

# **SP and CST Technologies A new generation of cost saving curatives in rubber processing - Part 2**

**By: Laurent KEROMNES, Alfredo DEFRANCISCI,  
Arnaud PREBE and Leonard H. PALYS\***



**Arkema  
Peroxides Department  
Centre de Recherche Rhone-Alpes  
Rue Henri Moissan  
69493 Pierre-Benite, FRANCE  
011 +33 4 92 33 79 05 / 011 +33 4 72 39 8244**

**Arkema Inc.\*  
Organic Peroxides R&D  
900 First Avenue, King of Prussia, PA 19406-0936  
(800)-626-3404 ext 6068 (610)-878-6068**

**LUPEROX®**  **ORGANIC PEROXIDES**

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**\*Speaker**

# SP and CST Technologies - A new generation of cost saving curatives in rubber processing – Part 2

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**Arkema Inc., Organic Peroxides**

## **ABSTRACT**

Improving the productivity of rubber compounding by increasing the mixer speed or replacing two-pass mixing with a one-pass mixing step has been a challenge when using organic peroxides. Attempting these productivity improvements can lead to higher mixing temperatures that could result in “scorch” or premature crosslinking. To address the issue of scorch during rubber compounding, peroxides with higher thermal stability have been used by the rubber industry. Unfortunately, these more thermally stable peroxides will also provide slower crosslinking rates that lower productivity for crosslinking operations, unless cure temperatures can be increased.

Previously, to answer this contradictory challenge, Arkema Inc.<sup>1</sup> introduced two new commercially available peroxide grades based on di(t-butylperoxy)diisopropylbenzene; Luperox® F40M-SP and Luperox® F-CST. These peroxides were designed specifically for crosslinking EPDM based upon novel “SP” Scorch Protected and “CST” Controlled Speed Technology. F40M-SP provides a two to three fold improvement in scorch time safety when compounding EPDM with no loss in cure rate, and significantly better elastomer flow properties with a 25% longer scorch time at cure temperatures for better mold-filling, compared to the standard peroxide. Thus F40M-SP provides increased productivity for EPDM compounding and crosslinking operations. The F-CST<sup>2</sup> is a unique peroxide grade that provides the same superior scorch time as the SP, but with a 20% faster cure rate in EPDM without changing the cure temperature, compared to the standard peroxide.

In this paper we review F40M-SP and F-CST and introduce three new SP peroxides: Luperox 231XL40-SP, Luperox 230XL40-SP and Luperox F40P-SP. 231XL40-SP and 230XL40-SP are two new “SP” peroxides designed for crosslinking EPDM and HNBR. Based on 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane and n-butyl-4,4-di(t-butylperoxy)valerate respectively, these Peroxyketal peroxides offer significantly faster cure rates at lower temperatures while providing up to three times the ts5 Mooney scorch time at compounding temperatures. 231XL40-SP and 230XL40-SP provide improved elastomer flow during injection molding and prevent scorch during cure that results in poor tear-trim, poor hot-tear, and backrinding problems. The third new SP peroxide, Luperox F40P-SP, contains an enhanced SP package specifically designed for use in HNBR and CPE compounding and crosslinking. F40P-SP provides much longer scorch times during the compounding of chlorinated polyethylene (CPE) even when mixing very reactive crosslinking coagents to provide faster cure rates in continuous vulcanization (CV) steam tube lines, used extensively in wire & cable manufacture.

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## INTRODUCTION

This paper reviews the benefits of the new Luperox® “SP” and “CST” peroxide crosslinking technologies developed by Arkema Inc. The SP and CST peroxide products are being sold to the rubber industry by our distributor, R. T. Vanderbilt Company, Inc, under the Varox® tradename<sup>3</sup>. “SP” (Scorch Protection) and “CST” (Controlled Speed Technology) provide very efficient scorch protection, where scorch is defined as unwanted or pre-mature crosslinking that can occur during mixing or extrusion or during the actual crosslinking process. The various organic peroxides used in this paper for crosslinking EPDM, HNBR and CPE can be found in Table 1, below.

**Table 1**  
**Organic Peroxides Used in this Paper**

Arkema Inc.	R. T. Vanderbilt Company, Inc.	Peroxide Abbreviations used in Paper & General Description
Luperox® F40KEP	Varox® 802-40KE	<b>F40KEP</b> m/p-di(t-butylperoxy)diisopropyl benzene dispersed in clay powder
Luperox <sup>◊</sup> F40M-SP	Varox <sup>◊</sup> 802 SP-40MB	<b>F40M-SP</b> SP (Scorch Protection) grade of m/p-di(t-butylperoxy)diisopropyl benzene in EPDM pellet masterbatch
Luperox <sup>◊</sup> F40P-SP	Varox <sup>◊</sup> 802 SP-40C	<b>F40P-SP</b> SP (Scorch Protection) grade of m/p-di(t-butylperoxy)diisopropyl benzene dispersed in calcium carbonate powder. Contains higher level of SP, designed for NBR, HNBR.
Luperox <sup>◊</sup> F-CST	Varox <sup>◊</sup> 802-40CST	<b>F-CST</b> CST (Controlled Speed Technology) grade of m/p-di(t-butylperoxy)diisopropyl benzene on calcium carbonate filler
Luperox® 230XL40	Varox® 230 XL	<b>230XL</b> n-butyl 4,4-di(t-butylperoxy)valerate on calcium carbonate
Luperox <sup>◊</sup> 230XL40-SP	Varox <sup>◊</sup> 230 XL-SP	<b>230XL-SP</b> SP (Scorch Protection) grade of n-butyl 4,4-di(t-butylperoxy)valerate on calcium carbonate
Luperox® 231XL40	Varox® 231 XL	<b>231XL</b> 1,1(di-t-butylperoxy)-3,3,5-trimethylcyclohexane on calcium carbonate
Luperox <sup>◊</sup> 231XL40-SP	Varox <sup>◊</sup> 231 XL-SP	<b>231XL-SP</b> SP (Scorch Protection) grade 1,1(di-t-butylperoxy)-3,3,5-trimethylcyclohexane on calcium carbonate

