Chemical-Loaded Molecular Sieves as Latent Curing Aids

A Resin Curing System for Butyl Rubber

F. M. O'CONNOR and R. L. MAYS
Linde Co., Division of Union Carbide Corp., Tonawanda, N. Y.

BUTYL RUBBER is a synthetic rubber obtained by copolymerization of isobutylene and isoprene. Usually, only 1 to 3 mole % isoprene is present. The polymerization process is conducted in the temperature range −50° to −100° C. in a liquid hydrocarbon medium with an aluminum chloride-type catalyst. Butyl rubber when properly compounded and cured resists chemical attack and aging even at high temperatures, is relatively impermeable to gases, and has good vibration insulation characteristics.

A new curing system for butyl rubber (*8*) is being used in formulating butyl rubber compounds for a variety of applications. There are other patents relating to this process (*2, 6, 7*). In this curing system, frequently called "resin cure," a para-substituted dimethylophenolic resin is used as the cross-linking agent in place of sulfur or a dioxime. The primary advantages of resin-cured formulations are outstanding resistance to dry heat, good compression set, and nonblooming and nonstaining properties. The heat reactive dimethylolphenol is in itself sufficient to cure butyl rubber formulations under normal production conditions of heat and pressure, but these formulations cure relatively slowly. Therefore, the cure rate must be increased to more practical ranges by using catalysts or accelerators with the phenolic resin.

The field of possible catalysts for the resin cure of butyl rubber is still relatively unexplored. Materials such as heavy metal halides, chlorinated paraffin wax, polychloroprene, chlorosulfonated polyethylene, and organic sulfonic acids have been the most common accelerators used. Some of these accelerators are so active that formulations containing them are difficult to process because of premature curing of the rubber. Also, some of these active compounds cause corrosion and excessive sticking of the compound to processing equipment. The less active catalysts, on the other hand, must be used either at relatively high vulcanization temperatures or for long curing cycles at conventional temperatures.

Ideally, the accelerator for the resin cure of butyl rubber should be relatively inactive during the various stages of processing, and cause no premature curing of the formulation, no corrosion, and no sticking of the rubber compound to equipment. It should, however, be active enough during vulcanization to provide a rapid cure rate. The combination of anhydrous hydrogen chloride with a Linde Molecular Sieve produces a unique accelerator for the resin cure of butyl rubber. This accelerator, designated Chemical-Loaded Molecular Sieve CW-3615, provides a very fast cure rate without the concomitant disadvantages normally encountered when active catalysts are used. Previous reports (*3,-5*) have disclosed the latent curing aid principle and discussed its application in styrene-butadiene rubber and neoprene.

The Molecular Sieve powders used as the carrier for active accelerators are synthetic crystalline metal aluminosilicates chemically similar to many clays and feldspars and belonging to a class of minerals known as zeolites. These materials can be synthesized as fine powders having a particle size in the range of 1 to 5 microns. They are essentially inert and have little effect on the properties of the rubber during processing or after vulcanization. The powders disperse rapidly and completely in rubber formulations, when the standard mixing technique recommended in the ASTM Standards on Rubber Products is used.

The adsorption of anhydrous hydrogen chloride on Molecular Sieve is almost completely reversible. When hydrogen chloride is properly adsorbed on a Molecular Sieve, the resulting product is substantially free from acidic odor when handled and stored under proper conditions. About 15 weight % hydrogen chloride, which is the loading of hydrogen chloride in CW-3615, is the optimum for this application.

The highly corrosive nature of hydrogen chloride is well known. Loaded Sieve CW-3615, on the other hand, is noncorrosive under most conditions. To ensure that no corrosion occurs during processing or vulcanization, a minimum of about 1.0 p.h.r. zinc oxide is recommended for use with this product. In this way, any hydrogen chloride which does not act directly as a catalyst should react with the zinc oxide to form zinc chloride in situ which may also function as a catalyst. Laboratory tests of formulations containing hydrogen chloride-loaded Molecular Sieve and zinc oxide have caused no corrosion even on prolonged contact with metal specimens.

