Paper No. 9

SP and CST Technologies – A new generation of cost saving curatives in rubber processing.

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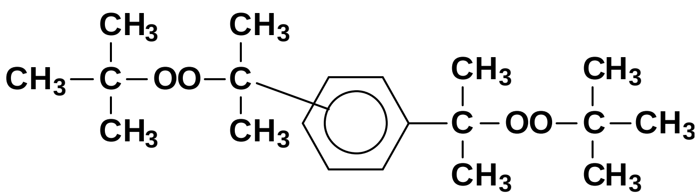
Two New Peroxide Grades based on LuperoxÒ F



m/p-di(t-butylperoxy)isopropylbenzene

LUPEROX F40M-SP

BENEFITS DURING COMPOUNDING:

- Outstanding scorch protection in EPDM formulations at compounding temperatures
- Speeds up your mixing operation. Possible to use a one-pass mixing step.
- Assists in compound development, making it possible to use lower particle sized fillers to achieve targeted physical properties without compromising scorch safety.

BENEFITS FOR YOUR PROCESS:

- Equal weight crosslinking efficiency compared to 40% peroxide assay grades
- Improved productivity for extrusion, compression molding and injection molding
- 20% Longer scorch time at cure temperature
- Commercially available as a 40% peroxide-EPDM masterbatch in a free-flowing pellet form

LUPEROX F-CST

BENEFITS DURING COMPOUNDING:

- Same scorch time performance as Luperox F40M-SP
- Outstanding scorch protection in EPDM formulations at compounding temperatures
- Speeds up your mixing operation. Possible to use a one-pass mixing step.

BENEFITS FOR YOUR PROCESS:

- 20% Faster cure rate without changing process temperatures (improved productivity)
- 20% Longer scorch time at cure temperatures (improved process safety)
- Equal weight crosslinking efficiency compared to 40% peroxide assay grades
- Improved productivity for extrusion, compression molding and injection molding
- Commercially available (end of 2004), as a free flowing powder on inert fillers with 40% peroxide activity.

SP and CST Technologies – A new generation of cost saving curatives in rubber processing.

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Arkema, Inc., Organic Peroxides Division

ABSTRACT

Improving processing time and scorch resistance of organic peroxide based curing systems is a constant objective that focuses on productivity increase, and consequently cost decrease. The improvement of processing time requires higher reactivity of the curing system, whereas an improvement in scorch resistance requires lower reactivity.

To answer this contradictory challenge, ATOFINA has developed two novel scorch protection technologies that can be applied to all peroxide grades. Initially, we have developed two grades of 1,3 & 1,4-di(t-butylperoxy)diisopropylbenzene, using SP and CST technologies. SP (Scorch Protected) technology provides an increased scorch time that is about three times higher than the standard grade at typical compounding temperature. CST (Controlled Speed Technology) simultaneously provides, increased scorch protection (equivalent to the SP grade), with a significantly faster cure (about 20% faster than standard grade). These new generations of organic peroxides have been developed to address the needs voiced by rubber processing customers.

INTRODUCTION

This paper describes two new peroxide crosslinking technologies called "SP" (Scorch Protection) and "CST" (Controlled Speed Technology) developed by ATOFINA that provide very efficient scorch protection. Scorch is unwanted or pre-mature crosslinking that can occur during mixing or extrusion operations, or even during the actual crosslinking process. Two new products, Luperox® F40M-SP and Luperox® F-CST have been commercialized based on the well-known Luperox® F peroxide, whose chemical name is 1,3 & 1,4-di(t-butylperoxy)diisopropylbenzene.

Luperox F40M-SP and Luperox F-CST can provide three times greater scorch protection, compared to the standard grade. There are many ways to take advantage of this scorch protection, for example; faster compounding, faster extrusion and faster molding operations at increased temperatures with no scorch threat and less scrap. In addition, Luperox F-CST exhibits faster curing at equivalent temperatures, which constitutes an extra source of productivity increase and cost saving. In this paper we compare the performance of these new peroxides grades to the standard peroxide in two EPDM elastomer compositions.

