

retarders for rubber cures

Depth and Understanding: Choosing the correct retarder for a situation may involve a number of variables: cost, efficiency, effect on the compound, and in-house availability. This Solutions examines the various retarders in use and how to optimize your choice of retarder depending on the polymer and cure system.

Retarders in the rubber industry are in an unusual position — some rubber technologists insist that retarders aren't needed and are the sign of a poorly thought-out cure system. Yet copious amounts of retarders are consumed in the rubber business every year. While there is some truth to the fact that retarders are sometimes quick-fix bandages for problem stocks, their utility in a variety of situations makes them a critical component of a rubber compounder's toolbox of rubber technology.

The idealized retarder would have the following attributes:

- scorch time at processing temperatures (as measured by the 2, 3 or 5 point rise at 250-270°F — best known as T₂, T₃ or T₅) is increased significantly,
- scorch time at molding temperatures may be slightly longer but not much,
- time to reach 90% of cure (T₉₀) is not delayed,
- maximum rheometer torque (state-of-cure) is not changed significantly,
- cost is not prohibitive.

Of course, no retarder meets all these qualities. As a compounder, one must decide which retarder gives the maximum benefit with minimum deficiencies. Choice of the retarder depends on the polymer to be used, the cure system, the curing parameters needed (a steam vulcanizer-cured part could afford to lose some T₉₀ cure rate without an effect on part cost; an injection molded part must keep T₉₀ time to a minimum), inventories (is it worth bringing in a new raw material to have the optimized retarder or can a currently inventoried retarder satisfy the minimal requirements?), and finally in choosing your retarder, the sometimes essential details: discoloration, possibility of bloom, FDA status, ability of some retarders to reduce reversion, cost, etc.

While virtually all compounders know how retarders are used in the rubber industry, there are a few applications for retarders that might spark some thoughts:

- The most common use of retarders is to give a marginally processing stock a little more scorch time. This might involve increasing the flow time in a mold or allowing a calendar to be run at a higher temperature to smooth a calendared sheet. You may have developed a compound that meets all the required specifications, the mold is cut and sample parts need to be made. However, the cavities continue to underfill — increasing the shot or preform weight just leads to thick flash and flow lines.

If you can make minor changes in the compound, the simplest treatment is to use a small amount of retarder to gain some flow time. You want to choose a retarder that minimizes final physical property changes so an enormous amount of re-testing is not required. You may even choose retarders that improve certain marginal properties (a good example is using Retarder SAFE in nitriles where the retarder improves processing time and also raises the state-of-cure and reduces compression set).

- A stock runs consistently well for nine months out of the year. But during the summer months the combination of higher ambient temperatures, oppressive warehouse temperatures, hotter running processing equipment, and higher humidity lead to curing problems.

RETARDERS FOR RUBBER CURES: c o n t i n u e d

A small amount of retarder can often relieve this seasonal variation without affecting the compound properties. Some companies run a summer stock and a winter stock. It's probably a better idea to leave the retarder in year-round rather than having two stocks that you have to stay aware of making the next seasonal change.