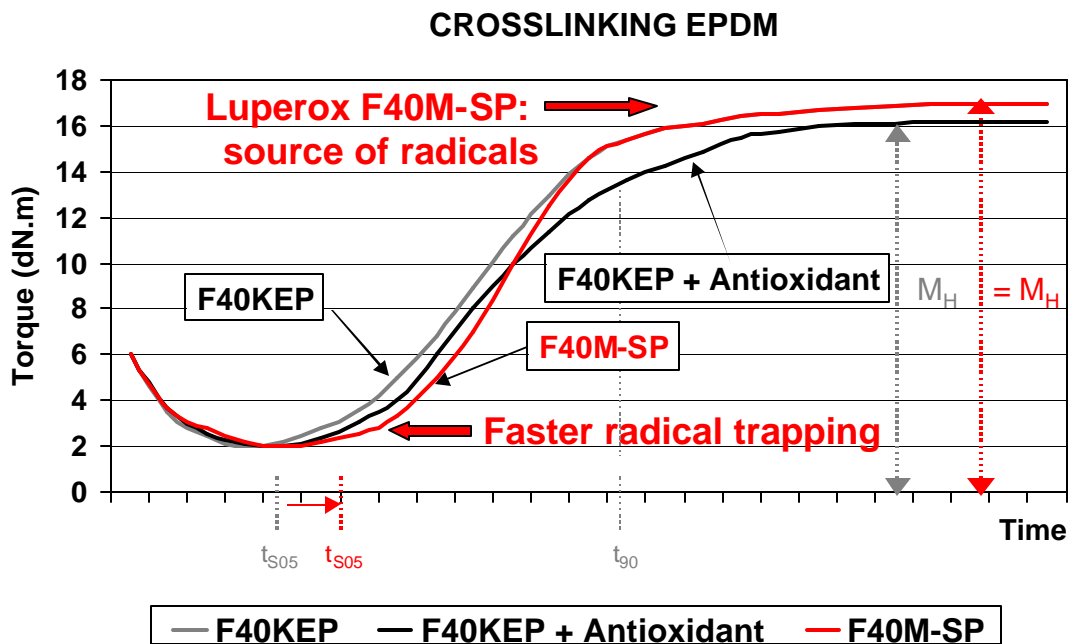
## DISCUSSION

### “SP” - Scorch Protected Technology; Crosslinking EPDM

“SP” organic peroxides provide superior scorch time protection during compounding and crosslinking, with equivalent crosslinking and cure rate performance in EPDM versus the standard peroxide grade. This is possible, as “SP” peroxides trap free radicals quickly and efficiently, then these trapped radicals are released for use during the crosslinking reaction. As shown in Figure 1, the SP technology overcomes all the serious limitations encountered with classical antioxidant scorch retarders that permanently trap radicals to provide scorch protection, with the distinct disadvantage of reduced crosslinking.

**Figure 1**

**Comparing Cure profiles of standard Luperox® F40KE, Luperox® F40KE plus a classical Antioxidant, and Luperox® F40M-SP a new “SP” grade**



**Figure 1:** The “SP” grade of peroxides are faster and more efficient in trapping free radicals, providing significantly longer scorch time protection compared to the use of classical antioxidants. The advantage of the SP peroxide is that these trapped radicals are then released for efficient crosslinking. Antioxidants provide some scorch protection, but reduce crosslinking efficiency, as the radicals are permanently destroyed and no longer available for crosslinking.

## **EPDM: “SP” Peroxides Increase Productivity during Compounding and Crosslinking**

### **Luperox® F40M-SP: Designed for EPDM Compounding**

Luperox F40M-SP was specifically designed for use in EPDM, to provide an increase in productivity for compounding and crosslinking operations. It is commercially available as a 40% peroxide EPDM masterbatch in pellet form. Luperox F40M-SP provides equal weight crosslinking performance compared to Luperox F40KEP, the standard 40% di(t-butylperoxy)diisopropylbenzene on inert clay filler.

When compounding the standard F40KEP in EPDM, the typical mixer “drop” temperature range is 125°C to 130°C. F40M-SP provides a  $t_{S5}$  Mooney scorch time that is three times longer than the standard peroxide over this temperature range. This significantly longer scorch time safety provides the option of going from a two-pass to a one-pass mixing step, or to increase mixer speed to provide faster compounding and improved productivity.

Not shown in Figure 2, is that F40M-SP also provides a 20% to 25% increase in scorch time when crosslinking EPDM at 190°C, versus the standard F40KEP. This longer scorch time protection is beneficial in an injection molding process to provide uniform mold filling. Furthermore, a longer scorch time will allow a 5°C to 10°C increase in cure temperature with a scorch time that is equivalent to the standard peroxide’s result at the original temperature. This will provide a significant decrease in the crosslinking cycle time and thus, increase the productivity of the injection molding operation.

R. T. Vanderbilt<sup>4</sup> conducted several DuPont spider mold flow tests on a Nordel IP4640 EPDM compound at 177°C. The improved mold flow properties provided by F40M-SP (Varox 802SP-40MB) at crosslinking temperatures is clearly shown in Figure 3. The “spider” molded part produced with F40M-SP weighed 15g. Thus the “SP provides ~20% more mass flow into the mold, vs. only 12.8g. for the standard F40KEP peroxide.

### **Luperox® F-CST: Designed for EPDM to provide Long scorch times during Compounding and 20% Faster Cure Rate**

“Seeking The Ideal Peroxide Formulation.” The EPDM elastomer crosslinking industry has been seeking an ideal peroxide formulation with slower reactivity at compounding temperatures and faster reactivity at cure temperatures. These are the precise benefits of Luperox F-CST when used to crosslink EPDM.

F-CST provides excellent scorch safety during compounding, equivalent to F40M-SP. However, F-CST can significantly increase productivity by providing a 20% faster cure rate for injection molding of EPDM, without increasing the cure temperature (Figure 4).