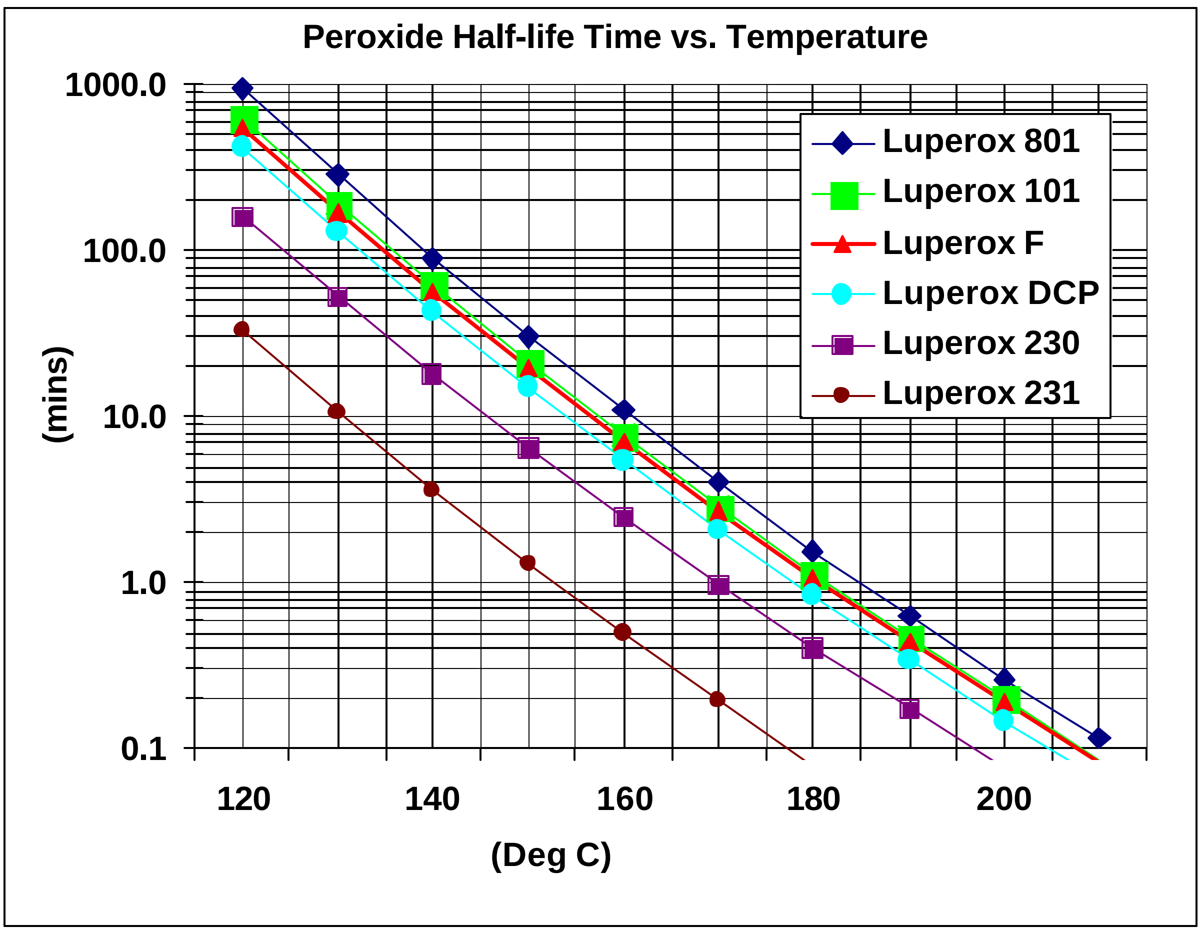
DISCUSSION

Atofina manufactures seven different classes of organic peroxides and a total of approximately fifty different unique molecules. For crosslinking various elastomers and engineering rubbers, there are two important organic peroxide classes: the Dialkyl peroxides and the Peroxyketals[1,2]. Dialkyl peroxides are by far the most efficient and cost-effective organic peroxide class for a wide range of crosslinking applications. The most common Dialkyl peroxides[3] are: dicumyl peroxide (Luperox DC), 1,3&1,4-di(*tert*-butylperoxy)diisopropylbenzene (Luperox F) and 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (Luperox 101). When faster reactivity at lower temperatures is required, Peroxyketal peroxides are selected, particularly when crosslinking unsaturated elastomers or when coagents are used[4]. The two most common Peroxyketal peroxides used in crosslinking are 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox 231) and n-butyl-4,4-di(t-butylperoxy)valerate (Luperox 230).

The chemical structures of these peroxides govern their kinetic behavior during thermal decomposition. Other properties are also affected, such as, the energy of the free radicals produced, the physical form of the peroxide (solid or liquid), its solubility, volatility, flash point, storage temperature and self accelerating decomposition temperature[5], etc.

Scorch time and cure time are key parameters for crosslinking applications. These parameters strongly depend on the chemical structure, and more specifically, on the time-temperature half-life[6] profiles of the organic peroxides (see Fig 1).

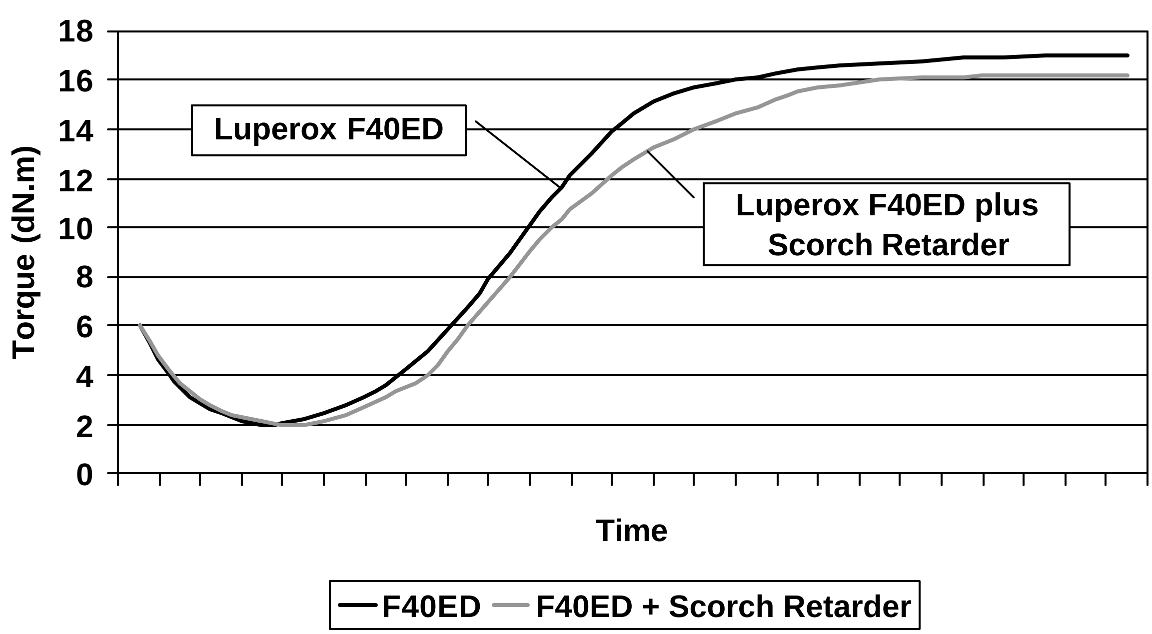
Fig 1: Half-life time vs. temperature in n-dodecane.



However, it is possible to adjust both scorch time and cure time using certain additives. In particular, traditional antioxidants[7] have been used as “scorch retarders” to increase scorch time, which is the length of time before any significant crosslinking begins. Typically, these classical antioxidants are merely free radical scavengers whose role is to react with the free radicals generated by the organic peroxide and therefore prevent them from prematurely reacting with the polymer.

However, to be fully efficient, the reaction between the free radical and the “scorch retarder” must be faster than the reaction between the free radical and the polymer. The resulting trapped free radicals must then be available later on for crosslinking. This goal is very difficult to achieve in EPDM based compounds. Moreover, it is worth pointing out that the free radicals trapped by these classical “scorch retarders” are not able to subsequently participate in the crosslinking process. The end result is a significant loss of crosslink density as shown below in Fig 2, often accompanied with an increase in the time to cure. Using more peroxide to compensate for this loss in crosslinking will reduce the scorch time, creating a vicious circle. Thus these inefficient classical scorch retarders merely produce an irreversible reduction in the actual peroxide concentration. The result is very similar to merely adding less peroxide, which of course, reduces the crosslink density, increases scorch time, and unfortunately increases the cure time as well.

