

fire retardant (fr) systems and techniques

The ability of a rubber part to resist burning has become ever more critical. A further issue, in addition to fire resistance, is limiting smoke production in a fire. It is a fact that more people die in fires due to smoke inhalation than are killed by the fire itself. This solution will outline flame retardant techniques used in rubber. Included are some tips to improved compounds as well as some things to avoid. Also, compounding methods to minimize smoke evolution during a fire will be discussed. Because test methods vary widely, these compounding recommendations can't guarantee a material will pass every type of flame testing but experience shows that most specifications can be met by standard compounding.

Getting Started:

The first thing to consider is what kind of flame resistance is required. If it simply has to meet HB specs (Horizontal Burn), minor compounding changes will usually do, since most rubber burns relatively slowly when held horizontally. All it has to do is not burn too quickly; in some tests it doesn't even need to extinguish the flame. However, most testing is done vertically (rubber strip is held vertically in a flame so the fire is more likely to propagate), which is more difficult to pass. The most common specification is UL 95, which requires a vertical flame to go out almost immediately once the flame source is removed. V-0 (flame goes out in less than 5 sec) can normally be met by standard techniques using a combination of halogens (Cl or Br) and antimony trioxide. ATH (alumina trihydrate) is sometimes also used in this combination. V-1 requires that the flame go out in 25 seconds (in both V-0 and V-1, any drips cannot ignite cotton located under the burning sample). V-1 allows more latitude in compounding but it makes more sense to compound toward V-0, if possible, rather than tightrope the V-1 spec.

There is a wide and varied assortment of flame testing in the rubber and plastics industries. It will benefit you to become very familiar with the test method you need to meet. You can usually do rudimentary testing in the lab by simulating the test method. You have to remember, though, that if the lab test isn't run virtually identical to the actual test, results can differ. There was a compounder whose lab-tested compound extinguished quickly when a vertical flame was removed. But certified lab testing failed the rubber. It turned out the compounder was testing a thick 0.25" cross-section sample and the actual test called for a thin sample of about .06" (a thin sample burns more readily than a thick one). This was enough to make his product fail.

A strong push is toward low smoke compounding. Minimum smoke emission requires that no halogens or antimony oxide be used. Ideally, other burnable materials like black and petroleum oils are minimized. Besides providing less burnable material, non-black fillers tend to reduce smoke generation vs. carbon black. Use of halogens creates an acidic smoke that in a closed space (train car, mines, underground subway, and tunnels) can be deadly. Thus, more low smoke specifications are being issued. This is troublesome in some cases because older specifications call out polychloroprene to be used because of its inherent flame resistance (due to the Cl in the polymer backbone). The presence of the chlorine means smoke is a problem right away. The best low smoke is done with EVA and Vamac® elastomers. These polymers are somewhat resistant to flame propagation and can hold the large amounts of ATH (50-60% of the total compound may have to be ATH in order to meet V-0 specifications) required in low smoke formulas while remaining processable. EPDM, although very combustible, is popular for low smoke simply because of its good overall properties, acceptance of high loadings, and lower cost.

Flame resistant packages:

If the goal is to simply put the flame out, the tried-and-true formula of halogens/antimony oxide (Sb₂O₃) and possibly ATH is the least expensive and easiest method. The “standard package” below can be added to many compounds that meet other needed requirements without significantly affecting final properties. The improved package is for those tests that are more stringent (for example, a flame produced from butane will burn hotter and cause more problems passing a test) and this may require other changes to the compound to fulfill all the product application properties.

STANDARD PACKAGE	IMPROVED PACKAGE
Akrochlor R-70 (70% Cl by wt) 15-20 phr E-29072 (90% antimony trioxide) 5-10 phr Alumina Trihydrate (ATH) 25-40 phr	up to 30 phr (use liquid Cl for better processing) 8-12 phr Sb ₂ O ₃ 50-75 phr ATH