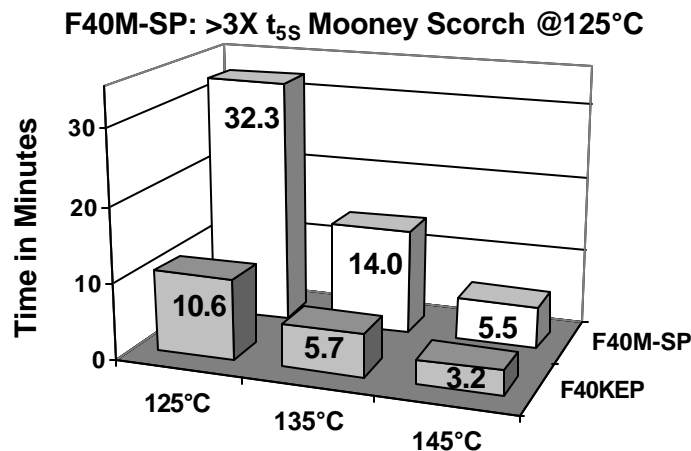
In Figure 5, Luperox F-CST provides a longer scorch time (about three times more than the standard F40KEP when compounding EPDM at 130°C and the same scorch time as the “SP” peroxide, F40M-SP). However, Figure 4 shows that F-CST clearly has a shorter cure time, providing a 20% faster crosslinking rate for improved productivity vs. F40KEP and F40M-SP, when crosslinking EPDM at 190°C. Luperox F-CST provides equal weight crosslinking efficiency compared to F40M-SP and F40KEP when curing EPDM as per Figure 6.

In Figure 7, DuPont Spider Mold Flow Tests<sup>4</sup> performed by The R. T. Vanderbilt Company, Inc., show the superior mold flow performance for Varox 802-40CST (Luperox F-CST) when curing EPDM at 177°C, compared to the standard peroxide Varox 802-40KE (Luperox F40KEP). This clearly highlights the unique advantages of the F-CST. Luperox F-CST provides an unprecedented combination of equal weight crosslinking performance in EPDM, a 20% faster cure rate without increasing the cure temperature, while providing better mold filling capability. The “spider” molded part made with F-CST weighed 14.2 g. versus only 12.8 g. for the standard peroxide.

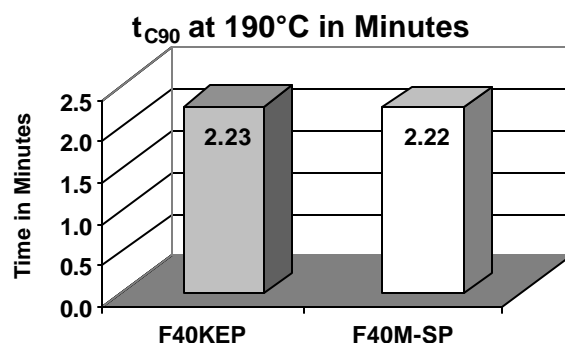
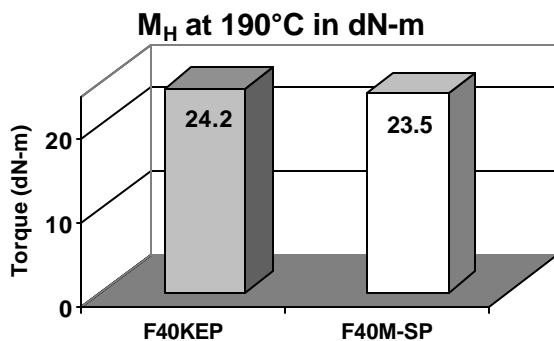
**Figure 2**

**Luperox® F40M-SP provides superior scorch time protection during compounding with equal weight cure performance to the standard peroxide, F40KEP**

**SUPERIOR EPDM COMPOUNDING PERFORMANCE AT 125°C WITH F40M-SP**



**... AND EQUAL WT. CROSSLINKING EFFICIENCY IN EPDM**



**Figure 3**

**Luperox® F40M-SP (Varox 802SP-40MB) Spider Mold Flow Test<sup>4</sup> in EPDM at 177°C**

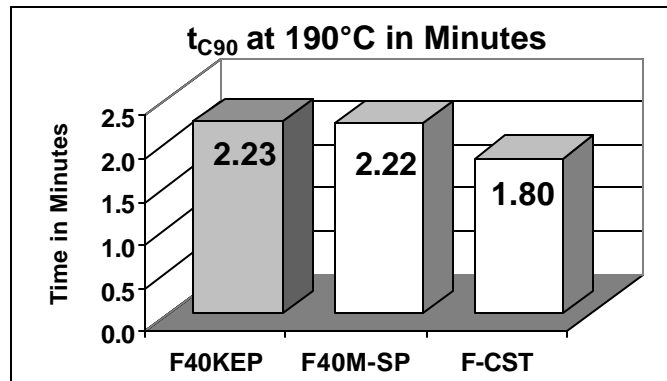


**(15.0 g.) 8 phr Luperox® F40M-SP**

**(12.8 g.) 8 phr Luperox® F40KEP**

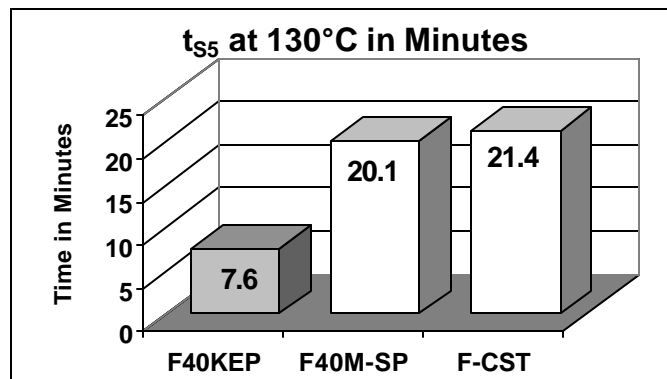
**Figure 4**

**Luperox® F-CST provides 20% Faster Crosslinking of EPDM at 190C**



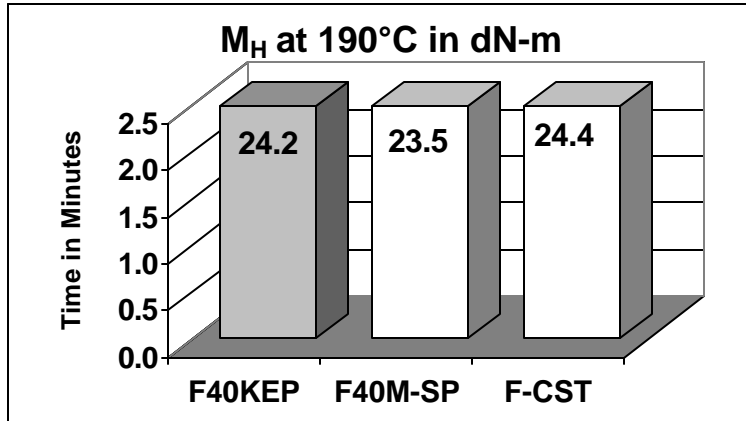
**Figure 5**

**F-CST Provides Three Times Longer t<sub>S5</sub> Mooney Scorch Time@130°C**



**Figure 6**

**F-CST & F40M-SP provide equal state of cure vs Standard Peroxide  
(Crosslinking EPDM)**



**Figure 7**

**Luperox® F-CST (Varox® 802-40CST) vs F40KEP, Spider Mold Flow Test<sup>4</sup> at 177°C  
(Crosslinking Nordel IP 4640 EPDM)**



**(14.2 g.) 8 phr Luperox® F-CST**

**(12.8 g.) 8 phr Luperox® F40KEP**

## Luperox® 231XL40-SP and Luperox® 230XL40-SP: Curing EPDM

Luperox 231XL40-SP and Luperox 230XL40-SP are two new “SP” (Scorch Protected) peroxide grades that were specifically formulated for compounding and crosslinking EPDM and HNBR type elastomers.