- Recovery of scorchy material: The cooling water chiller breaks down and ten batches of a finely tuned injection stock are mixed with excess heat input. Compound properties are OK, but there is no way the presses can handle the short scorch. Adding a retarder while minimizing property changes can allow the stock to be molded. There are various ways to get the retarder in: run the stock back through the mixer; mill mix on a cold mill (a predispersed masterbatch of the retarder is preferred here); or for stock so marginal that reworking is questionable, add retarder to fresh batches and add the scorchy stock to the fresh batches on a cold dump mill and mill blend. The trick in retarder selection is whether you can bring a stock back without large physical property changes or without having to use so much retarder that bloom occurs.
- Certain products require the raw stock to be warehoused for long times. Or stocks may have to be transported long distances in hot trucks. While refrigerated trucks are an option, a sufficient safeguard in many cases may be to add some retarder to the compound.
- Increase Productivity: This may take the form of parts that can be molded at higher temperatures; stocks that can be run hotter and faster through an extruder or calendar; or going from a two-pass mix to a one pass. For example: Production mixing time is at a premium. Mixing is done on one shift only plus some overtime. Reducing a two-pass mixed stock to a single-pass mix will not only reduce the cost of that stock, but reduce overtime needs as well. Conversion to a one-pass mix starts with a good retarder. However, the use of a retarder to allow the addition of cure in a higher-temperature-mix is only one part of converting a two-pass mix to one-pass. The mixer must be in good enough shape to adequately mix the stock in a shorter overall mix time. Good cooling should be present in the mixer and the dump mill. Finally, certain materials may be a problem when one-passed, like insoluble sulfur, reactive phenolic resins, and fabric bonding systems.

So far we've only discussed retarders in generalities. Let's look at specific retarders and how they differ from one another.

SUMMARY OF RETARDERS FOR SULFUR CURES

<u>Akrochem Retarder</u>	<u>Chemical Type</u>	<u>Uses and Comments</u>
Retarder BA and BAX	benzoic acid	Weak acid; improves shelf aging; activates cure; reduces compound viscosity.
Retarder SAX	salicylic acid	Moderate acid; moderate retarding of thiazoles; promotes reversion resistance; activates cure.
Retarder PX	phthalic acid	Best retarding acid with thiazoles; minimal effect on state-of-cure.
Retarder AK	modified phthalic acid	Phthalic acid with activation added. Retards sl. less than PX but cures faster.
Retarder SAFE	sulfonamide	Good retarder in most systems; v. strong cure activation; reduces reversion. High cost.
Retarder CTP	N-(cyclohexylthio) phthalimide	Outstanding retarder with most systems; very effective with sulfenamides. Low dosages (0.10-0.40 phr) are typical.
Retrocure G	4, 5 methylbenzotriazole	Use with halobutyls and sulfur-modified polychloroprene. Not for mill addition.

RETARDERS FOR RUBBER CURES: c o n t i n u e d

See Table I and Table II for a brief look at the effectiveness of various retarders with a sulfenamide or a thiazole accelerator.

