ANGUS® CHEMICAL COMPANY

CHAINGUARD® I-15 SYNTHETIC RUBBER

CHAINGUARD® I-15 Shortstop for free-radical polymerizations
CAS Reg. no. 5080-22-8 EINECS No. 225-791-1

Key Performance Advantages

- Efficiently stops polymerization reaction
- Prevents popcorn polymer
- Minimizes emission problems

Synthetic Rubber

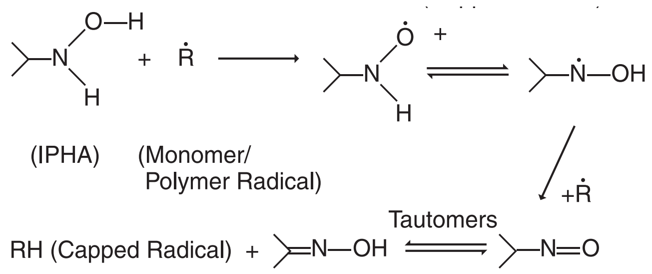
CHAINGUARD® is a very efficient free-radical scavenger which is used worldwide to shortstop emulsion styrene-butadiene and acrylonitrile-butadiene polymerization reactions in the production of SBR and NBR elastomers. These reactions are stopped short of complete conversion (monomers to polymer), to produce elastomers that have the required physical properties.

CHAINGUARD I-15 is an excellent multi-purpose shortstop that can be used alone to provide both excellent Mooney Viscosity control and effective popcorn polymer prevention. Traditional shortstop systems normally consist of two components, a non-volatile product to provide Mooney Viscosity control and a volatile product to prevent popcorn polymer formation in monomer recovery areas. Because of its unique physical properties, IPHA partitions almost equally between the latex and vapor phases during monomer recovery, thus providing excellent control in both phases.

CHAINGUARD I-15 is also expected to effectively stop other commercially important free-radical processes, such as suspension polymerization of vinyl chloride, and emulsion polymerizations of chloroprene and fluorinated olefins.

Free-Radical Termination Mechanism

One possible mechanism for scavenging of free radicals by CHAINGUARD (IPHA) is shown below:



In this reaction scheme, one IPHA molecule scavenges two monomer/polymer radicals, forming acetone oxime (tautomer) as a by-product. This mechanism has not been verified by experiment and other reactions are also possible. It is expected that IPHA deactivates the peroxide (or persulfate) and redox systems, thereby preventing generation of radicals that could reinitiate polymerization.

CHAINGUARD I-15 offers the following benefits to producers of SBR and NBR:

- Efficient stopping of polymerization reaction (excellent Mooney Viscosity stability)
- Prevention of popcorn polymer in monomer recovery units (reduced maintenance and downtime)
- Possible cost savings vs. conventional shortstops
- Nitrosamine-free rubber
- Avoids emission problems associated with other shortstops
- Minimizes corrosion problems
- Favorable elastomer color
- Reduced carryover of shortstop into recycled monomer

Performance Benefits

Efficient Stopping of SBR Polymerizations

CHAINGUARD I-15 is widely used for shortstopping styrene-butadiene emulsion polymerizations in the manufacture of styrene-butadiene rubber (SBR). CHAINGUARD is normally added at a rate of 0.27-0.33 parts per hundred monomer or pphm (0.04-0.05 pphm active IPHA) for standard 23.5% bound styrene cold polymers such as SBR-1502. Slightly higher levels may be required for high styrene recipes, such as the 40% bound SBR-1721. Hot SBR recipes (1000 series) will typically require similar IPHA levels to the cold recipes.

The effectiveness of CHAINGUARD I-15 at shortstopping a generic cold SBR recipe has been investigated at ANGUS research laboratories. The recipe described below was used for this study. Polymerization was carried out in glass bottles at 10°C until a conversion of 60-70% was reached; conversion was determined by measuring percent solids and correcting for added solids such as potassium hydroxide.

The degree of conversion was measured immediately prior to IPHA addition and again after 24, 48 and 72 hours of latex aging at 70°C. This aging was an attempt to simulate heat stresses that the latex might experience during stripping of monomers and during storage prior to coagulation. This test is more severe than plant environments because the unreacted monomers were left in the latex. Little or no conversion increase in this test indicates that Mooney Viscosity stability in most plant situations should be very good.