These two new “SP” formulations can be used to solve many manufacturing problems that require lower temperature curing, e.g., crosslinked rubber over thermoplastic parts, and faster curing at lower temperatures to improve productivity. The 231XL-SP and 230XL-SP peroxides can provide desirable and desperately needed shorter cure cycles at lower crosslinking temperatures, while avoiding the major concern of premature crosslinking, or scorch during compounding and injection molding, due to the novel “SP” Scorch Protected technology.

Scorch is a major concern when compounding and curing elastomers with the standard Luperox 231 and Luperox 230 peroxides. These “231” and “230” peroxides have considerably lower thermal stability compared to Luperox F, as shown in Table 2 below.

**Table 2**

### **Peroxide Half-Life<sup>5</sup> Time in Seconds vs Reaction Temperature in Deg. C**

(Deg C)	Luperox 231 (seconds)	Luperox 230 (seconds)	Luperox F (seconds)
160°C	29.8	148.6	423.2
165°C	18.6	93.1	259.7
170°C	11.7	58.9	161.1
175°C	7.5	37.7	101.0
180°C	4.8	24.3	64.0
185°C	3.1	15.8	41.0
190°C	2.1	10.4	26.5

The typical mixer drop temperatures used by the rubber industry for the “231” and “230” peroxides are 90°C and 100°C respectively, to prevent scorch or premature crosslinking in the internal mixer.

In Figure 8, when compounding EPDM, 231XL-SP provides a  $t_{S5}$  Mooney scorch time at 110°C that is 2.66 times longer than the standard 231XL peroxide. In regard to crosslinking EPDM, 231XL-SP provides similar  $M_H$  (dN-m) and  $T_{C90}$  (mins.) values vs. the standard 231XL peroxide on an equal weight basis.

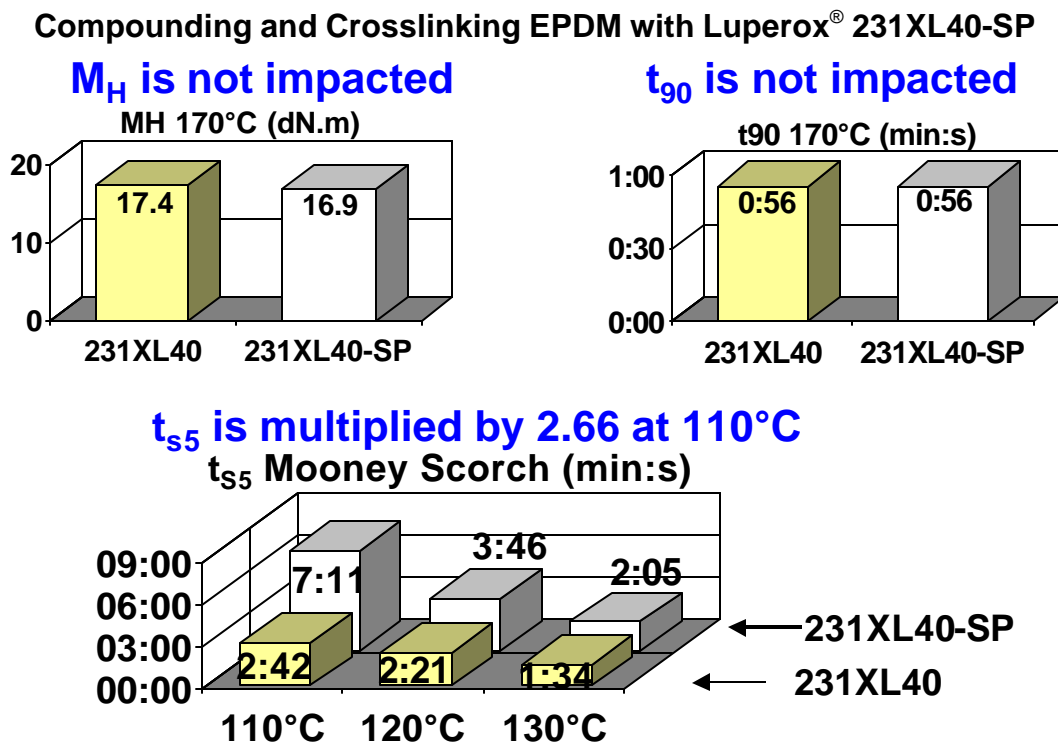
In Figure 9 at the compounding temperature of 110°C, Luperox 230XL-SP provides a  $t_{S5}$  Mooney scorch time that is four times longer than the standard 230XL peroxide in EPDM. Luperox 230XL-SP provides similar  $M_H$  (dN-m) and  $T_{C90}$  (mins.) values vs. the standard 230XL peroxide on an equal weight basis, when crosslinking EPDM.

In a recent report<sup>6</sup> kindly provided by the R. T. Vanderbilt Company, 230XL-SP was found to provide twice the scorch safety time at 132°C, compared to the standard product. Note: the typical “drop” temperatures for this peroxide is 100°C or less. They also concluded that Varox 230 XL-SP (Luperox 230XL40-SP) and Varox 231 XL-SP (Luperox 231XL40-SP) provided similar  $M_H$  and  $T_{C90}$  values when evaluated on an equal weight to the standard Varox peroxides in Nordel IP EPDM. Some of this data can be found in Table 3.

In addition, both 230XL-SP and 231XL-SP demonstrated superior mold flow at 157°C and 140.5°C respectively, based on DuPont spider mold flow tests. The photographs of the crosslinked spider mold test specimens for 230XL-SP and 231XL-SP in EPDM are provided in Figure 10 and Figure 11.