One of the largest volume uses for butyl rubber vulcanized by the resin cure system is in making tire curing bags. These bags are used continuously at very high temperatures in the vulcanization of tires. Resistance to severe mechanical abuse and to deterioration of physical properties on exposure to high temperatures for extended periods of time is required. Resin-cured butyl rubber is well suited to this type of service because of its superior heat-aging properties and toughness. Also, there is no tendency for the resin-cured rubber to overvulcanize because of migration of sulfur from the tire formulation. In a tire curing bag formulation, a safe-processing, fast-curing stock is desired which will maintain a minimum tensile strength of about 1000 p.s.i. and a minimum elongation of about 200% after being aged in air at 300° F. for six days. Formulations accelerated with CW-3615 have these desirable characteristics. The versatility of formulations containing this accelerator should also offer advantages in resin-cured butyl rubber used for many other applications.

Table I gives a typical resin-cured butyl rubber tire curing bag recipe. This formulation is the base compound which was used in obtaining the data presented here.

Table I. Typical Butyl Tire Curing Bag Recipe

Compound	P.H.R.	Compound	P.H.R.
Butyl 218	100.0	Stearic acid	1.0
HAF black	60.0	Amberol ST 137 resin	12.0
Process oil	10.0	Accelerator	Variable

Chloride-containing compounds have been widely used as accelerators for this type of curing system. Table II shows the effect of various catalysts on the scorch time, cure rate,

Table II. Effect of Various Accelerators on the Resin Cure of a Typical Butyl Tire Curing Bag Formulation

	Recipe, P.H.R.			
	1	2	3	4
Base compound	183	183	183	183
Neoprene W	5.0	...	...	5.0
Stannous chloride	...	2.0	...	...
CW-3615	...	...	3.0	3.0
Zinc oxide	...	...	5.0	5.0
	Mooney Scorch at 250° F., Minutes to 5-Point Rise			
	100+	9	96	78
	Ultimate Tensile, P.S.I.			
Minutes at 320° F.				
15	465	1505	1350	1315
30	1340	2400	1890	1885
45	1385	2475	2075	1980
	Ultimate Elongation, %			
15	1000+	410	865	860
30	1000	475	750	705
45	745	415	685	590
	Shore A Hardness, Units			
15	62	65	67	66
30	62	66	68	70
45	63	67	70	71
Physical Properties after 6 Days at 300° F. of Samples Cured 30 Min. at 320° F. (*1*)				
Ultimate tensile, p.s.i.	1050	2045	880	1525
Ultimate elongation, %	270	170	330	210
Shore A hardness, units	82	78	76	87

and aging characteristics of the typical butyl tire curing bag formulation. Neoprene W (recipe 1, Table II) is typical of the halogenated elastomer type accelerators which generally provide safe-processing stocks with relatively slow rates of cure and acceptable heat-aging characteristics. Stannous chloride (recipe 2, Table II), on the other hand, is typical of the very active heavy metal halide-type accelerators. These accelerators give very rapid curing formulations which are difficult to process, and generally have good tensile strength but poor elongation after heat aging. This formulation was very difficult to blend on a two-roll mill because of excessive sticking of the compound to the rolls. The use of CW-3615 with zinc oxide (recipe 3, Table II) gave essentially the same rate of cure as stannous chloride without the undesirable decrease in processing safety, and did not cause any sticking of the compound to processing equipment. The product, however, could not meet the tensile strength specification for curing bags after heat aging. The addition of Neoprene W to the formulation containing CW-3615 and zinc oxide (recipe 4, Table II) gave the desired improvement in heat-aging properties while maintaining a rapid rate of cure and satisfactory processing characteristics. The data show that the combination of CW-3615, zinc oxide, and Neoprene W provides a versatile acceleration system for the resin cure of Butyl rubber. Proper choice of the concentration of each accelerator provides processing, curing, and heat-aging characteristics which will meet a wide variety of specifications.

Weight per Cent Loading of Hydrogen Chloride. The efficiency with which Moelcular Sieves can isolate an adsorbed chemical from a formulation in which they are dispersed is, in part, determined by the weight per cent loading of active chemical. The loading which provides the best handling characteristics and optimum performance in a given application must be determined. Loadings of up to 15 weight % hydrogen chloride on Molecular Sieve gave products with virtually no acidic odor. Higher concentrations, however, resulted in products with the pungent odor characteristic of hydrogen chloride. Table III shows that, at a constant concentration (0.6 p.h.r.) of hydrogen chloride, the processing safety and rate of cure are a function of the weight per cent loading of hydrogen chloride on the Molecular Sieve. Shorter scorch times and faster cure rates are obtained at higher loadings of hydrogen chloride. Even at 20 weight % hydrogen chloride on the Molecular Sieve, however, the scorch time is considerably improved over that obtained with other active accelerators. It is generally desirable to use as high a loading as possible of active chemical on Molecular Sieve. About 15 weight % hydrogen chloride on Molecular Sieve (CW-3615) gives a product which provides good processing safety and a rapid rate of cure in butyl rubber formulations.