Fig 2: Comparison of Curing Profiles of Luperox F40ED and Luperox F40ED + Classical Scorch Retarder (Crosslinking EPDM)



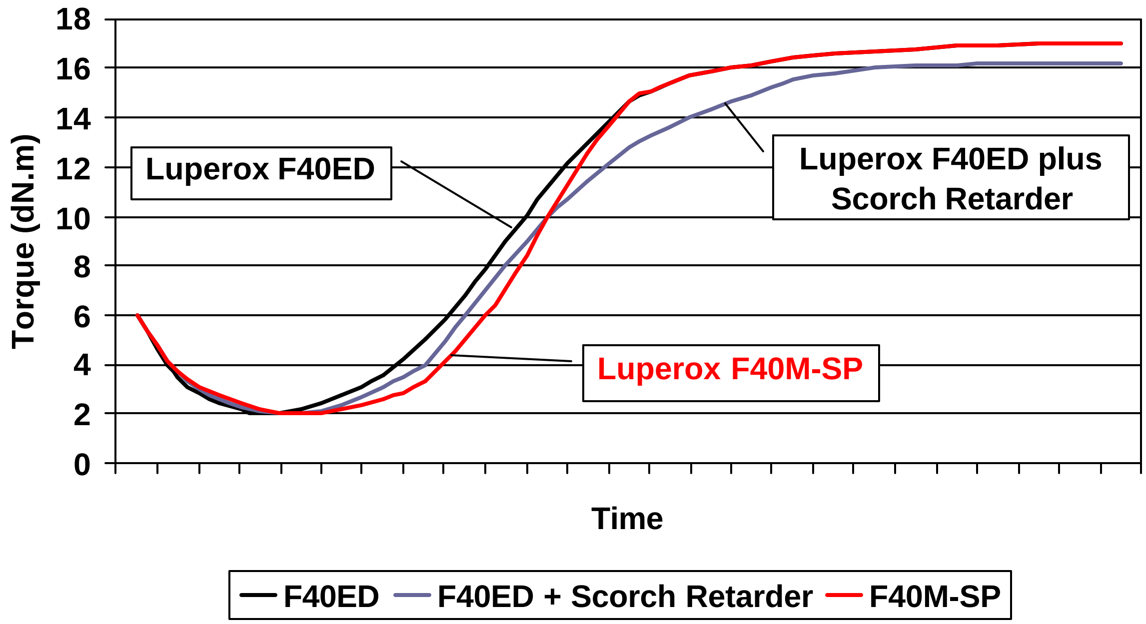
Note: Luperox F40ED is the traditional organic peroxide 1,3&1,4-di(tert-butylperoxy) diisopropylbenzene peroxide at 40% assay as a polymer masterbatch in pellet form, for easier and faster compounding. It is used in Figure 2, with and without a classical antioxidant-type “Scorch Retarder” that imparts scorch time, but sacrifices crosslinking.

"SP" - Scorch Protection Technology

ATOFINA has developed organic peroxides compositions based on a new scorch protection technology that provides outstanding benefits when crosslinking EPDM. This technology overcomes all the aforementioned serious limitations encountered with classical antioxidant scorch retarders.

As shown in Fig 3, the main benefit of the new "SP Technology" is its faster and efficient free radical trapping ability, providing significantly longer scorch time protection compared to the classical retarder, with a crosslinking efficiency equivalent to the standard peroxide with additive.

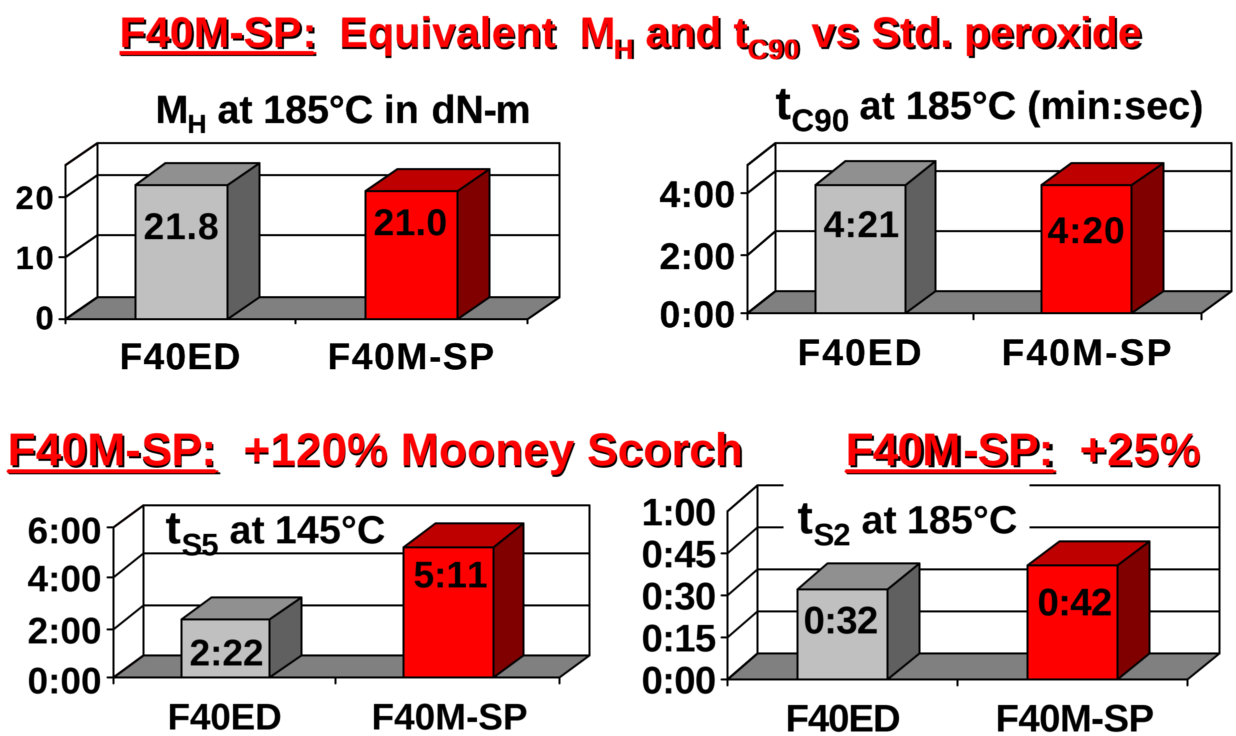
Fig 3: Comparison of cure profiles of Luperox F40ED; Luperox F40ED + Scorch Retarder, and Luperox F40M-SP (Crosslinking EPDM)



Luperox F40M-SP is the first peroxide grade commercialized using the "SP" technology, based upon 1,3 & 1,4-di(t-butylperoxy)diisopropylbenzene. Luperox F40M-SP is a proprietary scorch resistant peroxide polymer masterbatch, compounded at 40% assay in EPDM. *The physical form of Luperox F40M-SP is a free-flowing EPDM polymer pellet.* Luperox F40ED is the standard 40% peroxide EPDM masterbatch, in pellet form. In this paper we provide the results obtained using two proprietary, commercial EPDM formulations representing two different applications: seals and automotive.