Generic Cold SBR Polymerization Recipe

Monomer Phase	**pphm (actives)**
Styrene	29.00
T-Dodecyl Mercaptan	0.20
Diisopropylbenzene Monohydroperoxide[1]	0.05
Butadiene	71.00
Aqueous Phase	**pphm (actives)**
DI Water	185.00
Disproportionated Tall Oil Rosin Soap[2]	1.69
Whole Cut Tallow Fatty Acid[3]	2.61
Potassium Hydroxide	0.57
Sodium Alkyl Sulfates[4]	0.10
Potassium Chloride	0.30
Disodium EDTA	0.003
Potassium Hydroxide	Adjust to pH 10.3
Initiator Phase	**pphm (actives)**
EDTA Iron (III), Sodium Salt Hydrate[5]	0.02
Sodium Formaldehyde Sulfoxylate Dihydrate[6]	0.06
DI Water	10.00

The performance data for CHAINGUARD I-15 are presented in Figure 1, where conversion is plotted against latex aging time for various active IPHA levels. A baseline conversion of 65% is assumed, while in reality baselines ranged from 60-70%.

Figure 2 shows the results of a laboratory study on a cold NBR recipe (10°C) utilizing pinene hydroperoxide and iron-EDTA. IPHA was effective at 0.05 pphm in this system.

Figure 1. CHAINGUARD 1-15 Shortstop Efficiency in Cold SBR

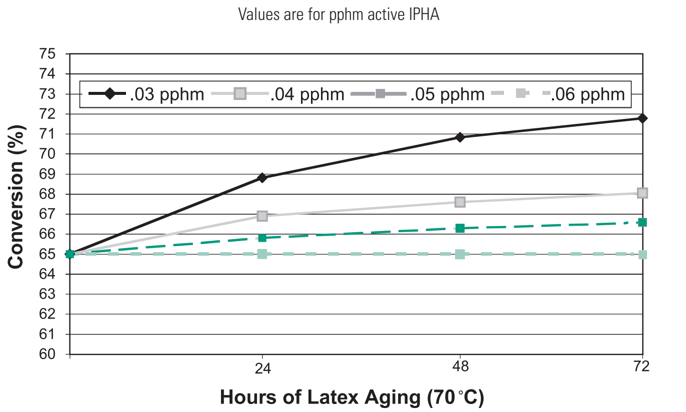
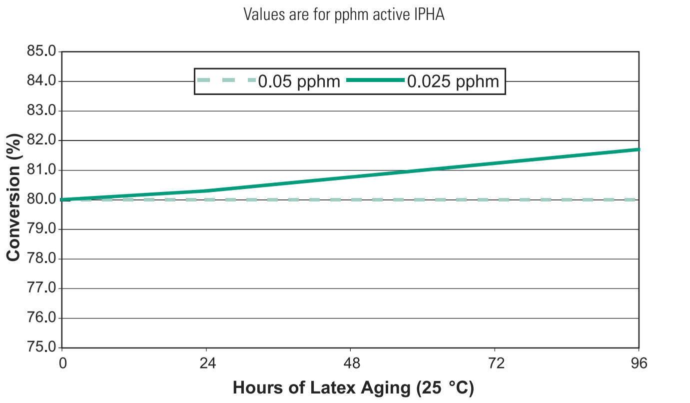


Figure 2. CHAINGUARD 1-15 Shortsop Efficiency in Cold NBR



These data show that, under the severe conditions of this test, IPHA completely stops the reaction at 0.06 pphm; conversion remains at 65% even after 72 hours at 70°C. At 0.04 pphm, a conversion increase of 3% occurs after 72 hours. Since good field performance (Mooney stability) is normally observed with 0.04-0.05 pphm IPHA, this means that a conversion increase of 3% or less after 72 hours should equal acceptable field performance.

The optimum dosage of IPHA will vary with the SBR recipe, polymerization temperature and plant operating conditions. For example, the type of peroxide is an important factor, since some peroxides are more reactive than others. The polymerization temperature is also important because it can influence the rate of generation and longevity of radical species. Plant operating conditions, particularly stripping temperature/vacuum/time, are believed to also play an important role in shortstop performance. Severe stripping (higher temperature/vacuum) to achieve low residual monomer levels, can place greater demands on the shortstop. At higher temperatures, radicals may be more easily regenerated and more shortstop will be stripped from the latex along with the monomers. Latex storage time/temperature prior to coagulation can also influence shortstop performance.