Table III. Effect of Weight per Cent Loading of HCl on Performance of HCl-Loaded Molecular Sieve in Resin Cure of a Typical Butyl Tire Curing Bag

	Recipe, P.H.R.			
	1	2	3	4
Base compound	183	183	183	183
Neoprene W	5.0	5.0	5.0	5.0
Zinc oxide	5.0	5.0	5.0	5.0
HCl-loaded molecular sieves,				
5 wt. % HCl	12.0	...	...	...
10 wt. % HCl	...	6.0	...	...
15 wt. % HCl (CW-3615)	...	...	4.0	...
20 wt. % HCl	...	...	...	3.0
	Mooney Scorch at 250° F., Minutes to 5-Point Rise			
	55	27	25	19
	Ultimate Tensile, P.S.I.			
Minutes at 320° F.				
15	1410	1695	1745	1975
30	1845	1880	1975	2265
45	1935	2000	2120	2205
	Ultimate Elongation, %			
15	545	630	690	640
30	495	580	560	490
45	465	530	535	590
	Shore A Hardness, Units			
15	75	70	69	72
30	77	72	70	75
45	78	74	72	75
Physical Properties after 6 Days at 300° F. of Samples Cured 30 Min. at 320° F. (*1*)				
Ultimate tensile, p.s.i.	1185	1445	1570	1634
Ultimate elongation, %	235	230	230	210
Shore A hardness, units	87	87	88	88

Concentration of CW-3615. Chemical-Loaded Molecular Sieves can generally be added to rubber formulations at various concentrations without affecting the processing safety. With very volatile chemicals, such as hydrogen chloride, however, greater effects are expected than are obtained with relatively nonvolatile compounds. Table IV shows that the processing safety and rate of cure are affected by the concentration of CW-3615. The Mooney scorch time decreases and the rate of cure increases as the concentration is increased. The heat-aging properties, however, appear to be independent of the concentration of CW-3615 in this formulation. Compression set was improved at higher accelerator concentrations. Scorch time

Table IV. Effect of Concentration of CW-3615 on Resin-Cure of a Typical Butyl Tire Curing Bag Formulation

Compound	Recipe, P.H.R. 1	2	3	4
Base compound	183	183	183	183
Neoprene W	5.0	5.0	5.0	5.0
Zinc oxide	5.0	5.0	5.0	5.0
CW-3615	1.0	2.0	3.0	4.0
	Mooney Scorch at 250° F., Minutes to 5-Point Rise			
	106	102	78	25
	Ultimate Tensile, P.S.I.			
Minutes at 320° F.				
15	1180	1280	1315	1745
30	1810	1950	1880	1975
45	2120	1990	1980	2120
	Ultimate Elongation, %			
15	905	905	860	690
30	770	755	705	560
45	660	745	590	535
	Shore A Hardness, Units			
15	65	65	66	69
30	68	70	70	70
45	72	70	71	72
Physical Properties after 6 Days at 300° F. of Samples Cured 30 Min. at 320° F. (*1*)				
Ultimate Tensile, p.s.i.	1750	1520	1525	1570
Ultimate elongation, %	230	205	210	230
Shore A hardness, units	88	88	87	88
Compression Set (Method B), %				
70 hr. at 212° F., plugs cured 60 min. at 300° F.	61.6	57.2	57.5	53.3

dropped most severely when the concentration of CW-3615 was increased from 3.0 to 4.0 p.h.r. It appears, therefore, that about 3.0 p.h.r. CW-3615 provides the best combination of curing and processing characteristics.

Zinc Oxide Concentration. The presence of zinc oxide in resin-cured butyl rubber formulations employing CW-3615 as accelerator ensures that no corrosive effects will be obtained from any excess hydrogen chloride. Zinc oxide functions as a retarder when used with metal halides and has an activating effect with elastomer type catalysts. Table V shows that increasing the concentration of zinc oxide considerably improves Mooney scorch time and retards the rate of cure to some extent. This is similar to the behavior of zinc oxide with metal halides. The compression set and heat-aging characteristics, however, appear to be independent of the concentration of zinc oxide. These data indicate that by adjusting the amount of zinc oxide in a formulation using this type of acceleration system, varying degrees of processing safety can be obtained while maintaining a rapid cure rate.