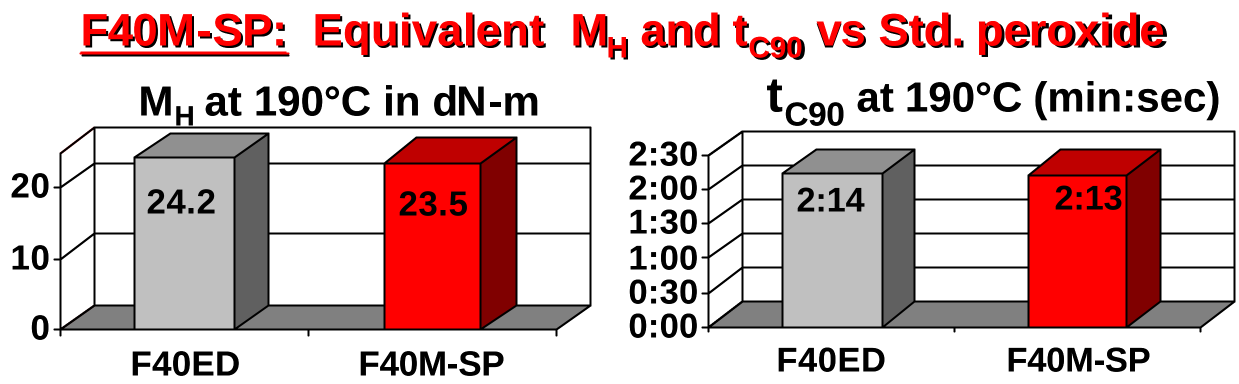
The comparison of Luperox F40M-SP with Luperox F40ED using an EPDM seal formulation is shown in Fig 4. The crosslink density and the time to final cure have been found to be comparable. Scorch time has been measured at two different temperatures, at 145°C using a Mooney viscometer and at 185°C using an RPA[8]. The scorch time attained by Luperox F40M-SP at 145°C is more than two times longer than the standard peroxide Luperox F40ED. This advantage is even larger at lower compounding temperatures. We found that Luperox F40M-SP can provide a scorch time that is about three times longer that the standard peroxide at 130°C, which is a commonly used mixing or “drop-temperature”. More interestingly for this EPDM seal application, the scorch time difference at 185°C is about 25% longer with F40M-SP. This result clearly indicates possible reduction in scrap and even a shorter mold cycle time (cure time), leading to improved productivity. Indeed, with such a scorch time improvement, one can envision an increase in mold temperature, which would result in a much shorter cycle time without scorch related problems.

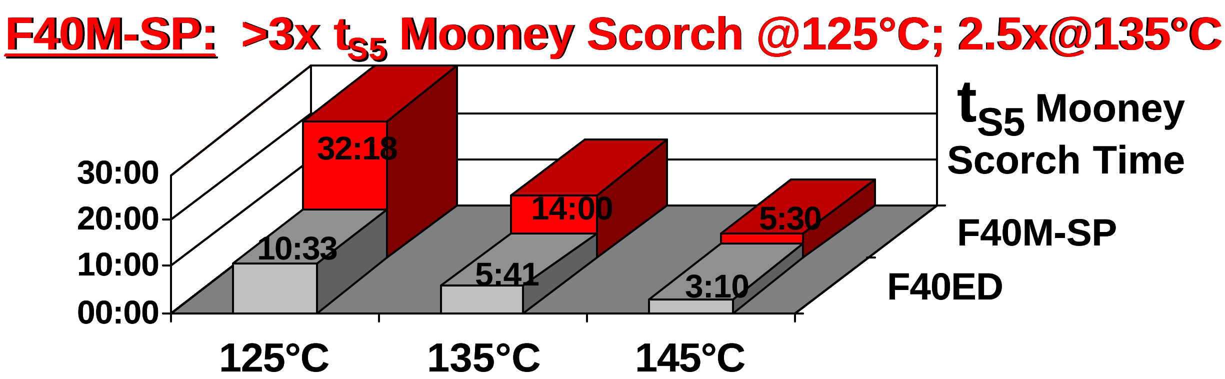
Fig 4: Performance comparison between Luperox F40ED and F40M-SP
(EPDM Seal type compound)



In Fig 5, we compare the standard Luperox F40ED to the new Luperox F40M-SP in a proprietary automotive EPDM compound. We find that Luperox F40M-SP offers a scorch time that is three times longer when compounding at 125°C, based upon the t_{S5} Mooney scorch time values. Time to 90% of final cure (t_{C90} mins.) and final crosslink densities (M_H in deciNewton-meters) are comparable when crosslinking at 190°C using an RPA. Thus, F40M-SP provides significant improvement in scorch time with virtually no change in the other important cure characteristics.

Fig 5: Performance Comparison Between Luperox F40ED and F40M-SP
(EPDM based Automotive Compound)





“SP” Peroxides Provide The Benefit Of Greater Productivity

The scorch protection shown in Fig 5 can directly improve productivity. One may increase mixer speed to provide faster compounding (as more process safety is obtained). Other options include going from a time consuming two-pass mixing step to a more efficient one-pass mixing step. One-pass mixing is typically not economical with the standard peroxide due to scorch issues that necessitate slower mixer speeds making the process too costly. The SP peroxide provides the benefits of a faster and more economical mixing process due to greater scorch time protection at compounding temperatures.

For extrusion compounding, faster screw speed (higher RPM) may be possible, again due to the significantly greater scorch time protection. Faster screw speeds provide higher productivity (throughput). Normally faster screw speeds would not be possible with the standard peroxide, as that would also increase melt temperatures due to shear-heating, thereby increasing the risk of scorch. This scorch protection would be particularly appreciated in injection molding processes, where scorch strongly penalizes production rate.

Note: This “SP” technology is being extended to include other Dialkyl type peroxides, e.g., Luperox 101, and Peroxyketals, e.g., Luperox 231 and Luperox 230.