A COUPLE OF REPRESENTATIVE FORMULAS:			
Good Quality Hose Cover		Conveyor Belt Edging (“skirtboard”)	
	PHR		PHR
Buna EPT 6850	100.00	SBR 1500	78.00
Spheron 5000A Black	80.00	SBR 1009	22.00
Zinc Oxide	5.00	N330 Black	50.00
Stearic Acid	1.00	Zinc Oxide	5.00
Heavy paraffinic oil	60.00	Stearic Acid	1.00
Akrochlor R-70	40.00	Akrochlor L-60	20.00
E-29072 90% Sb ₂ O ₃	10.00	E-29072 90% Sb ₂ O ₃	6.00
Micral 632 ATH	30.00	Micral 632 ATH	25.00
Sulfur	1.50	TMTM	0.25
MBTS	1.50	Sulfur	1.80
TMTD	0.70	CBTS	1.00
DPTT	0.70		
Passes UL-95 V-0		Passes MSHA (Mine Safety & Health Adm.) tests	

Adding 5-10 phr Zinc Borate helps either system. One half as much antimony can be used if Zinc Borate is present. Use of a bromine halogen donor in place of the chlorine donor allows less FR material to be used. The Br radical reacts 2300 times faster and is more efficient than Cl but the Cl is usually less expensive overall. Br is used mostly in plastics where they take advantage of the lower loadings needed. There are, however, rumblings that Br flame resistors may have PCB-like (DDT insecticide) characteristics and may eventually be banned. A recent article in the *Wall Street Journal* noted that PBDE's (polybrominated diphenyl ethers) appear to be building up in human tissue at a rate doubling every two to five years. Their persistence in the environment recalls PCB's continuous escalation in natural systems. Computer hardware is one of the heaviest users of PBDE's.

Chlorinated paraffins are a primary source of Cl for fire fighting. The liquid chlorinated paraffins (Akrochlor "L" products) are good plasticizers for medium and high polarity elastomers like Hypalon®, polychloroprene, and NBR. Color is good; high temperature properties are good; low temperature is adequate. Akrochlors have very good heat stability. This is important for better color consistency and minimizing corrosion from Cl release. The various chlorinated paraffins available are listed below:

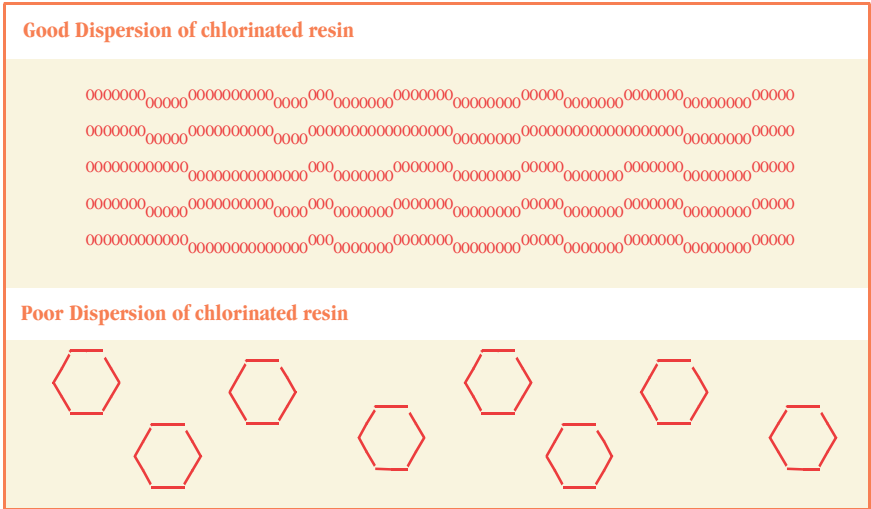
TYPICAL PROPERTIES - LIQUID GRADES:								
Grade	Chlorine WT %	Specific Gravity	VISCOSITY			VOLATILITY		STABILITY JQD method %HCl 4 hrs. @ 175°C
			SUS 210°F	SUS 100°F	Poises 77°F	4 hrs. 150°C	24 hrs. 100°C	
L-40	40	1.11	90	1300	8	2.0	0.5	0.3
L-42	42	1.15	149	3900	29	1.5	0.8	0.3
L-45	45	1.16	50	390	2.5	7.0	1.5	0.2
L-57	57	1.30	50	1100	13	18	6.0	0.25
L-60	60	1.35	63	1700	20	14	4.0	0.25
L-61	61	1.38	78	4000	60	11	3.0	0.1
L-70LV	67	1.52	350	>10 ⁷	>10 ⁷	5.2	0.6	0.25
L-170HV	70	1.54	530	>10 ⁹	>10 ⁷	1.0	0.1	0.25