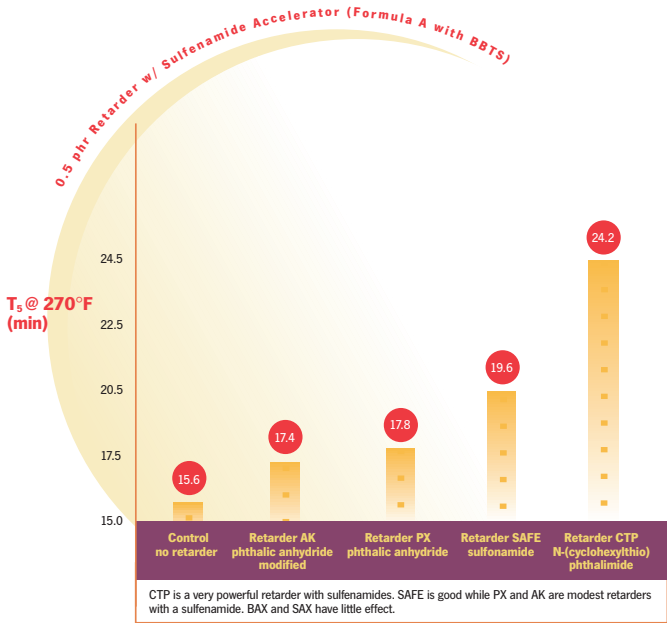


TABLE I

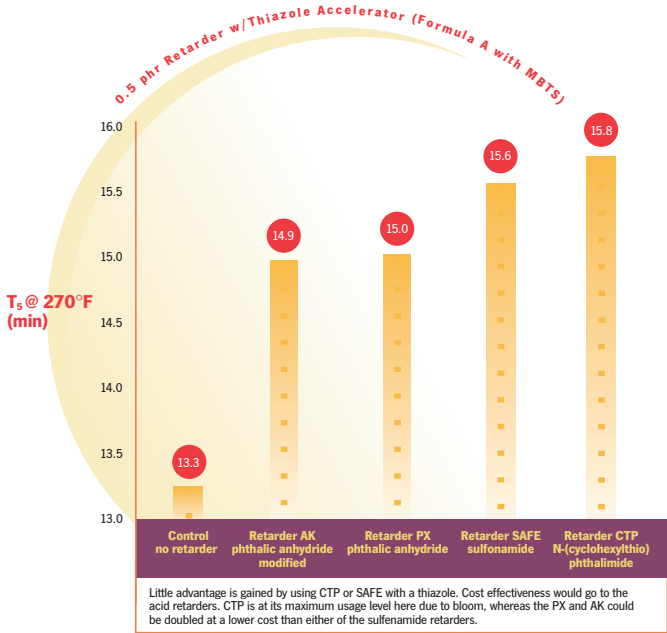


TABLE II

acid retarders

Akrochem's Retarder BAX (benzoic acid), Retarder SAX (salicylic acid), Retarder AK (modified phthalic anhydride), and Retarder PX (phthalic anhydride) represent the range of acid retarders.

Acid retarders are most effective with basic accelerators like MBT, MBTS, DPG, DOTG, and Accelerator 40B (aldehyde-amine). Following is a summary of acid retarder characteristics:

- Highly effective with thiazole (MBT, MBTS) primary accelerators. Only moderately effective (PX and AK) or ineffective (SAX, BAX) with sulfenamides (CBTS, BBTS, OBTS).
- The weaker acids (BAX and SAX) have a pronounced activating effect. Similar to stearic acid, these two acid retarders will mildly retard thiazoles and then activate the cure. All the acid retarders do a good job of retaining the compound's state-of-cure. BAX and SAX will result in slightly higher final maximum rheometer torque, while AK and PX will usually be just slightly lower. This is in contrast to Retarder CTP where state-of-cure is almost always lower (see sulfenamide-type retarders) and SAFE where the state-of-cure is sometimes much higher.
- BAX has minimal scorch retarding effect at hotter processing temperatures (above 225°F). This makes it useful for improving shelf aging of a stock without affecting curing time. BAX will also reduce compound viscosity. SAX improves scorch up to about 260°F before activation starts to occur. AK and PX improve scorch up to about 280°F.
- SAX and PX have FDA status under 177.2600 regulations, "Rubber articles intended for repeated use". Benzoic acid (the oil-treated Retarder BAX is also FDA) is acceptable under GRAS regulation 184.1021 (Generally Recognized As Safe).
- The acid retarders all **reduce natural rubber reversion**. A natural rubber compound with 2.0 parts sulfur (compound A in Appendix), was cured at 380°F:

Retarder (0.5 phr)	Max Torque	T ₉₀ (sec)	T _{max-2} (sec) (2-pt reversion)	% overcure allowed (Overcure of the T ₉₀ before reversion occurs)
None	29.3	95	148	56
BAX	30.5	104	180	73
AK	27.2	102	180	76
PX	26.3	105	184	75
SAX	30.2	107	196	83
SAFE	33.7	108	196	81
CTP	24.4	110	171	55

As can be seen, all the acid retarders lengthened time to reversion (as measured by time to a 2-point loss from maximum) with salicylic acid (SAX) providing the most protection from overcure (last column — largest % of overcure of the T₉₀ before reversion). Among the sulfenamide retarders, SAFE reduced reversion, as well as SAX, but raised the state-of-cure significantly. CTP had no effect on reversion and lowered state-of-cure.