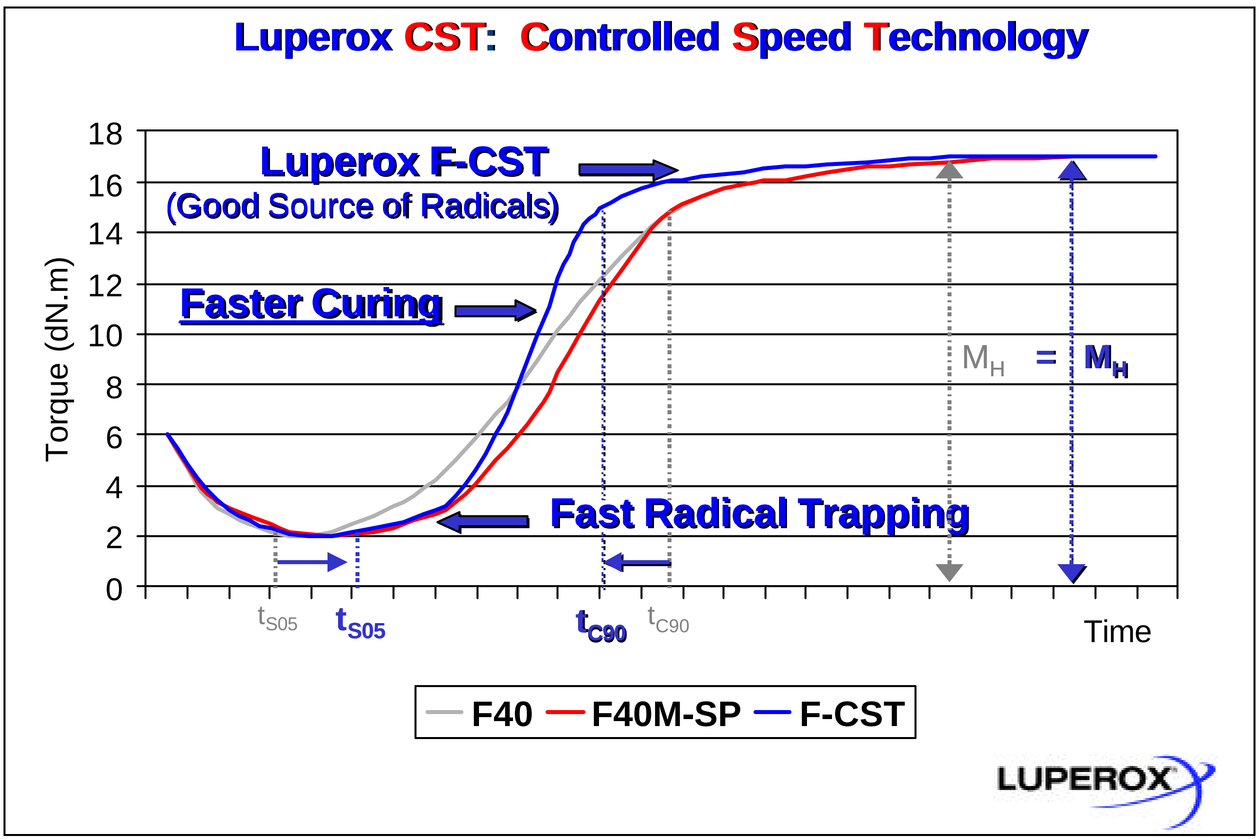
“CST” - Controlled Speed Technology

This is a new and very unique grade of peroxide with enhanced benefits, based upon the previously mentioned scorch protection technology. The CST peroxide grade was designed to provide the same scorch protection as the “SP” grade, however overall, the peroxide formulation is much more active. As a result, the time to final cure is significantly shorter. Thus CST provides the benefit of a significantly longer scorch time equivalent to that of the “SP” with a shorter cure time to further increase productivity.

In Fig 6, the rheometer cure curves show that Luperox F-CST provides the same scorch time protection as Luperox F40M-SP with a much faster rate of cure, thus a shorter cure time. The state of cure for both F40M-SP and F-CST products are equivalent to the standard 40% assay product F40ED, on an equal weight basis.

NOTE: The physical form of the Luperox F-CST peroxide is a free-flowing powder on inert filler.

Fig 6: Comparison of curing profiles of Luperox F40ED ; F40M-SP ; F-CST
(Crosslinking EPDM Elastomer)



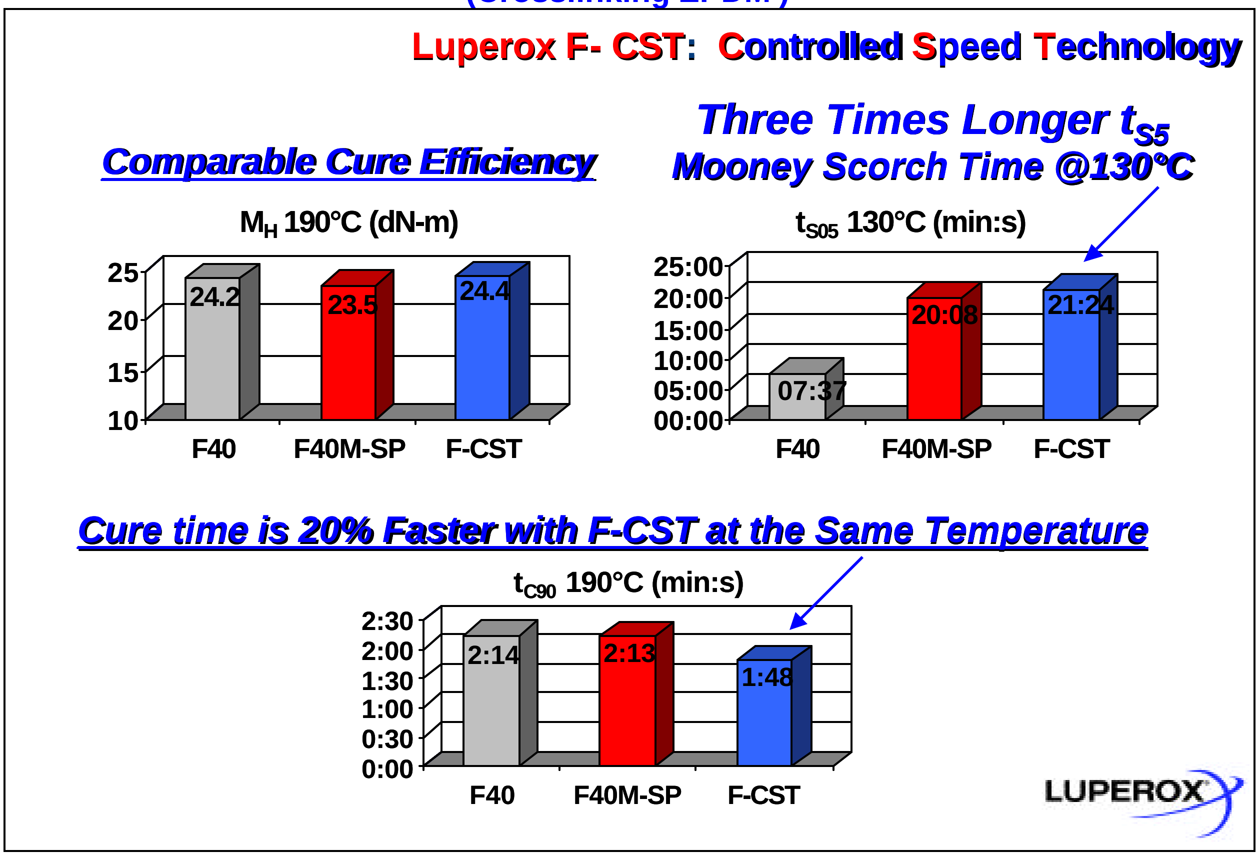
"Seeking The Ideal Peroxide Formulation"

