

Cost-Effective, High-Performance Vulcanizing Agent for Chlorinated Polyethylene

ECHO[®] A vulcanizing agent is designed for use with halogenated elastomers such as chlorinated polyethylene (CPE). It is supplied as an off-white powder with a specific gravity of 1.46. ECHO[®] A is a blend of esters of 2,5-dimercapto-1,3,4-thiadiazole.

In general, CPE compounds exhibit good resistance to oil, heat, and ozone. The appropriate choice of vulcanization system and formulating ingredients is the key to the ultimate performance and cost effectiveness of CPE compounds. Peroxides have commonly been used as the cross-linker for CPE in applications requiring optimum compression set and heat resistance. For less stringent applications, the use of ECHO[®] A vulcanizing agent allows for a more highly-extended, lower-cost compound than is possible with peroxides. The resultant vulcanizates cured with ECHO[®] are high-performance compounds with heat resistance only slightly less than that obtained by peroxide cures.

The Advantages of the ECHO[®] vulcanizing agent Cure System are:

- Single pass mixing.
- No bloom or surface stains.
- Cure rate that can be accelerated.
- Cures not inhibited by oxygen.
- Lead-free compounds.
- Low compound cost.

Compounding With Echo[®] A Vulcanizing Agent

ECHO[®] A vulcanizing agent functions as a di-nucleophile, vulcanizing any elastomer containing replaceable halogen atoms. Because of this, many inexpensive fillers, oils, and plasticizers can be used with ECHO[®] A. The cure mechanism of ECHO[®] A involves hydrolysis of the thioester bonds within ECHO[®] A to form a dimercaptide intermediate. This di-nucleophilic species then displaces halogens on the two elastomer backbones to become a cross-link.

ECHO[®] A vulcanizing agent should be used in conjunction with an amine accelerator and a basic metal oxide acid acceptor/cure activator. The cure rate can be increased by increasing the level of the amine accelerator or of the metal oxide; however, this often results in reduced heat-aging performance. Cure rate can also be accelerated by including a water donor such as Epsom salts in the formulation.

To illustrate the compounding flexibility of ECHO[®] A vulcanizing agent, Table I lists the physical properties and aging performance of model compounds.

Table I
CPE Cured with Echo[®] A - Model Formulations and Properties

Component	Formulation (phr)		
	Minimally Extended	Moderately Extended	Highly Extended
CPE-Tyrin 0136	100	--	--
Sundex [™] 790	30	--	--
Maglite [®] D	5.0	--	--
Vanax [®] 808	0.8	--	--
Echo[®] A Vulcanizing Agent	1.7	--	--
SRF-N762	50	80	100
FEF-N550	--	--	20
Atomite	--	--	10
DOP	--	10	25
Cured 20 min at 320 [°] F(171 [°] C)			
	Original Properties		
Modulus at 100% elongation, MPa	4.27	4.69	4.76
Modulus at 200% elongation, MPa	8.00	7.93	7.65
Tensile strength, MPa	11.86	10.41	8.41
Elongation, %	500	460	210
Shore A hardness, points	70	78	93
	Air-aged 70 hrs at 257 [°] F(125 [°] C)		
Modulus at 100% elongation, MPa	4.55	7.31	7.10
Modulus at 200% elongation, MPa	8.41	10.41	--
Modulus at 300% elongation, MPa	11.10	11.03	--
Tensile strength, MPa	12.96	11.45	9.52
Elongation, %	450	320	160
Shore A hardness, points	77	91	95

Acid Acceptors

ECHO[®] A vulcanizing agent requires an inorganic base to activate the cure and to stabilize the compound from acid-catalyzed degradation during heat-aging. It is believed that this base enhances the nucleophilic cross-linking mechanism and reacts with the resultant chloride ions to prevent HCl formation. Compounding parameters, such as scorch safety, shelf life, and state of cure are related to the chemical nature and surface area (particle size) of the base. Since the base is insoluble in the compound, its basicity is dependent on the exposed surface area. In general, 5 to 6 phr of a readily dispersible, high-activity¹ magnesium oxide such as Maglite[®] D or Elastomag[®] 170 provide excellent results. A comparison of the performance of a "high-activity" and a "low-activity" magnesium oxide is shown in Table II.