TYPICAL PROPERTIES - RESIN GRADES:								
Grade	Chlorine WT %	Sp. Grav 25°/25°C	Particle Size Thru 50 Mesh	Color Gardner	Volatility	Soft Pt. B&R, °C	Particle 4 hrs. at 175°C	
R-70	70	1.60	94	< 1	N.V.	102	0.3	
R-70S	70	1.60	94	< 1	N.V.	102	0.1	

The resinous R-70 is probably the most widely used product of this type because it provides high levels of chlorine, improves rubber viscosity and flow, is more compatible than the liquid products, and has the least effect on physical properties.

—The chlorinated paraffins are not very compatible with EPDM. Excessive use of Akrochlor L liquid products in EPDM will lead to an oily bleed. About 10 phr is okay. Using antimony oxide at higher than needed levels can help compatibilize chlorinated paraffins. The higher molecular

weight, solid Akrochlor R-70 resin can be used at 25-30 phr in EPDM. Make sure R-70 is melted during mixing (220°F minimum). Mill-mixing R-70 sometimes results in molding flaws and poorer flame resistance. In general, good dispersion of the flame retarders is essential. Imagine two identical compounds, one with finely dispersed ingredients; the other with poor dispersion:



In this simulation, the poorly dispersed particles of chlorinated resin are large chunks in the path of the fire. The fire will easily bypass these chunks and move on. With good dispersion, there is no easy path for the fire to propagate along and there will be better flame retardation throughout the sample. This was evident in a customer's formula that passed flame tests when his mixer Banbury-mixed the stock but when the customer mixed it on his own mill and did not melt the resin, the stock would not pass. The concept of good dispersion aiding overall flame resistance is applicable regardless of which materials you use.

— Antimony oxide is usually used at 1/4 to 1/3 the level of the chlorinated paraffins. Some formulas use higher levels of antimony but tests have shown this extra Sb_2O_3 adds little to the overall flame resistance. It should be noted that antimony oxide by itself has no value as a flame retarder. There must be halogens present for Sb_2O_3 to work. Note that antimony trioxide (“trioxide” is the proper term, while the simple antimony “oxide” is the more commonly used – both terms describe the same material) is a skin irritant and an IARC Group 2B carcinogen and thus Akrochem does not sell the straight, powdered material. We offer an 85% active rubber-bound version as well as the more economical version, 90% Sb_2O_3 powder de-dusted with 10% liquid chlorinated paraffin. This way even the de-dusting material helps with the flame resistance.

—The use of ATH along with the halogen/antimony materials helps with smoke and flame reduction.

It also provides filler that helps prevent “drips” and sticky rubber forming if the compound burns or melts. Drips are typically more of a plastic concern than rubber.

Smoke and Flame Resistance:

As noted, low smoke formulas (SS or smoke suppressing) should not contain any halogens or antimony oxide. Thus the polymer itself should not contain any halogens. The main method of flame resistance in low smoke formulas is very high loadings of ATH and/or Mg(OH)₂. These materials release water at fire temperatures:



This is intended to not only put the fire out but also dampen down any evolving smoke. It requires high loadings (50-60% of total formula) of these water-releasing fillers to reach V-0 resistance in a rubber or plastic that is not inherently flame resistant (such as EPDM, PE, or PP). A blend of ATH and Mg(OH)₂ will produce a better “char” (a burnt carbon remnant that shields the unburned rubber) than ATH alone. Both FR fillers form heat reflective metal oxides during decomposition, which act as insulating barriers. Take note that the high loadings of ATH and/or Mg(OH)₂ limit the properties available to this kind of compound (for example, it is very difficult to make low durometer FR/SS EPDM's).