As mentioned in our introduction, the elastomer crosslinking industry has been seeking an ideal peroxide formulation with the benefits of slower reactivity at compounding temperatures, while simultaneously possessing faster reactivity at cure temperatures. These are the precise benefits of the F-CST peroxide grade.

Luperox F-CST exhibits the same enhanced scorch time protection as the "SP Peroxide grade" Luperox F40M-SP, while simultaneously providing a 20% faster cure rate at equivalent crosslinking temperatures. Thus F-CST provides the benefits of increased compounding safety with the ability to further improve productivity by providing faster cure rates without increasing crosslinking temperatures.

As shown in Fig 7, Luperox F-CST has a longer scorch time (about three times more than Luperox F40ED at a standard compounding temperature) and a shorter cure time, more than a 20% faster cure rate compared to Luperox F40ED and Luperox F 40M-SP.

Fig 7: Performance comparison: Luperox F40ED – Luperox F-CST (Crosslinking EPDM)



Another way to express the gain in scorch time is to consider an increase in compounding temperature without reducing scorch time when compared to the standard peroxide grade with no retarder. This increase in compounding temperature might result from a faster mixing speed to reduce mix time or a perhaps a problematic, highly mineral-filled compound.

In Fig 8, F40M-SP and F-CST provide equivalent scorch time profiles that are clearly superior in performance compared to the standard peroxide Luperox F40ED. Fig 8 shows that the t_{S5} (min) Mooney scorch times of Luperox F40M-SP and Luperox F-CST **at 142°C** are equivalent to the scorch time of the standard peroxide F40ED being compounded at a lower temperature of **130°C**. *This represents a 12°C difference in mixer temperature with equivalent scorch time when using SP or CST peroxides.*

Using the SP or CST type peroxides, it is possible to use a faster mixing speed that generates a 12°C higher mixing temperature. Specifically, we found that F40M-SP and F-CST have the same scorch time protection at 142°C versus 130°C for the standard peroxide, F40ED. *Higher mixer temperatures would indicate faster mixer speeds and shorter compounding cycles, helping to reduce process cost.*

Hence these new peroxide grades provide the benefit of a wider processing window and the opportunity to improve productivity by providing the ability to shorten mixing time by increasing mix speed compared to the standard peroxide grade.

Fig 8: Mooney Scorch time comparisons at various temperatures in EPDM

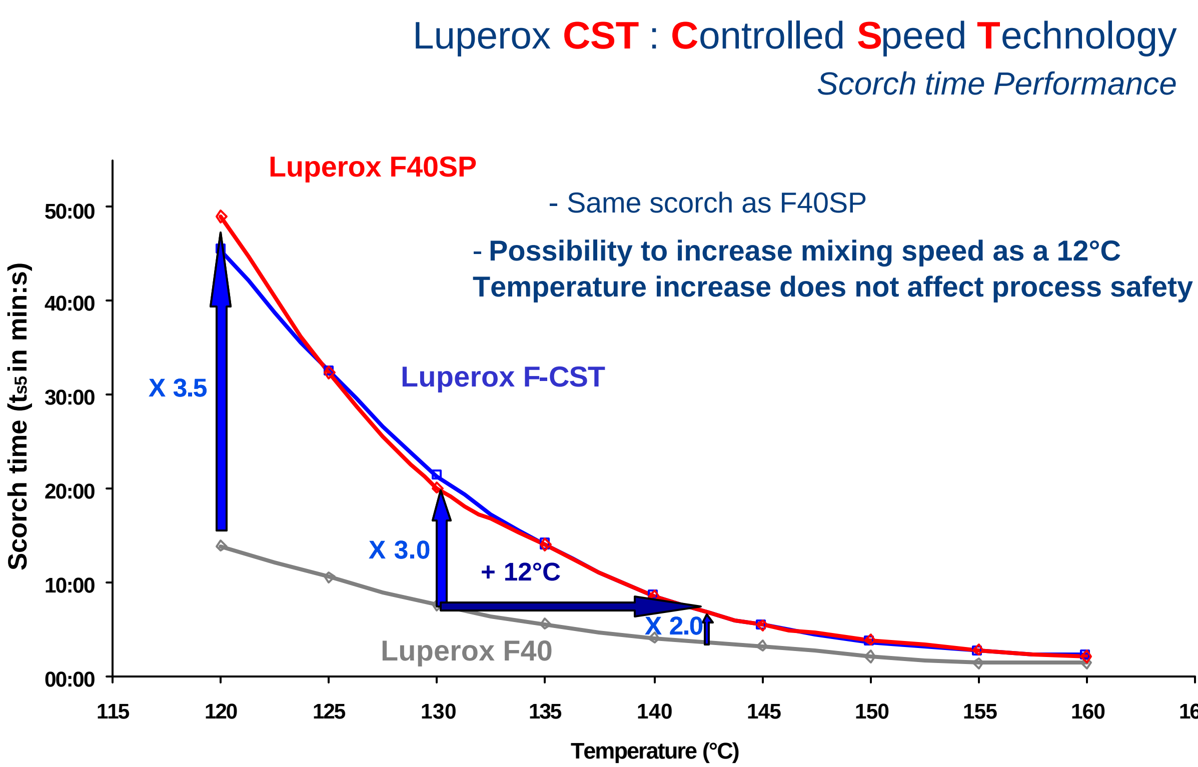


Fig 9 lists the RPA crosslinking data at 190°C and Mooney scorch time data (at the lower temperatures), for Luperox F40ED, Luperox F40M-SP and Luperox F-CST. These peroxide systems were compared on an equal weight basis of 8.0 phr.