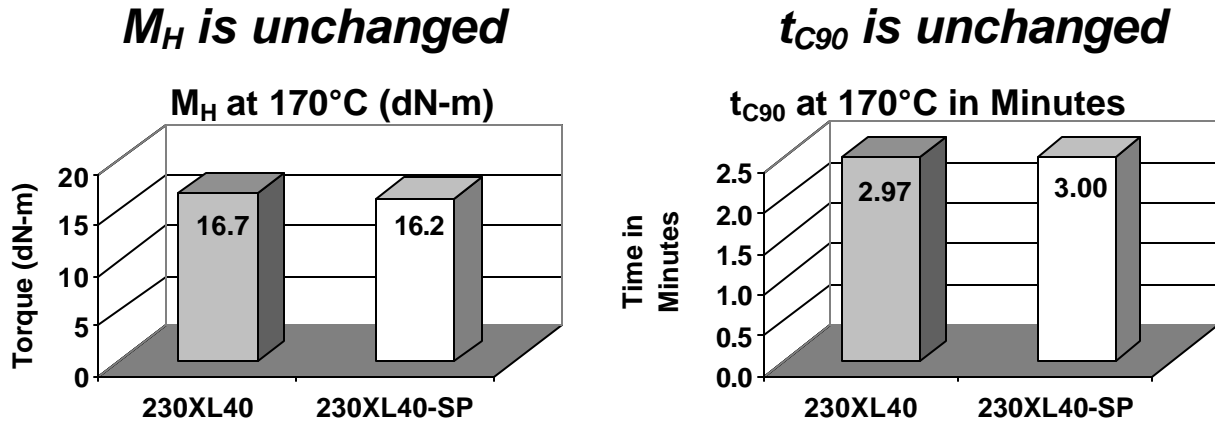
In summary, 231XL-SP and 230XL-SP greatly improve the compounding and crosslinking scorch time performance versus the standard reactive Peroxyketal peroxides. These two “SP” peroxides are recommended for EPDM and HNBR. Furthermore, the “SP” peroxide formulations provide enhanced molding filling (increased scorch protection) at cure temperatures to improve both productivity and quality of the finished crosslinked part.

**Figure 8**

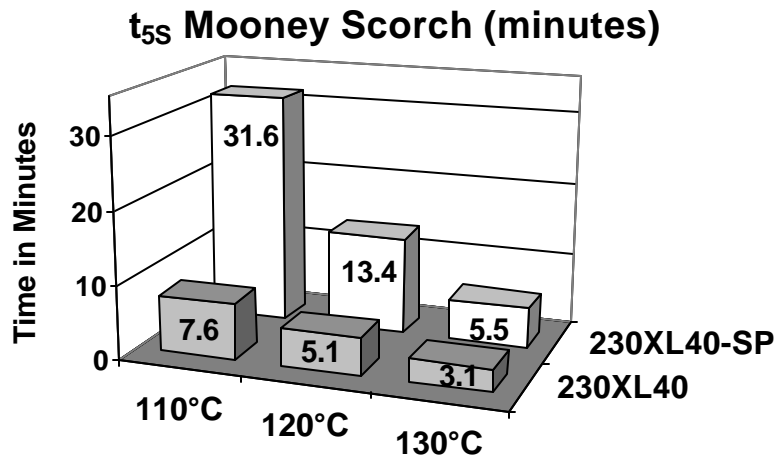


**Figure 9**

**Compounding and Crosslinking EPDM with Luperox® 230XL40-SP**



**230XL40-SP:  $t_{S5}$  Mooney Scorch is multiplied by 4 @110°C**



**Table 3****EPDM Formulation used by R. T. Vanderbilt Company, Inc.**

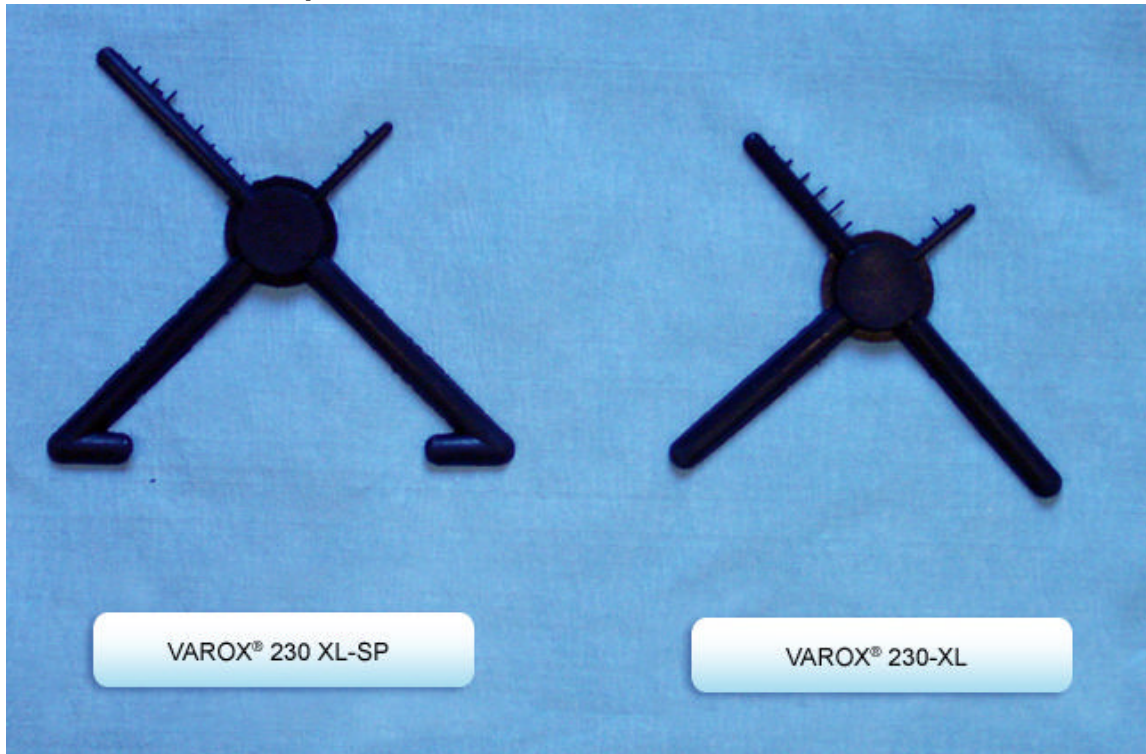
Ingredient	Parts
NORDEL IP 4640	100
Zinc Oxide	5
N990	35
N660	65
Sunpar 2280	20
Total	225