Neoprene W Concentration. Neoprene W is a member of the class of halogenated elastomers which function as mild accelerators for the resin cure of butyl rubber. Formulations containing this type of catalyst are generally safe processing and relatively slow curing, and possess good heat-aging characteristics. Table VI shows that in the absence of Neoprene W, a formulation containing CW-3615 (recipe 1, Table VI) was safe processing and fast curing but did not retain a high tensile strength when aged at high temperatures. The addition of Neoprene W to this recipe (recipe 2, Table VI) reduced the processing safety slightly and had little effect on the cure rate but improved the retention of tensile strength by heat-aged samples. There was a signficant decrease in the elongation of aged specimens. Increasing concentrations of Neoprene W (recipes 3 and 4,

Table V. Effect of Zinc Oxide Concentration on Resin Cured Butyl Tire Curing Bag Formulation Containing CW-3615 as Accelerator

	Recipe, P.H.R. 1	2	3	4	5	6
Base compound	183	183	183	183	183	183
Neoprene W	5.0	5.0	5.0	5.0	5.0	5.0
Zinc oxide	1.0	2.0	3.0	4.0	5.0	10.0
CW-3615	3.0	3.0	3.0	3.0	3.0	3.0
	Mooney Scorch at 250° F., Minutes to 5-Point Rise					
	32	48	58	68	74	80
	Ultimate Tensile, P.S.I.					
Minutes at 320° F.						
15	1850	1555	1475	1470	1400	1305
30	2145	2000	1950	1875	1900	1900
45	2020	2075	2165	2170	2095	2075
	Ultimate Elongation, %					
15	625	705	765	805	825	830
30	560	615	625	650	715	690
45	500	515	580	575	615	575
	Shore A Hardness, Units					
15	70	70	70	70	70	68
30	72	70	71	71	70	70
45	73	73	73	73	73	72
Physical Properties after 6 Days at 300° F. of Samples Cured 30 Min. at 320° F. (*1*)						
Ultimate tensile, p.s.i.	1415	1440	1490	1505	1565	1505
Ultimate elongation, %	225	240	220	210	225	195
Shore A hardness, units	87	86	86	87	87	88
	Compression Set (Method B), %					
70 hr. at 212° F., plugs cured 60 min. at 320° F.	53.5	53.8	56.5	54.3	...	...

Table VI. Effect of Neoprene W Concentration on Resin-Cured Butyl Tire Curing Bag Formulation Containing CW-3615 as Accelerator

	Recipe, P.H.R.			
	1	2	3	4
Base compound	183	183	183	183
Neoprene W	. . .	3.0	5.0	10.0
Zinc oxide	5.0	5.0	5.0	5.0
CW-3615	3.0	3.0	3.0	3.0
	Mooney Scorch at 250° F., Minutes to 5-Point Rise			
	96	80	78	52
	Ultimate Tensile, P.S.I.			
Minutes at 320° F.				
15	1350	1300	1315	1525
30	1890	1870	1880	2025
45	2075	2075	1980	2175
	Ulitmate Elongation, %			
15	865	945	860	750
30	750	765	705	600
45	685	655	590	540
	Shore A Hardness, Units			
15	67	67	66	67
30	68	70	70	70
45	70	71	71	72
Physical Properties after 6 Days at 300° F. of Samples Cured 30 Min. at 320° F. (*1*)				
Ultimate tensile, p.s.i.	880	1480	1525	1510
Ultimate elongation, %	330	245	210	165
Shore A hardness units	76	87	87	93
Compression Set (Method B), %				
70 hr. at 212° F., Plugs cured 60 min. at 320° F.	51.1	54.6	57.5	. . .

Table VII. Effect of Ratio of CW-3615 to Zinc Oxide and Neoprene W on Resin-Cured Butyl Rubber

	Recipe, P.H.R.			
	1	2	3	4
Base compound	183	183	183	183
Neoprene W	3.0	1.0	3.0	2.0
Zinc oxide	3.0	1.0	1.0	2.0
CW-3615	3.0	3.0	3.0	3.0
	Mooney Scorch at 250° F., Minutes to 5-Point Rise			
	50	48	52	72
	Ultimate Tensile, P.S.I.			
Minutes at 320° F.				
15	1430	1630	1545	1475
30	1855	2010	1930	1930
45	2000	2110	2010	2030
	Ultimate Elongation, %			
15	790	700	720	750
30	640	590	575	640
45	550	520	505	550
	Shore A Hardness, Units			
15	70	72	73	72
30	74	75	75	75
45	76	76	75	75
Physical Properties after 6 Days at 300° F. of Samples Cured 30 Min. at 320° F. (*1*)				
Ultimate tensile, p.s.i.	1430	605	1065	1195
Ultimate elongation, %	220	300	250	250
Shore A Hardness, units	87	80	85	85
Compression Set (Method B), %				
ASTM, 70 hr. at 212° F., Plugs cured 60 min. at 320° F.	56.5	44.3	45.8	54.4