The data clearly underscores the benefits of the new SP and CST peroxide grades. Significantly higher Mooney t_{S5} (min) scorch time protection is achieved with F40M-SP and F-CST at the lower compounding temperatures. The lower the temperature, the greater the performance advantage compared to the standard peroxide. This is particularly important when compounding standard peroxides into highly filled or reactive systems that are typically mixed at very controlled speeds to prevent scorch. Furthermore, Luperox F-CST provides a significantly faster rate of cure based on the t_{C90} values at 190°C. **Therefore F-CST also provides the benefit of improved productivity (e.g., a 20% cure time) with no change in process temperature!**

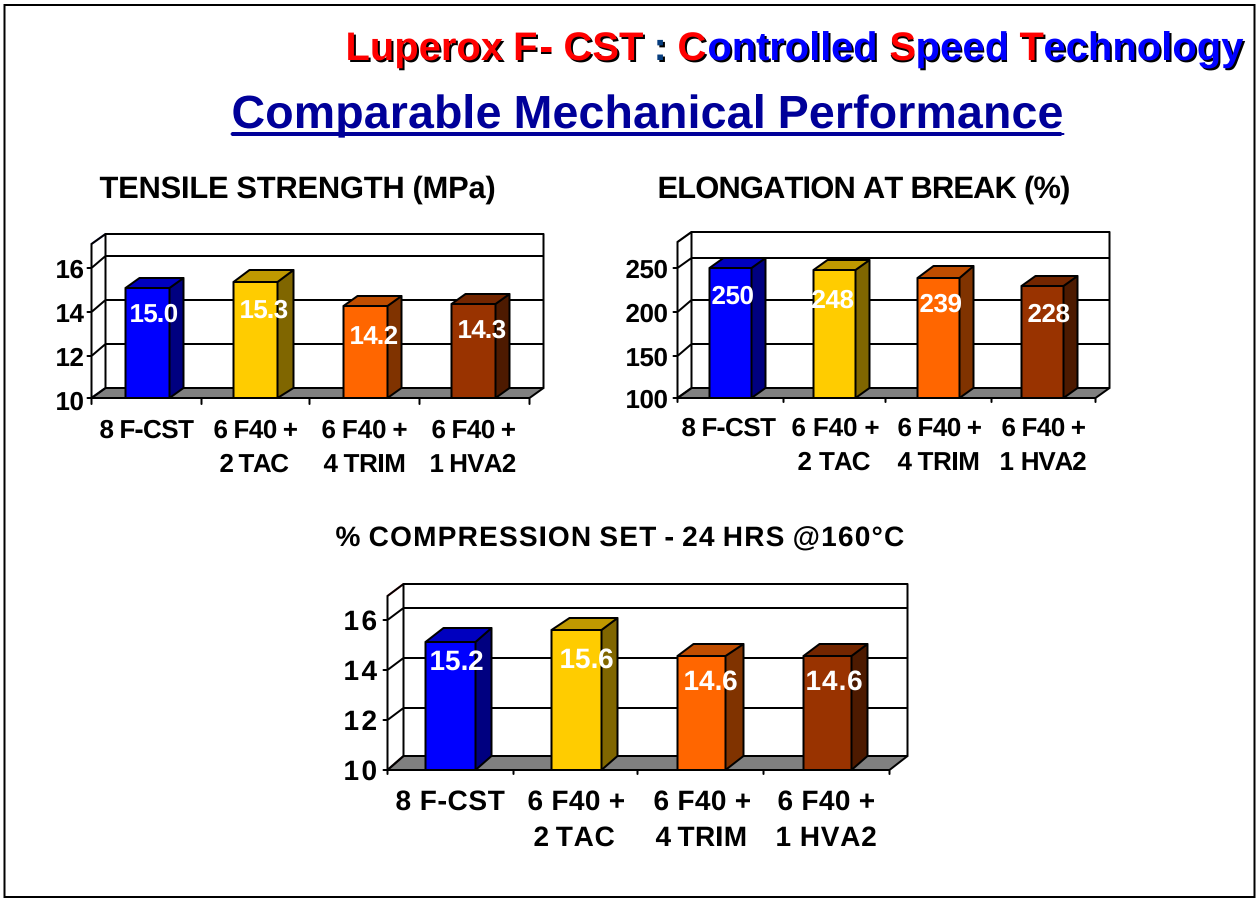
Fig 9: Comparison F40ED, F40M-SP and F-CST

Luperox type	8 phr F40ED	**8 phr F40M-SP**	**8 phr F-CST**
M_H (dN.m) at 190°C	24.2	23.5	24.4
t_{C90} (min:s) at **190°C**	2:14	2:13	**1:48**
t_{S5} (min:s) at **120°C**	13:56	**48:53**	**45:29**
t_{S5} (min:s) at **130°C**	7:37	**20:08**	**21:24**
t_{S5} (min:s) at **140°C**	4:09	**8:39**	**8:38**

We also studied the performance of Luperox F-CST compared to the standard peroxide Luperox F40ED blended with various crosslinking coagents. In Fig 10 we compare the various mechanical properties obtained with Luperox F-CST to Luperox F40ED blended with three of the mostly commonly used coagents: TAC (triallyl cyanurate or Sartomer SR507), TRIM (also known as TMPTMA, trimethylolpropane trimethacrylate or Sartomer SR350) and HVA-2 (N,N'-phenylene bismaleimide, also called Vanax MBM or Sartomer SR525)[9,10]. Note: The amount of coagent used in each case was adjusted to obtain comparable M_H values. The phr values of coagent and peroxide used are provided below each bar graph in Fig 10.

Interestingly, it was found that for the most part, Luperox F-CST provides an equivalent crosslink level (M_H value) when compared on an equal weight basis, to the blends of the standard peroxide (Luperox F40ED) and coagent. Furthermore, Luperox F-CST leads to comparable tensile strength, elongation at break and compression set values. This data suggests an opportunity for increased cost-savings, as the use of a coagent may not be necessary when using F-CST.

Fig 10: Mechanical properties comparison with typically used coagents



To complete the comparison of Luperox F-CST versus the standard peroxide F40ED blended with various coagents, we show our Mooney scorch time and RPA crosslinking data for these blends. The results are summarized visually in bar graph form in Fig 11 and in tabular form in Fig 12.