Once you have made the decision to use a non-halogen FR/SS system, you need to consider the type of filler you want to use in such a system. ATH can be used at processing temperatures up to about 420°F. If processing temperatures exceed 420°F, water may be released, causing blistering. For higher processing temperatures, magnesium hydroxide, with a release of hydration beginning at 617°F (325°C), must be used to prevent premature release of water. Typically, ATH is used in most molded goods because of its good cost. Mg(OH)₂ is used in hot processing plastics, salt bath extrusions, and those parts where premium flame resistance is required. Magnesium hydroxide has less smoke evolution and greater char formation than ATH but is more expensive. The endothermic (heat absorbing) decomposition of ATH absorbs 280 cal/gm of heat energy. Magnesium hydroxide absorbs 328 cal/gm. This means that both fillers will absorb heat from the fire before releasing their water of hydration. A 50:50 blend of ATH and Mg(OH)₂ seems to be the best ratio of flame resistance and economics. Beyond the selection of ATH or Mg(OH)₂ is the exact type of the particular product to use. For example within ATH, differences exist in particle size, morphology, surface treatment, and brightness.

The advantages, if any, of smaller particle-sized ATH are not clear. Smaller particle means more surface area is exposed to the fire and that would imply a faster initial flame resistance reaction. Studies do

indicate that a smaller particle filler increases the time to initial ignition of a fire, but once the flame has ignited, the difference between small and large-particle fillers is essentially overwhelmed. The smaller particle, higher surface area fillers may drive up viscosity of the polymer and thus limit how much filler can be added (see surface-treating below). High loadings are essential to good FR, so lower surface area fillers should help in this regard. Dispersion is also better with the lower surface area materials and as noted earlier here, the better the dispersion, the better the FR and the consistency of the FR. Finally, the reinforcement value will be moderately better with the smaller particle size filler. If reinforcement is important, look at surface-treating your filler. Thus, while a small particle/high surface area filler may have some advantage on a part-for-part basis, this advantage may disappear when comparing possible total loadings.

Surface treatments of both ATH and Mg(OH)₂ vary from processability improvement like stearic acid to silane coupling agents that improve reinforcement and reduce compound viscosity. Some versions of treated Mg(OH)₂ are included below:

TYPICAL PROPERTIES:	VERSAMAG®	VERTEX®	VERTEX® ST	ZEROGEN® 50SP
Treatment	none	Silane	Stearic Acid	Silane
Mg(OH) ₂ , % typical	98	97.5	97.5	99.6
Free Moisture (105C, 2 hrs) ¹ , %	0.9*	0.30	0.29	0.10
Average Particle Size ¹ , microns	2.0	1.8	1.8	0.7
Calcium as Ca, %	0.5	0.3	0.3	0.06
325 Mesh Residue, %	0.1	0.10	0.05	0.01

* - low moisture versions available 1-tests performed on unmodified material

The Vertex are very economical versions of treated Mg(OH)₂ typically used in high-volume, low-cost applications like roofing while the Zerogen is a very high quality Mg(OH)₂ for demanding applications. Zerogen is also designed to prevent “pinkening” (thermal degradation caused by the high alkaline Mg(OH)₂) in chlorinated polymers like PVC. The stearic-treated Vertex will allow better dispersion of the polar hydroxide in a non-polar rubber compound. The silane treatments will not only help reinforce but also lower compound viscosity, which permit higher loadings. Versamag, or untreated Mg(OH)₂, is used in everyday applications and many plastics.

Treated ATH includes Micral® 9402 and the Hymod® ATH series. Treatment (silanes and/or processing promoters) first provides maximum particle dispersion of the FR filler. Not only will better dispersion make FR better at a particular loading, but also lower loadings may be required due to the improved dispersion. The heightened compatibility with the polymer will reduce viscosities and permit higher loadings of the FR fillers without causing undue processing problems. Silane treatments improve modulus values, tensile and abrasion, electrical resistivity, and lower water swell. While not needed for many routine fire-resistant formulas, the treated materials may make the difference in a more complicated specification when properties are tougher to meet

One of my favorite stories concerning ATH and $Mg(OH)_2$ concerns a compounder with whom I helped formulate an extremely flame resistant compound for fabric coating of firemen's clothing. The compound passed all the stringent tests but the customer then learned of one final test that had to be met. A coated fabric sample had to go into a $550^\circ F$ oven for 6 minutes without exhibiting cracking or bubbling. This simulated a fireman kneeling in hot embers. It turned out the compound we had designed bubbled badly when exposed to these temperatures. Of course, as you're reading this, the answer may be obvious. But at that time it was a real cause for concern since so much effort had been put into the basic compound's development and testing. It soon occurred to me that at $550^\circ F$, the ATH was releasing water, which turned to steam and caused the blisters in the stock. A simple change to magnesium hydroxide solved the problem. This is a good example of why it is important that all potential tests be known up-front so the proper compound can be designed.