**Benefits of 230 & 231 “SP” Peroxyketal Peroxides when Compounding & Crosslinking EPDM for Improved Productivity**

Run Number:	1	2	3	4
EPDM Formulation	225	225	225	225
<b>230 XL-SP</b>	<b>8.0</b>	-	-	-
Varox 230 XL	-	8.0	-	-
<b>231 XL-SP</b>	-	-	<b>8.0</b>	-
Varox 231 XL	-	-	-	8.0
Mooney Scorch at 132°C (270°F)				
Minimum Viscosity, mu	49.2	49.3	53.3	58.2
t5 (minutes)	10.16	5.65	4.16	3.21
ASTM D5289 - MDR at Spider Mold Flow Temperatures, 0.5° Arc				
	157°C (315°F)		140.5°C (285°F)	
M <sub>L</sub> (dN-m)	1.2	2.1	2.5	2.5
M <sub>H</sub> (dN-m)	19.7	22.1	21.43	23.03
M <sub>H</sub> – M <sub>L</sub> (dN-m)	18.51	20.0	18.94	20.44
t <sub>S1</sub> , minutes	1.05	0.73	1.35	0.83
t <sub>C90</sub> , minutes	11.94	11.89	15.89	14.36
ASTM D412, Method A, Die D – Stress Strain Tests				
Tensile Strength, MPa	16.43	16.51	17.55	18.05
Elongation, %	299	278	292	264
ASTM D2240 – Shore A Durometer				
Points	67.8	67.2	65.8	65.7
<b>DuPont Spider Mold Flow Test</b> 3/8” Orifice, 20 Tons, 30.0g Charge, T90 Cure				
	157°C (315°F)		140.5°C (285°F)	
Weight, g	13.56	10.98	12.63	11.02
<i>( Please see the pictures of the Spider Mold Test, Figs. 3 &amp; 4 )</i>				

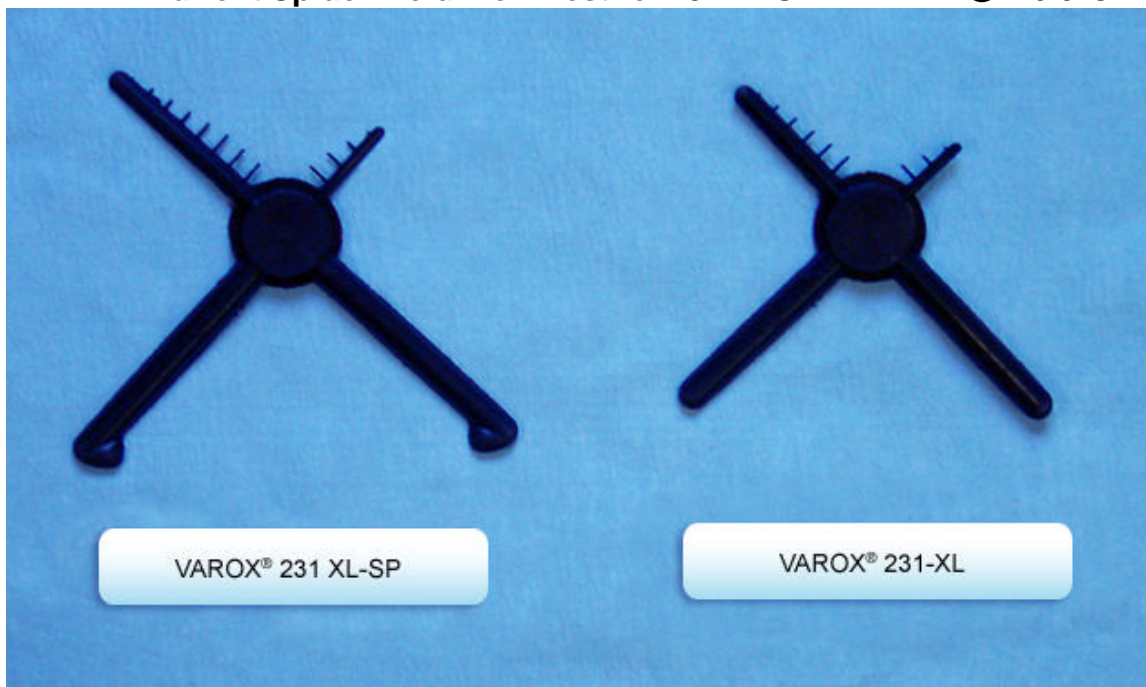
**Figure 10**

**DuPont Spider Mold Flow Test<sup>6</sup> of 230XL-SP in EPDM @157°C**



**Figure 11**

**DuPont Spider Mold Flow Test<sup>6</sup> of 231XL-SP in EPDM @140.5°C**



## **HNBR: “F40P-SP” Increases Productivity during Compounding and Crosslinking**

### **Luperox® F40P-SP: Curing & Compounding HNBR**

Luperox F40P-SP was recently developed specifically for compounding and crosslinking HNBR elastomers\*. This new F40P-SP peroxide contains a significantly enhanced SP scorch protection package, compared to F40M-SP, which was optimized for EPDM. However, HNBR rubber formulations can pose more difficult scorch time issues during compounding and crosslinking, compared to EPDM. F40P-SP provides significantly greater scorch time protection for HNBR and based on our results. However, it must be noted that 10t% to 15% more Luperox F40P-SP is required by weight, compared to the standard Luperox F40KEP peroxide, to maintain the same level of crosslinking.

In Table 4, 4.5 phr Luperox F40P-SP is needed (12.5% more of the F40P-SP) compared to 4.0 phr of the standard peroxide F40KEP, to provide a similar degree crosslinking ( $M_H-M_L$ ) and cure rate ( $T_{C90}$ ) for the Lanxess Therban C3446 HNBR elastomer. However, there are significant differences in the scorch time performance for the F40P-SP at the 180°C crosslinking and 130°C compounding temperatures.