The results show that Luperox F-CST has good crosslinking efficiency on a weight basis compared to F40ED blended with coagents. However, F-CST also provides one of the fastest rates of cure, about 30% faster than a F40ED-TAC based system, and is equivalent in speed to the HVA-2 (m-N,N'-phenylenebismaleimide) coagent system. However, the bismaleimide coagent is very reactive and can create scorch problems. This is clearly seen when measuring Mooney T_{S5} scorch times at 125C and 135C.

By far the best system for scorch time is the F-CST. When looking at these scorch time values, the reader fully realizes the exceptional behavior of Luperox F-CST which provides the shortest cure process with the best (longest) scorch time protection.

Fig 11: Comparison Luperox F-CST with typically used coagents

Benefit: ***LuperoxÒ F-CST gives faster cures & longer scorch times at equal cure***

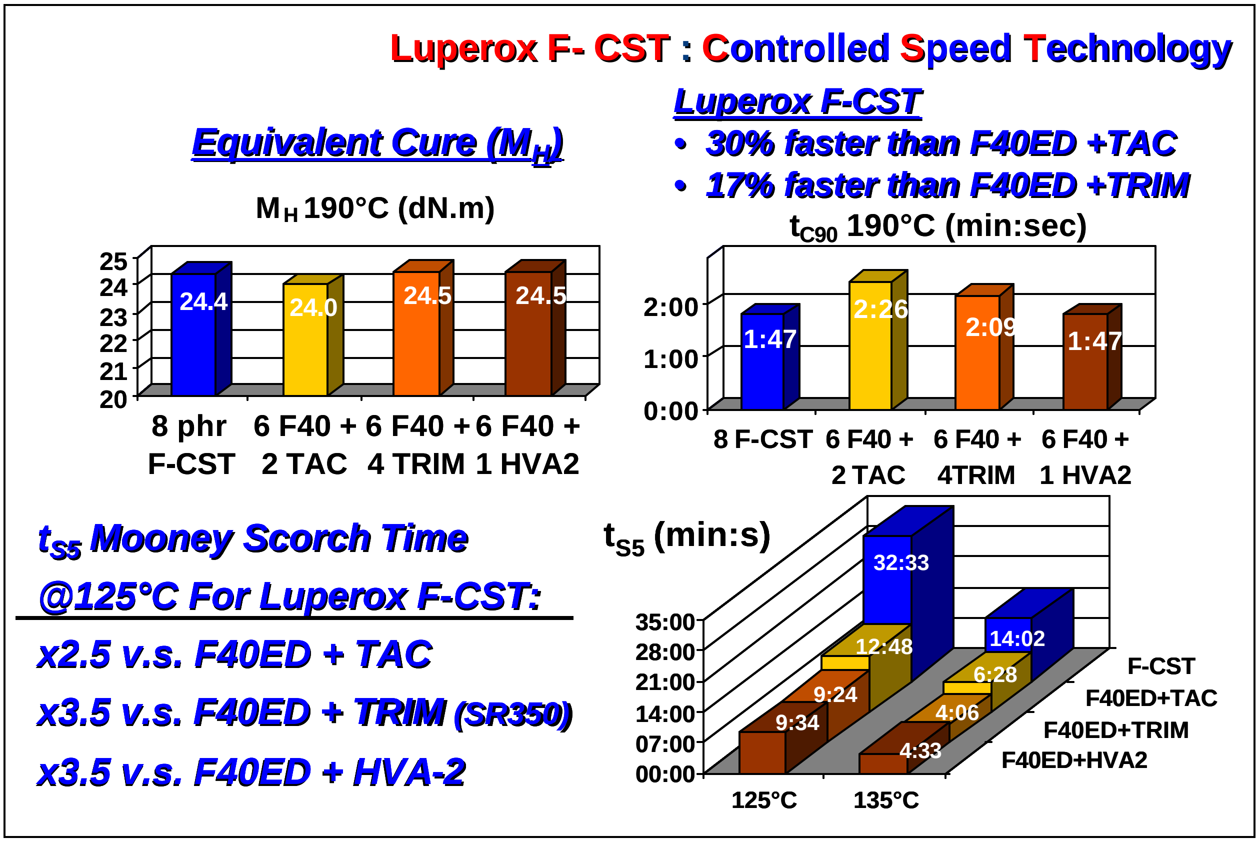


Fig 12: Comparison Luperox F-CST with typically used coagents

Luperox type	**8phr F-CST**	6 phr F40ED	6 phr F40ED	6 phr F40ED
Coagent type	- - -	2 phr TAC	4 phr TRIM	1 phr HVA-2
M_H (dN.m) at 190°C	24.4	24.0	24.5	24.5
t_{C90} (min:sec) at 190°C	**1:47**	2:26	2:09	*1:47*
t_{S5} (min:sec) at 125°C	**32:33**	12:48	9:24	9:34
t_{S5} (min:sec) at 135°C	**14:02**	6:28	4:06	4:33
Tensile strength (MPa)	15.0	15.3	14.2	14.3
Elongation (%)	250	248	239	228
Compression set (%)	15.2	15.6	14.6	14.6

CONCLUSION

Arkema Inc., has commercialized two new grades of peroxide based on a novel and efficient scorch protection technology. This technology has been applied to one of the most widely used and efficient Dialkyl type peroxides, Luperox F, to create two new commercial products: Luperox F40M-SP and Luperox F-CST. The physical form of Luperox F40M-SP is a free-flowing polymer pellet; Luperox F-CST is a free-flowing powder on inert filler.

Luperox F40M-SP provides outstanding scorch protection (three times the scorch time of the standard product, Luperox F40ED) while maintaining equal weight cure performance. Luperox F-CST is a remarkable evolution of Luperox F40M-SP as it concomitantly offers a better scorch time (same as Luperox F40M-SP) and a shorter cure time (20% faster than F40M-SP or F40ED). It is also demonstrated in this paper that Luperox F-CST may possibly replace some peroxide and coagent blends. The extension of SP and CST technologies to other peroxide grades is in progress.

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[9] Sartomer is a tradename of Sartomer Company; Oaklands Corporate Center; 502 Thomas Jones Way; Exton, PA 19341, telephone 610-363-4100. See website for additional info. www.sartomer.com

[10] Vanax and Varox are tradenames of the R. T. Vanderbilt Company, Inc.; 30 Winfield Street; Norwalk, Ct 06855; telephone 800-243-6064; See website: http://www.rtvanderbilt.com/vnews

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