- The acid retarders will not bloom when used at levels within recommended range (up to 1.5 phr).
- Use acid retarders in white and transparent articles due to excellent resistance to discoloration.
- Phthalic anhydride is a good retarder for carboxylated NBR (Krynac®) and carboxylated HNBR (Therban® XT).

sulfenamide retarders

These retarders have structures similar to the sulfenamide class of accelerators. They tend to be more effective retarders and are often used at lower levels than acid retarders. However, the sulfenamide (SFA) retarders cost more; thus, a cost/performance consideration must be made when choosing a retarder.

CTP (better known as “PVI”) is an outstanding retarder at low concentrations (a predispersed masterbatch may be preferred for more precise weigh-ups and improved dispersion). It is particularly potent when used with sulfenamide accelerators (OBTS, BBTS or CBTS in order of most-to-least improvement in scorch when used with CTP). CTP will retard thiazoles, but acid retarders are probably more cost effective.

CTP will bloom a shiny crystal if used above approximately 0.5 phr. If a hot-running stock needs more than 0.5 phr, it is better to blend CTP and SAFE (0.5:1 ratio) to maximize scorch safety without bloom as well as minimize loss in state-of-cure. State-of-cure is usually lowered by CTP addition. If more than 0.25 phr CTP is used, some compensation may be needed to boost the state-of-cure back to the original level. Additional sulfur and/or additional accelerator should be added. If additional sulfenamide is used to boost the state-of-cure this may also help the scorch retardation.

SAFE behaves similar to a sulfenamide accelerator. Scorch is retarded and state-of-cure is maintained or even raised in most sulfur systems. SAFE is particularly effective in nitriles (NBR). Bloom does not occur at levels under 1.5 (possibly 2.0) phr. SAFE’s main drawback is its cost — the price/effectiveness ratio may not be as good as another retarder.

- FDA status: neither CTP nor SAFE have food contact permission under FDA 177.2600 regulations. Both, however, are acceptable under German Health Ministry Recommendation XXI, Category 4 which would indicate neither has adverse properties in contact with food.
- SAFE will reduce natural rubber reversion on overcure. CTP has no effect on reversion.

other sulfur cure retarding tips

- One way to improve scorch and cure speed in a thiazole (MBT, MBTS) accelerated compound is to add a small amount of OBTS sulfenamide. An SBR (Compound B in Appendix) with MBTS and DPG acceleration had standard retarders, as well as OBTS added to it.

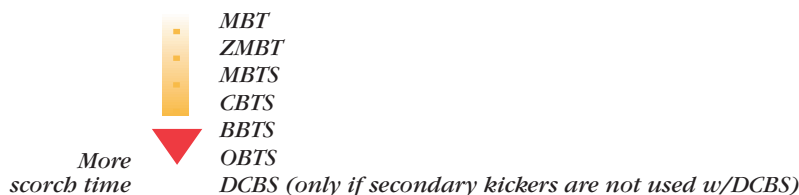
<u>Retarder</u>	<u>PHR added</u>	<u>T₂ @ 250°F</u>	<u>T₉₀ @ 340°F</u>
None	—	14.1	5.44
SAX	1.0	17.1	8.01
AK	1.0	16.3	7.14
PX	1.0	16.9	7.30
CTP	0.5	18.2	6.32
SAFE	1.0	18.5	8.47
OBTS	0.5	16.1	5.05
OBTS	1.0	18.0	4.42

0.5 phr of OBTS provides scorch resistance, a faster cure, a good state-of-cure, all at a reasonable cost. In the same vein, if a stock is badly scorched, a blend of CTP, OBTS and SAFE may be used to recover the stock without bloom or loss of properties.

- Often a retarder is used to reduce scorch when a simple change of the primary accelerator will provide sufficient scorch safety. Moving step-wise to more scorch resistant primary accelerators may sometimes be less disruptive to a formula than addition of a retarder.