Table VI) resulted in higher tensile strength and lower elongation after heat aging. Thus, by altering the concentration of Neoprene W, varying heat-aging requirements can be met. If high tensile strength is desired and relatively low elongations are satisfactory, relatively high concentrations of Neoprene W should be used. If, on the other hand, high elongation must be maintained, lower concentrations of Neoprene W should give the desired effect.

Relative Concentrations of CW-3615, Zinc Oxide and Neoprene W. Previous data have shown the effects of varying the concentration of CW-3615, zinc oxide, or Neoprene W on the processing safety, rate of cure, heat-aging characteristics, and compression set of resin-cured butyl rubber. The required processing, curing, and aging characteristics may be obtained in a variety of applications by the proper choice of concentration of each of these materials. Table VII shows the effect of different concentrations of both zinc oxide and Neoprene W, when used in conjunction with CW-3615, on the properties of a resin-cured butyl rubber formulation. The use of 3.0 p.h.r. each of CW-3615, zinc oxide, and Neoprene W (recipe 1, Table VII) gave good proceesing safety, a rapid cure rate, and acceptable heat-aging properties.

If a faster rate of cure is desired and some loss in processing safety and tensile strength after heat aging can be tolerated, the concentration of both zinc oxide and Neoprene W should be lowered without changing the CW-3615 concentration. Reduction of both zinc oxide and Neoprene W concentrations to 1.0 p.h.r. (recipe 2, Table VII) gave a faster rate of cure and a slight reduction in Mooney scorch time. The tensile strength was lower and elongation higher than in recipe 1 after aging at elevated temperatures.

To increase the tensile strength after heat aging, the concentration of Neoprene W should be increased. Neoprene W (3.0 p.h.r.) and zinc oxide (1.0 p.h.r.) used with 3.0 p.h.r. CW-3615 (recipe 3, Table VII) gave a recipe having processing and curing characteristics similar to recipe 2, but provided the desired improvement in tensile strength after heat aging.

If a longer Mooney scorch time is desired, it is recommended that the concentration of zinc oxide be increased and the concentration of Neoprene W decreased. The use of 2.0 p.h.r. each of zinc oxide and Neoprene W along with 3.0 p.h.r. CW-3615 (recipe 4, Table VII) gave a formulation having a rate of cure and heat-aging properties comparable to recipe 3 and considerably improved Mooney scorch time.

LITERATURE CITED

(1) Am. Soc. Testing Materials, Philadelphia, Pa., ASTM D 865-54T.

(2) Batts, H.J., Delang, T.G., (to U.S. Rubber Co.) U.S. Patent **2,734,877** (Feb. 14, 1956).

(3) O'Connor, F.M., Thomas, T.L., Dunham, M.L., *Ind. Eng. Chem.* **51**, 531 (1959).

(4) O'Connor, F.M., Thomas, T.L., Dunham, M.L., "Chemical-Loaded Molecular Sieves as Latent Curing Aids. Secondary Accelerators in Styrene-Butadiene Rubber," Division of Rubber Chemistry, ACS, Cincinnati, Ohio, May 1958.

(5) O'Connor, F.M., Thomas, T.L., "Chemical-Loaded Molecular Sieves as Latent Curing Aids. Accelerators for the Vulcanization of Neoprene," Division of Rubber Chemistry, ACS, Chicago, Ill., September 1958.

(6) Peterson, L.C., Batts, H.J., (to U.S. Rubber Co.), U.S. Patents **2,734,039** (Feb. 7, 1956); **2,726,224** (Dec. 6, 1955); **2,727,874** (Dec. 20, 1955).

(7) Schaefer, W.E., Batts, H.J., Brafford, D.A., *Ibid.*, **2,749,323** (June 5, 1956).

(8) Tawny, P.O., Little, J.R., (to U.S. Rubber Co.) *Ibid.*, **2,701,895** (Feb. 15, 1955).

RECEIVED for review June 5, 1959. Accepted October 19, 1959. Division of Rubber Chemistry, ACS, Los Angles, Calif., May 1959.