When crosslinking HNBR at 180°C, F40P-SP provides a 40% increase in scorch time safety, based on the  $t_{S1}$  scorch time, as per Table 4 and Figure 12. This data demonstrates that F40P-SP will improve HNBR rubber flow in the mold at 180°C cure temperatures and would be especially useful for more complicated or convoluted molds by preventing poor knit lines that result in hot-tear problems. Alternatively, one could use F40P-SP in HNBR at perhaps 185°C and possibly match the scorch time of F40KEP at 180°C, to obtain a shorter mold cycle (faster cure rate) for improved productivity.

In HNBR at the 130°C “drop” temperature, F40P-SP provides a nearly a 300% increase in scorch time protection as per the  $t_{S1}$  values in Table 4 and Figure 13 and the rheograph curves in Figure 14. Thus, F40P-SP could be used to increase the uniformity of the peroxide concentration in the HNBR compound by increasing mixing time. This would reduce the standard deviation on the measured physical properties of the HNBR crosslinked parts from batch to batch, as long as mixing capacity is not an issue. Alternatively, due to the higher scorch safety of F40P-SP, one could increase the mixing capacity of the plant and improve productivity of the compounding operation by increasing the mixer speed without concern for scorch.

\*Note: We used the Lanxess Inc. Therban® C 3446 HNBR elastomer in all of the HNBR experiments in this paper.

**Table 4**

**Typical HNBR Formulation used for Luperox® F40P-SP Evaluation**

	Sample 1	Sample 2
HNBR	100	100
N-550	50	50
ZnO	3	3
MTBZ	1	1
TOTM	3	3
F40KEP	4	-
<b>F40PSP</b>	-	<b>4.5</b>

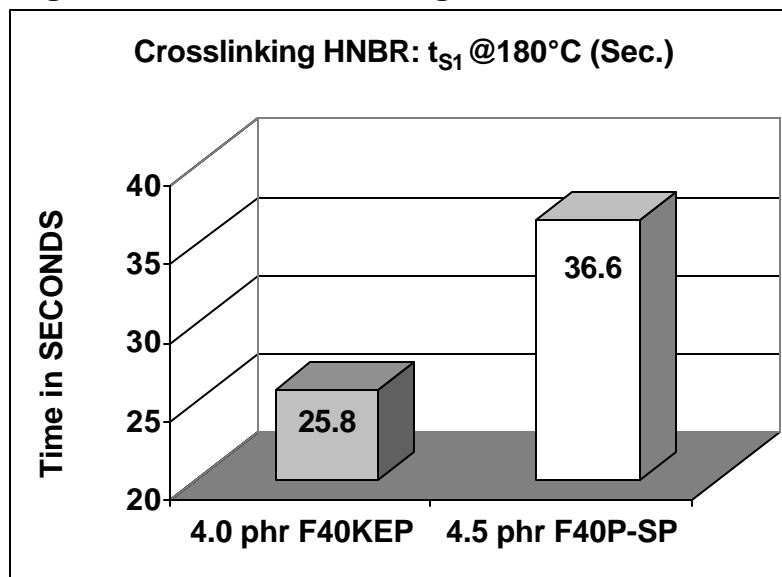
<b>Crosslinking HNBR: MDR @180 C</b>		
M <sub>H</sub> (dN-m)	32.26	31.19
M <sub>L</sub> (dN-m)	2.63	2.32
<b>MH- ML (dN-m)</b>	<b>29.63</b>	<b>28.87</b>
t <sub>C90</sub> (min)	5.06	5.15
t <sub>S1</sub> (sec)	25.80	36.60
t <sub>S2</sub> (sec)	32.40	43.60

<b>Compounding HNBR: MDR @ 130 C</b>		
t <sub>S0.2</sub> (minutes)	9.7	41.3
t <sub>S0.4</sub> (minutes)	14.5	53.2
t <sub>S0.6</sub> (minutes)	18.6	61.7
t <sub>S1</sub> (minutes)	26.8	75.0

Notes for Table 4: TOTM = trioctyl trimellitate ; MTBZ = mercaptobenzimidazole zinc salt ; HNBR = (Lanxess Inc.) Therban® C 3446, ACN = 34%, Double bonds = 4%