¹ - Surface area greater than 120 m²/g.

Table II
The Effect of Magnesium Oxide Activity

Component	Formulation (phr)	
	Low Activity	High Activity
CPE 0136	100	100
SRF N-762	50	50
Sundex [™] 790	30	30
Stanmag 112	5.0	--
Elastomag [®] 170	--	5.0
Vanax [®] 808	0.8	0.8
Echo[®] A Vulcanizing Agent	1.7	1.7

Press cured 25 min at 340^oF

ODR cure at 340 ^o F		
t ₉₅ (95% cure), min	25.8	23.0

Original Properties

Modulus at 100% elongation, MPa	2.41	2.48
Modulus at 200% elongation, MPa	4.96	5.58
Tensile strength, MPa	10.20	12.69
Elongation, %	530	540
Shore A hardness, points	63	63
Compression set, % 70 hrs at 257 ^o F	62	37

Most other metal oxides commonly used in rubber compounding are less effective than magnesium oxide and are not recommended for use with ECHO[®] A vulcanizing agent. Antimony oxide can be used for its flame-retardant characteristics, but it should not be used to replace magnesium oxide.

Accelerators

ECHO[®] A vulcanizing agent is activated by alkaline ingredients. Strong bases such as calcium hydroxide and strongly basic amine accelerators should be avoided because they significantly reduce scorch safety and shelf life.

Vanax[®] 808 rubber accelerator, a butyraldehyde-aniline condensation product, is recommended for use at 0.8 phr in CPE compounds cured with ECHO[®] A vulcanizing agent. Other basic amine accelerators can also be used to enhance scorch safety. Table III provides a comparison of a few of these ECHO[®] accelerators in a basic CPE compound. These materials, in combination with magnesium oxide, can provide a good balance of cure rate, scorch safety, and physical property generation. High concentrations of amine accelerators may be used to produce a faster cure rate but this practice is not generally recommended, since this can adversely affect heat-aged properties as well as seriously reduce scorch safety.

Table III
Comparison of Amine Accelerators
Formulation (phr)

Component	1	2	3	4	5
CPE CM0136	100	100	100	100	100
N550 Black	50	50	50	50	50
TOTM	35	35	35	35	35
Magnesium Oxide	5	5	5	5	5
Wingstay [®] 29	2	2	2	2	2
ECHO[®] A	2.5	2.5	2.5	2.5	2.5
Epsom Salts	2	2	2	2	2
Accelerators					
Vanax [®] 808	0.8				
Rhenofit [®] NC		3.5			
Vulkacit [®] 576			1.0		
Beutene				0.8	
Vanax [®] 808HP					0.5
ODR Data (360° F, 3° Arc, 100 cpm)					
Min. Torque (lb-in)	6.96	4.93	6.13	7.57	6.72
Max. Torque (lb-in)	61.85	60.20	60.67	58.99	59.79
Delta Torque (lb-in)	54.89	55.27	54.53	51.42	53.08
ts ₂ (minutes)	1.43	3.00	1.87	1.97	1.55
t ₉₀ (minutes)	5.32	10.25	5.77	7.58	5.20
Cure Conditions (Press Cure at 360° F)					
Cure Time (minutes)	6	10	6	8	6
Physical Properties of Cured Plaques					
Modulus _{100%} (Mpa)	4.83	3.864	4.83	4.83	4.899
Modulus _{200%} (Mpa)	10.557	7.728	10.212	10.005	10.212
Modulus _{300%} (Mpa)	15.18	11.178	14.835	14.421	14.628
Tensile Strength (Mpa)	16.767	15.111	16.146	16.56	16.836
Elongation (%)	340	430	340	360	370
Shore A Hardness	72	74	75	76	76