OTHER SULFUR CURE RETARDING TIPS: c o n t i n u e d

Primary accelerators in order of scorch resistance



- Low sulfur/high thiuram (TMTD, TETD, DPTT) cures are used for excellent heat aging and compression set in SBR and NBR. 0.5 - 1.0 phr of a sulfenamide like BBTS will retard this system and improve cure rate. Higher levels (3.0 phr) will reduce bloom normally associated with this cure system (of course, splitting the thiuram into several different thiurams will also reduce bloom, e.g., 2.0 phr of TMTD is often used in NBR. 1.0 phr each of TMTD and TETD will prevent bloom and provide similar properties). Once the BBTS has been added to the system, CTP can be used to retard further if needed.

RETARDERS FOR POLYCHLOROPRENE AND OTHER HALOGENATED ELASTOMERS

The acid and sulfenamide retarders should not be used in polychloroprene (CR-“Neoprene® or Baypren®”). They will either have no effect or negative results (CTP will severely depress state-of-cure). The standard way to retard CR is with TMTD, TMTM, MBTS, or a retarder for halogenated polymers, Retrocure G.

Sulfur-modified CR (S-CR or “G-types”)

Retrocure G (4- and 5-methyl benzotriazole) is an ideal retarder for sulfur-modified chloroprene. 1.0 phr of various retarders were added to formula C in the Appendix. The results are listed below:

Retarder	T_5 @ 250°F (mins)	T_{90} @ 340°F (mins)	Max Torque @ 340°F
None	17.4	6.9	102
Retrocure G	25.9	7.6	97
MBTS	20.4	5.2	92
TMTM	19.3	4.8	89
TMTD	21.6	4.3	94

Retrocure G improves scorch with a minimal effect on curing properties. The rounded, marching modulus that is typical with sulfur-modified-CR is the same with Retrocure G. Most of the other retarders result in a flattened plateau (which does reduce T_{90} time) and a lower state-of-cure. In some cases, this flatter plateau effect might be a benefit by getting a more exact T_{90} cure than the marching modulus provides. Also, the lower state-of-cure may result in better flex properties. Properties that require high states-of-cure like resistance to heat build-up, resilience and compression set should use Retrocure G as retarder.

OTHER SULFUR CURE RETARDING TIPS: c o n t i n u e d

Mercaptan-modified CR (M-CR or “W-types”)

Mercaptan-modified polychloroprene’s primary accelerator is ethylene thiourea (ETU). The best retarder for ETU in a black filled compound is TMTD. A half part of TMTD will add 40% scorch with minimum loss in T_{90} or maximum torque. MBTS will add a similar amount of scorch time but the maximum rheometer torque is lowered significantly. BBTS at 1.0 part will improve scorch significantly (65%) but has a very strong reduction in the state-of-cure. For non-black filled M-CR, MBTS is slightly better than TMTD with state-of-cure being good for both retarders and scorch, favoring MBTS slightly.

It is suggested that if a M-CR compound contains SBR, NR or PBD blend, the retarder should be a sulfenamide like BBTS (there should be sulfur or sulfur donor in the formula). While TMTD will retard the polychloroprene portion, it will contribute to the scorch of the general-purpose polymer. BBTS will retard the M-CR while providing delayed acceleration to the blended, unsaturated rubber.

Halogenated Butyls

For halogenated butyl (CIIR and BIIR), the first suggestion would be to not use the often suggested magnesium oxide as a retarder. While MgO (in fact, low activity MgO is traditionally used because of the extreme retardation caused by high activity MgO) will certainly retard, the lengthened T_{90} cure time is often too severe.

Retrocure G is a good retarder for most halogenated butyl cure systems. See below for a comparison of retarders in a chlorobutyl recipe (Formula D in the Appendix). Scorch is improved, T_{90} is nearly the same, and maximum torque is the same with Retrocure G.