Efficient Stopping of NBR Polymerizations

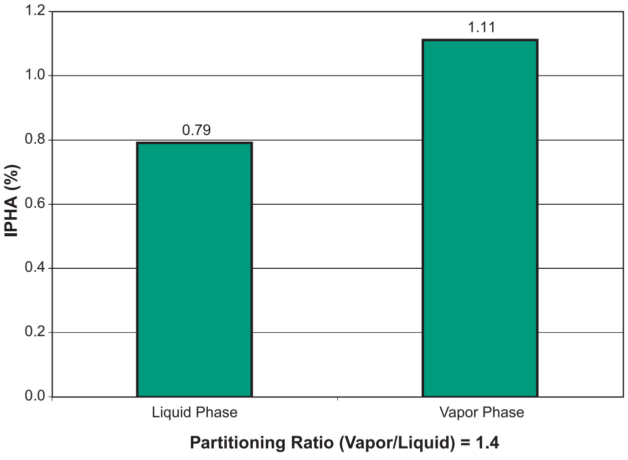
CHAINGUARD I-15 has also achieved commercial success as a shortstop for acrylonitrile-butadiene emulsion polymerizations in the manufacturing of acrylonitrile-butadiene rubber (NBR). Use of 0.40 pphm CHAINGUARD (0.06 pphm active IPHA) is very effective in stopping typical NBR recipies in the plant. ANGUS therefore recommends use of 0.06 pphm IPHA during initial lab/ plant evaluations. Optimum levels may be slightly higher or lower depending upon the recipe and plant operating conditions.

Prevention of Popcorn Polymer

Popcorn polymer is a highly crosslinked material which can form in the monomer recovery areas of processes containing dienes such as butadiene; these processes include manufacturing of SBR, NBR, BR and polychloroprene. Popcorn polymer is insoluble in organic solvents and causes costly maintenance shutdowns.

CHAINGUARD I-15 is very effective at preventing popcorn polymer formation in monomer recovery equipment, such as flash tanks and styrene strippers. IPHA has an almost ideal vapor/liquid partitioning ratio, with approximately equal amounts present in the liquid and vapor phases under typical monomer stripping con-ditions. This performance benefit of IPHA is illustrated graphically in Figure 3. A 1% aqueous solution of IPHA was heated in a closed loop system to 70°C at an absolute pressure of 353.3 hPa (265 mm Hg), which is typical for stripping of shortstopped SBR latex. After equilibration, the pot (simulated latex phase) and condensate (simulated vapor phase) were sampled and analyzed for percent IPHA.

Figure 3. Vapor/Liquid Partitioning of Aqueous IPHA



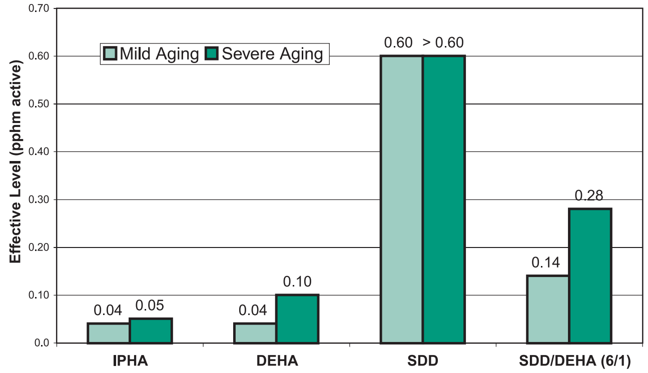
The data revealed that IPHA partitions slightly more into the vapor than the liquid phase. The partitioning ratio, which is the concentration of IPHA in the vapor divided by that in the liquid, is 1.4. Roughly equal amounts of IPHA are therefore present in the vapor (popcorn control) and liquid (Mooney Viscosity control). In contrast, shortstops such as sodium dimethyldithiocarbamate (SDD) and sodiumpoly- sulfide are essentially non-volatile (i.e. partitioning ratio ~0), providing no control of popcorn polymer.

The control of popcorn polymer with CHAINGUARD I-15 is demonstrated by results at an SBR production plant that formerly utilized sodium tetrasulfide as shortstop. While using the tetrasulfide system, the styrene stripper had to be shut down and cleaned every 1000 production hours (42 days). When tetrasulfide was replaced with CHAINGUARD I-15, cleaning intervals were increased to 2,200 hours (92 days). This resulted in reduced costs associated with maintenance and downtime.