It is probably a good time to note that not all flame resistance testing is as neat and straightforward as one would hope. Results vary from lab-to-lab. I worked one time with a customer on a FR compound that seemed to defy understanding. Virtually everything in the compound was flame resistant yet the compound failed the flame testing repeatedly. Frustrated, I asked the customer if there were another certified lab that could do the testing. Sure enough, the new lab passed the compound with flying colors. How do two labs come up with such different results? In this case, I never learned the reason. But it's clear a compounder has to be very cautious about lab testing. Whether the results are good or bad, take them with a grain of salt and whenever possible, confirm the results at a second lab. Of course, few people will want to pay for a second opinion if the first lab passes their material. And I guess I can't argue with that.

synergism

Synergism is a commonly used word in FR compounding. It simply means that if you use 1 phr of material A and 1 phr of material B, you get better results than you would if you used 2 phr of either A or B alone. In the complex reactions of a fire environment, there are many opportunities for materials to work hand-in-hand to better extinguish a flame. The best-known synergists in FR are antimony trioxide (Sb_2O_3) and halogens. Halogens (primarily Cl and Br) will form acids that help smother a fire. However this reaction is greatly enhanced by the presence of antimony trioxide. Antimony oxide (as it is more commonly known) alone has no flame retardant value. But by synergizing with HCl or HBr acids, a much more potent flame retarder is created.

An interesting synergistic material for flame resistance is Akrochem Zinc Borate HT ($4ZnO \cdot 6B_2O_3 \cdot 7H_2O$). It can be used in halogen-containing FR as well as low smoke/halogen-free versions. Its main

attribute is to form char. It also releases its water of hydration (“HT” indicates high temperature release of water – above 325°C) to quench the flame and suppress smoke. Zinc borate is synergistic with Cl-containing materials, ATH, phosphorus-containing material, as well as with antimony oxide. A brief summary of these synergies will make it evident that some zinc borate should be added to most FR formulas:

- 1) With HCl, zinc borate forms ZnCl which causes crosslinking to form char.
- 2) In combination with ATH or Mg(OH)₂, a hard residue is formed that resists further burning and shields unburned material.
- 3) With phosphorus-containing materials, zinc borate will form zinc phosphate and boric acid. Zinc phosphate forms phosphoric acid more easily than straight phosphorus plasticizer and the boric acid will form char readily.
- 4) Antimony oxide and zinc borate act together to delay the onset of flame ignition by 100°C in PVC and other chlorine-containing polymers.

It is possible to reduce the antimony oxide levels in a flame resistant compound by also using zinc borate. By using zinc borate in combination with ATH, the overall level of filler can be reduced. That is, instead of needing 190 phr of ATH to achieve V-0 fire status, 150 phr of ATH along with 10 phr of zinc borate may well give the same result. Zinc borate also suppresses afterglow, which is a test parameter in some flame testing. With Sb₂O₃, zinc borate forms a glassy char that resists further burning. Another interesting feature of zinc borate is that its refractive index is close to rubber and plastic so translucent goods are still possible with zinc borate. It is also a good fungicide with much less hazardous nature than normal fungicides. 2-3% in a compound can reduce mold growth. The borates are eco-friendly materials used to treat wood for inside housing frames to resist termites.

Another synergist is phosphorus-containing material that forms a phosphoric acid that results in char-formation with minimal smoke evolution. Ester plasticizers are the primary source of phosphorus in the rubber industry. The best flame resistance comes from triaryl phosphates like TCP (tricresyl phosphate) with a minimum phosphorus content of 8-9%. While good flame retarders, the aryls are not good plasticizers – they don’t soften as well nor are the low temperature properties very good. Alkyl phosphates (trioctyl phosphate is a good example) are excellent softeners and low temperature plasticizers but not as effective as flame retarders. Alkyl aryls are a good compromise.