Retarder	phr	$T_5 @ 270^\circ\text{F}$	$T_{90} @ 350^\circ\text{F}$	Max Torque
None	—	10.2	7.0	44
Active MgO	0.5	15.0	13.0	49
Retrocure G	0.5	13.0	7.6	43
Retarder CTP	0.5	11.9	12.0	39

retarding peroxide cures

Standard rubber peroxides like dicumyl and bis- (t-butyl peroxy) di-isopropyl benzene typically have good scorch at processing temperatures (less than 250°F). But as the temperature nears optimum curing temperatures there is often too little delay before scorch occurs. The best way to retard a peroxide is to scavenge the first free radicals formed as the peroxide opens up. Once the scavenger is used up, the reaction can proceed as usual. One of the best materials for this kind of peroxide retarding is Antioxidant BHT. BHT is an extremely active antioxidant such that little of it remains in the polymer after cure. For this reason, BHT is seldom used as a normal rubber antioxidant but rather to prevent gel in the polymerization process. But the trait of quickly reacting with free radicals (which prevents gel formation) makes BHT useful to delay the start of a peroxide cure.

BHT will nullify the initial peroxides formed. For this reason the final state-of-cure will be lowered by using the BHT. To regain the loss in torque, 20%-25% more peroxide can be added or a coagent that doesn’t effect scorch can be added. For EPDM, HNBR, EVA, and CPE (saturated polymers), a good coagent for this purpose is TAC (triallyl cyanurate). TAC will improve the state-of-cure with minimal effect on scorch. To study this, an EPDM formula (Formula E in the Appendix) was mixed and had BHT and TAC added to it:

RETARDING PEROXIDE CURES: c o n t i n u e d

Additive	phr	T ₂ @ 270°F	T ₉₀ @ 340°F	Max Torque
None	—	4.23	7.40	122
BHT	0.5	6.05	7.78	105
BHT	1.0	6.63	7.68	95
BHT/TAC	0.5/1.0	5.97	7.07	117
BHT/TAC	1.0/1.0	6.56	7.10	108

Adding 1 phr TAC for every 0.5 phr of BHT will improve scorch time by 40%, reduce the T₉₀ cure time, as well as retain most of the maximum rheometer torque. For an unsaturated elastomer like nitrile, TAC is ineffective. A retarded version of TMPTMA (trimethylolpropane trimethacrylate) should be used as the coagent in NBR and SBR.

conclusion

As time available for research diminishes for compounders, retarders can be a quick and efficient solution to formula development and factory problems. Hopefully this brochure will aid in the selection of the most suitable retarder for your application. To discuss specifics and get recommendations, please call Akrochem's Technical Service Department at 800-321-2260.

appendix

<u>Formula A</u>	<u>phr</u>	<u>Formula B</u>	<u>phr</u>	<u>Formula C</u>	<u>phr</u>
SMR 10	60.00	SBR 1805	212.50	Baypren KA 8786	100.00
Taktene 1359	92.00	ZnO	5.00	N990 Black	40.00
N550 Black	60.00	Stearic	1.00	Akromag Blue Bar	4.00
Aromatic Oil	18.00	MBTS	1.50	Akrozinc Bar 85	5.00
ZnO	5.00	DPG	0.60		
Stearic	2.00	Sulfur	1.50		
Sulfur	2.00	Retarder	as listed		
MBTS or BBTS	1.50				
TMTM	0.10				
Retarder	0.50				
<u>Formula D</u>	<u>phr</u>	<u>Formula E</u>	<u>phr</u>		
Bayer Chlorobutyl 1255	100.00	Buna EP T 2450	100.00		
N660 Black	65.00	N990 Black	40.00		
Sunpar 2280 oil	12.00	Sunpar 150 oil	10.00		
Stearic	1.00	Perkadox BC40B	10.00		
ZnO	3.00	(dicumyl)			
MC-98 Sulfur	0.50				
Vultac 5	1.00				
MBTS	1.00				
Retarder	as listed				



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