Possible Cost Savings vs. Conventional Shortstops

Research studies by ANGUS have shown that replacement of conventional shortstops, such as DEHA and SDD, with CHAINGUARD I-15 may result in cost savings. When tested in the generic SBR recipe described previously, using the indicated aging procedures, IPHA is equally or more effective than DEHA and SDD on a weight actives basis. This IPHA performance advantage increases with latex aging time. Figure 4 describes the minimum effective shortstop levels, assuming that a conversion increase of 2% or less relates to good Mooney Viscosity control in the plant, and 1) mild latex aging (24 hours at 70°C) or 2) severe aging (72 hours at 70°C) best represents the plant environment.

Figure 4. Shortstopping Efficiency (IPHA vs. Others)

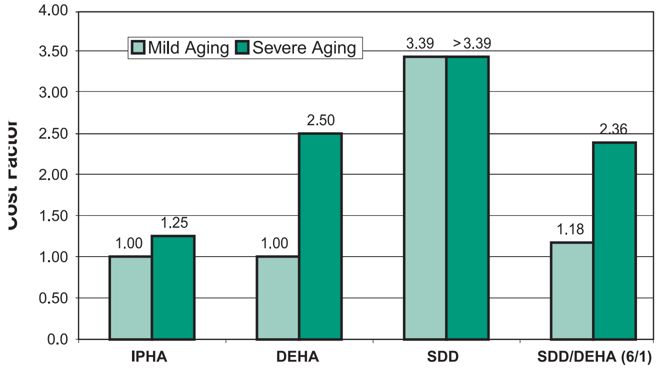


IPHA and DEHA are equally effective under mild conditions; however, IPHA is significantly more effective when conditions are more severe. The advantage of IPHA over DEHA is believed to be due in part to its more favorable vapor/liquid partitioning ratio. As shown previously, IPHA has a partitioning ratio of 1.4, while the ratio for DEHA is 5.9. Significantly less DEHA than IPHA is present in the liquid phase (latex) to prevent conversion increase (Mooney drift).

IPHA is clearly superior in performance to SDD and the combination of 6/1 SDD/DEHA (active basis). The SDD/DEHA combination has been widely used in the past because the non-volatile SDD protects the latex, while the volatile DEHA prevents popcorn polymer. These data demonstrate that IPHA can be used alone to replace this two-product system. This may be desirable not only from a performance standpoint, but from an inventory perspective as well.

Shortstop costs for SBR were compared for each of the above systems. The data (Figure 5) were calculated based on the results presented in Figure 4, using realistic shortstop prices. Overall, the relative use cost for IPHA is below that for the conventional systems.

Figure 5. Relative Shortstop Costs



The potential for cost savings will depend upon the polymerization recipes, plant operating conditions and local shortstop prices. Also, this analysis does not take into account the shortstop levels required to provide acceptable control of popcorn polymer. Each plant must therefore determine the optimum level of IPHA to provide the required Mooney Viscosity and popcorn polymer control.

Nitrosamine-Free Rubber

German regulations limit the allowable airborne levels of certain volatile nitrosamines. Synthetic rubber producers selling into the European market therefore want to supply nitrosamine-free products. SDD can form nitrosodimethyl-amine (NDMA), one of the volatile nitrosamines targeted in the German regulations; this can occur in the presence of strong acids (e.g. sulfuric) and nitrosating agents (e.g. sodium nitrite), which may be present during coagulation of the latex. Since NDMA can sometimes be detected in the finished rubber, use of SDD or SDD/DEHA is undesirable.

Use of CHAINGUARD I-15 as the sole shortstop has been shown not to lead to formation of detectable nitrosamines. To demonstrate this, the SBR recipe in Table 1 was prepared and shortstopped with 0.10 pphm IPHA, the highest level likely to be used in practice. The latex was coagulated, the rubber extracted with methanol and the extract concentrated for analysis by gas chromatography coupled to a thermal energy analyzer detector; this is the same technique used by an industry-recognized independent testing laboratory. No nitrosamines were detected in the extract and the rubber was therefore judged nitrosamine-free.

Analyses by an independent testing laboratory of commercial SBR and NBR shortstopped with IPHA, have likewise shown that these elastomers do not contain detectable levels of the specified nitrosamines.