Fillers

All carbon blacks provide normal reinforcement, based on particle size and structure, although not to the extent usually found in most elastomers. Non-black fillers must be carefully selected, however, based on their surface pH. Because of the chemical nature of ECHO[®] A vulcanizing agent and the resultant cross-linking mechanism, acidic fillers will retard the cure, while moderately basic and neutral fillers are acceptable. For example:

- Kaolin clays that are not surface-treated should be avoided. These materials are acidic and will retard cure.
- Silane-treated clays or silica can be used at levels up to 50 phr.
- The various calcium carbonate fillers (including ground oystershell) can be used as extenders, but they do not provide good reinforcement.

Plasticizers, Softeners, and Extenders

Esters, polyesters, and naphthenic and aromatic plasticizers and oils are generally compatible with CPE-based compounds cross-linked with ECHO[®] A vulcanizing agent. Vulcanizates of ECHO[®] and CPE can be inexpensively formulated for high-performance applications by the appropriate selection of plasticizer level and type. By using the lowest level of plasticizer required for the application and the most inexpensive aromatic oil possible, depending on the physical properties desired, the compounder can produce a high-performance, low-cost compound. These same extenders cannot be used in formulating with peroxides, since they would adversely affect cure.

Plasticizers containing olefinic unsaturation, such as butyl oleate, should not be used, since they react with the cure system and result in severe cure retardation. Phosphate esters, such as tricresyl phosphate, cause scorch problems.

Sundex[®] 790 aromatic oil and trioctyl trimellitate (TOTM) are recommended for CPE compounds containing ECHO[®] A vulcanizing agent. Sundex[®] 790 provides low compression set and volume swell, with advantage of low price and low specific gravity. TOTM is an excellent nonvolatile plasticizer for high-temperature performance. It provides low compression set and exhibits greater than 300% elongation after heat-aging at 302°F (150°C), with a durometer change of only 5 points.

Antioxidants

CPE cured with ECHO[®] A vulcanizing agent does not require antioxidants for normal service formulations. For improved long-term heat-aging, however, NBC and hindered phenols such as Irganox[®] 1425 provide additional protection.

Compounding Ingredients to Avoid

As described earlier, fillers that are too acidic interfere with cure, and those that are too basic cause scorch problems. Also, the disadvantages of using phosphate esters and unsaturated plasticizers have been established.

Additionally, a few other common compounding ingredients cause problems. Any lead compound causes severe cure retardation. Zinc oxide causes poor compound heat-aging. Common epoxy acid acceptors cause severe cure retardation. All these effects are a result of the specific chemistry of the ECHO[®] A vulcanizing agent molecule.

Suggestions For Processing Compounds Cured With Echo[®] A Vulcanizing Agent

Banbury[®] Mixing (Laboratory Procedure)

The Banbury[®] mixer should be on low speed with cooling water on. Mix in a Banbury[®] mixer following an upside-down mix procedure. Typically, the pre-blended mixture of reinforcing fillers, amine-type accelerator, and the acid acceptor is charged into the mixer first, followed by a mixture of the polymer, plasticizer, and ECHO[®] A vulcanizing agent. After 2 minutes of mixing, or when the compounded rubber reaches 200 to 230°F, raise the ram and sweep down the chute. Dump the compound after an additional mixing time of 1 to 2 minutes, or at a maximum temperature of 250°F (121°C), whichever occurs first.

Storage

Store ECHO[®] A vulcanizing agent in regular storage areas. Since it has a high melting point, it can be stored under most normal storage conditions. Care must be taken to ensure that unused ECHO[®] A is not exposed to moisture, since that will reduce ultimate scorch time and shelf life.

For additional information, or to place an order or sample request, call 1.800.331.7654.

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