If fire resistance is the main criterion, add all the TCP or similar plasticizer that the polymer can tolerate. Non-polar elastomers like EPDM can hold only about 10 phr of the phosphates without bleeding. Use of PEG (polyethylene glycol) as a process aid in EPDM will help compatibilize the

phosphorus material and possibly allow a little more to be used without bleed. As you go up in polarity of the rubber, more phosphorus plasticizer can be used. More polar elastomers (like CSM, CPE, or EVA) can be blended with EPDM to allow use of more phosphorus plasticizers.

low smoke formula

ATH 0 – 180 phr Mg(OH)₂ gives off less smoke, produces more char, results in higher LOI –

Mg(OH)₂ 180 – 0 phr (Limiting oxygen index or the amount of oxygen needed to allow flame to continue) but Mg(OH)₂ is higher priced. Blends with ATH are often used.

Zinc Borate 10 phr is typical. Up to 100 phr potentially could be used.

TCP 0 – 25 phr (depends on polymer and property requirements)

HERE ARE TWO EXAMPLES OF LOW SMOKE FORMULAS:

EPDM	PHR	EVA Title	PHR
Low mooney EPDM	100.00	Levapren 700HV	100.00
Zerogen 50SP Mg(OH) ₂	145.00	Hymod 632 SP ATH	190.00
Akrochem Zinc Borate HT	10.00	Akrochem Zinc Borate	15.00
Zinc Oxide	5.00	Akrochem VC-40K	6.00
Akrochem DDPH-50 peroxide	6.00	TAC	1.00
TAC	1.00	Proacid AC 18-DSA	2.00
Advawax 280	3.00	Zinc Stearate	1.00
		TCP	6.00
LOI-36		LOI-45	

As mentioned before, black and petroleum oil should be minimized in a low smoke formula. ATH is the least expensive way to gain flame resistance with minimal smoke, but alone, it is not effective enough to pass more stringent fire specifications unless the loadings are very high.

— Some further tips on flame resistance compounding: Tighter cures result in higher LOI numbers. LOI, or limiting oxygen index, is the amount of oxygen needed to make a product burn. It is a handy way to compare various FR methods. Normal atmosphere at sea level contains approximately 20% oxygen. If your FR compound has an LOI of 27, this means the oxygen in contact with this part must be 27% or more or the fire will extinguish. Moderately good FR compounds have LOI's in the high 20's and low 30's. Very good formulas are in the mid-30's to low 40's. In one study, simply adding more peroxide, and especially more co-agent or an additional co-agent, helped boost the LOI from 25 to as high as 42. Longer cures helped raise the LOI. The theory is that increasing crosslink density reduces the amount of combustible gases resulting from a fire (the rubber's overall molecular weight is higher so less gas is formed). The main point would be to not undercure a FR part as it may negatively affect fire resistance.

—Dispersion of all FR ingredients is very important. One study showed that the simple addition of 1 phr of stearic acid to a FR test compound raised the LOI number (from 25.5 without stearic to 34 with stearic). The only reasonable explanation for this startling jump was better dispersion. This is especially important when polar materials are being dispersed into non-polar elastomers. Even the surface of magnesium hydroxide is polar enough to create dispersion issues in EPDM. That is why better FR in EPDM is found with treated $Mg(OH)_2$ than untreated due to improved compatibility and dispersion.

—Calcium carbonate (whiting, limestone) should not be used in halogen-containing formulas since it will absorb the halogen acid that forms (the acid is what does the fire-fighting). ZnO and MgO should be limited in their use for the same reason (obviously, these materials are critically needed in certain formulas so you can't do without. The normal 4-5 phr usage will not interfere with FR). In low smoke recipes where no halogens are used, calcium carbonate can be used since it will act as a diluent to reduce flammable material.

—Chlorinated paraffins may affect color stability of a rubber compound. While the Akrochlores are very heat-stable and resist the loss of Cl that might cause a color change, it's a good idea to test a compound for color stability under conditions that simulate real-world usage.

Building a flame resistant compound can be simple or a complex endeavor depending upon the difficulty of the specification. If the rubber part "must not burn," this can be accomplished quickly and easily. But many, many additional requirements can be added that make compounding and part-testing much more difficult. When you get a request for FR rubber parts, ask a lot of questions. Get a thorough understanding of what is wanted (as well as what is actually needed) in the part. Don't try to marginally pass flame testing to save cost. It's better to have a wide margin for error, if possible, in these FR properties, than risk failure of a part.



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