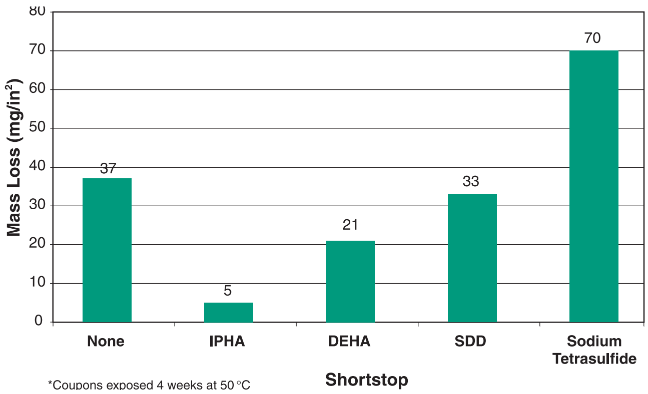
CHAINGUARD I-15 is therefore the shortstop of choice for nitrosamine-free recipes.

Favorable Elastomer Color

Elastomer color is important in applications such as footwear. It has been reported that in some instances elastomers shortstopped with CHAINGUARD I-15 have a more desirable color (lighter or more favorable shade) than those stopped with SDD/DEHA or DEHA alone. For example, in one case it was noted that NBR shortstopped with DEHA turned orange, while that with IPHA did not. In another case, NBR color improved when IPHA replaced SDD/DEHA. This color benefit with IPHA is expected to depend upon factors such as recipe type and processing conditions.

Figure 6. Corrosion of C-1010 Mild Steel*

(1% Shortstop Actives in Tap Water)



Avoids Emission Problems Associated with Other Shortstops

SDD can form poisonous, flammable carbon disulfide in the presence of strong acids (i.e. sulfuric acid during latex coagulation), and can also release toxic, flammable hydrogen sulfide if exposed to high temperatures. Sodium tetrasulfide releases hydrogen sulfide on exposure to acids. These toxic gases can potentially create an unsafe working environment and/or lead to plant emission problems. In the U.S., both carbon disulfide and hydrogen sulfide are regulated as hazardous air pollutants (HAPS) under the Clean Air Act. Replacement of SDD and sodium polysulfides with CHAINGUARD I-15 allows plants to avoid these concerns.

No Corrosion Problems

Sodium polysulfide shortstops are known to cause corrosion problems in monomer recovery units constructed of mild carbon steel, such as C-1010. The data in Figure 6 compare the corrosivity of dilute aqueous shortstop solutions and plain water (labeled "None") toward C-1010 steel. As expected, the sodium tetrasulfide solution is significantly more corrosive to C-1010 than plain water. The CHAINGUARD (IPHA) solution, on the other hand, inhibits corrosion of this alloy very effectively. The DEHA solution inhibits corrosion, but to a lesser degree than IPHA, while SDD neither promotes nor inhibits corrosion.

CHAINGUARD I-15 is therefore an excellent replacement for sodium polysulfide shortstops, thereby reducing corrosion problems in plants constructed of mild steel alloys.

Less Carryover into Recycled Monomer

In the production of NBR, unconverted acrylonitrile is often recycled to improve process economics and minimize waste volume. Because water has some solubility in acrylonitrile (~3% at 20°C), some of the shortstop (highly water soluble) that carries over with the recovered monomer/water mixture will reside in the acrylonitrile. The residual shortstop can inhibit polymerization of the recycled monomer, requiring upward adjustment of the initiator system (inconvenience, increased cost).

Shortstops having lower vapor/liquid partitioning ratios should be present at lower levels in the recycled acrylonitrile, meaning less need for initiator adjustment. Comparing IPHA (V/L ratio = 1.4) versus DEHA (V/L ratio = 5.9), less IPHA should be present in recycled acrylonitrile. Therefore, with CHAINGUARD I-15, there should be less need for initiator adjustment and cost savings may result.

Key to Raw Material Suppliers

[1]Eastman Chemical
[2]DSR-40; Arizona Chemical Co.
[3]T-11 Fatty Acid; Proctor & Gamble Chemicals
[4]Darvan WAQ; R.T. Vanderbilt Co.
[5]Aldrich Chemical Co.
[6]Fluka Chemie

Product Stewardship

ANGUS encourages its customers to review their applications of ANGUS products from the standpoint of human health and environmental quality. To help ensure that ANGUS products are not used in ways for which they are not intended, ANGUS personnel will assist customers in dealing with environmental and product safety considerations. For assistance, product Safety Data Sheets, or other information, please contact your ANGUS representative at the numbers provided in this document. When considering the use of any ANGUS product in a particular application, review the latest Safety Data Sheet to ensure that the intended use is within the scope of approved uses and can be accomplished safely. Before handling any of the products, obtain available product safety information including the Safety Data Sheet(s) and take the necessary steps to ensure safety of use.

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