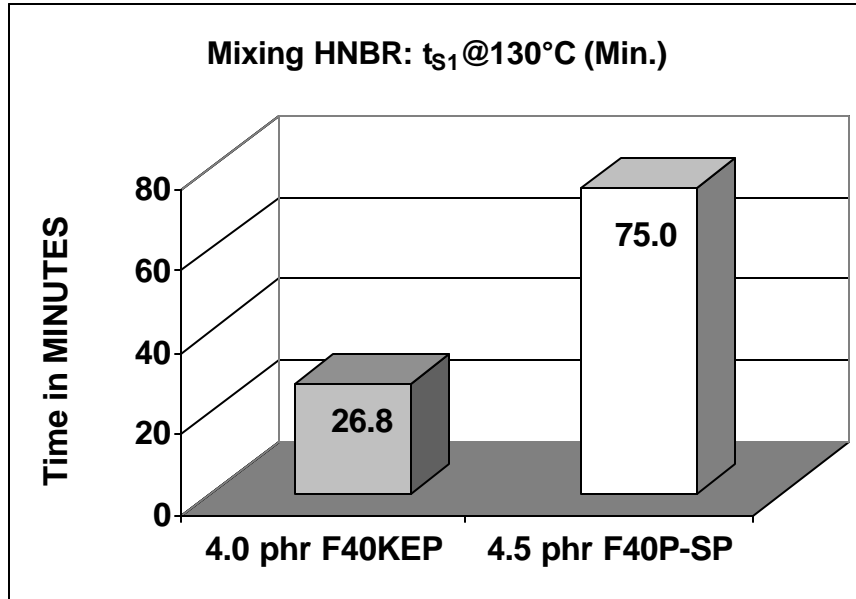
**Figure 12**

**Crosslinking HNBR @180°C: 40% longer t<sub>S1</sub> Scorch Time with F40P-SP**



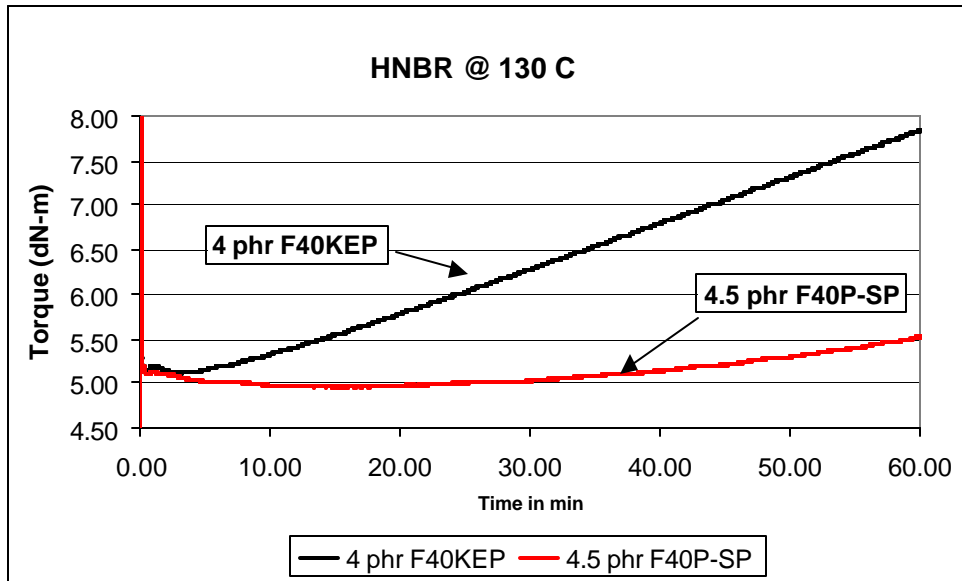
**Figure 13**

**Improved Compounding of HNBR at 130°C with Luperox® F40P-SP that Provides a ~300% Increase in the  $t_{S1}$  Scorch Time in Minutes.**



**Figure 14**

**Scorch Time Rheographs of Luperox® F40P-SP in HNBR at 130°C**



## **HNBR: Curing and Compounding with 231XL-SP to Improve Productivity**

Luperox 231XL-SP and Luperox 230XL-SP were designed for crosslinking EPDM and HNBR elastomers. Based on our data in Table 5 and Figure 15, we needed to add about 20% more Luperox 231XL40-SP to obtain a similar level of crosslinking ( $M_H-M_L$ ) for HNBR, compared to the standard Luperox 231XL40 peroxide. 231XL-SP gave an  $M_H-M_L$  of 30.2 vs only 28.7 for 231XL, so we might have only needed to add 18% more of the 231XL-SP, perhaps.

However, we obtained substantial increases in scorch time when curing and compounding the HNBR elastomer with the 231XL-SP peroxide formulation, compared to the standard product. When crosslinking HNBR at 152°C we noted in Table 5 and Figure 16, that one obtains 11 more seconds of mold filling time based on the improvement in  $t_{S1}$  scorch time, comparing 10 phr 231XL to 12 phr 231XL-SP. This is a 48% increase in scorch time safety for an injection molding process, when using 231XL-SP in an HNBR at 152°C.

Referring to Table 5 and Figure 17, we obtained a 228% increase in  $t_{S1}$  scorch time (a factor of >3 times greater scorch time) for 231XL-SP when compounding HNBR at 106°C. versus the standard 231XL peroxide. Again such a significant increase in scorch time gives the compounder the opportunity to increase mixer speed or move from a two-pass to a one-pass operation to improve compounding productivity.

## **HNBR: Compounding & Curing with Luperox® 230XL-SP**

Similar results are expected for Luperox 230XL-SP, based on several independent industrial evaluations when compounding and injection molding proprietary HNBR formulations<sup>7</sup>. The standard Luperox 230XL is lower in half-life than dicumyl peroxide, but it is the closest commercially available peroxide in regard to cure rate and scorch time performance. Using Luperox 230XL in place of dicumyl peroxide has always been problematic due to scorch issues during compounding and crosslinking or mold filling. Luperox 230XL-SP should be considered as a commercially viable replacement for the slower curing dicumyl peroxide, to improve productivity in compounding and crosslinking, and to eliminate the formation of acetophenone (odor) in the finished part.

**Table 5**

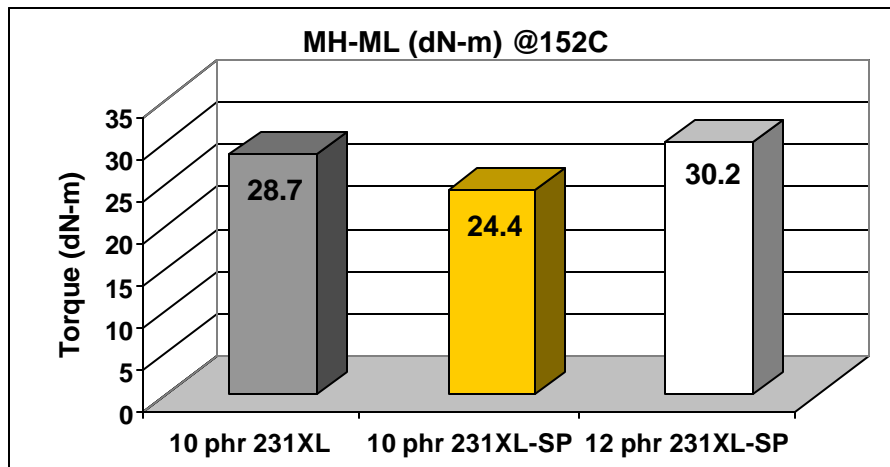
**Crosslinking and Compounding HNBR with Luperox® 231XL40-SP**

	Sample 1	Sample 2	Sample 3
*Therban HNBR	100	100	100
N-550	50	50	50
ZnO	3	3	3
MTBZ	1	1	1
TOTM	3	3	3
<b>231XL40</b>	<b>10</b>	-	-
<b>231XL40-SP</b>	-	10	<b>12</b>
<b>Crosslinking HNBR: MDR @152°C</b>			
M <sub>H</sub> (dN-m)	32.59	27.95	33.65
M <sub>L</sub> (dN-m)	3.94	3.56	3.43
M <sub>H</sub> -M <sub>L</sub> (dN-m)	28.66	24.39	30.22
t <sub>C90</sub> (minutes)	3.4	3.6	3.4
<b>t<sub>S0.5</sub> (seconds)</b>	20	31	<b>31</b>
<b>t<sub>S1</sub> (seconds)</b>	23	35	<b>34</b>
<b>t<sub>S2</sub> (seconds)</b>	28	42	<b>40</b>
<b>Compounding HNBR: MDR @106°C</b>			
t <sub>S0.5</sub> (minutes)	12.6	78.6	<b>67.2</b>
t <sub>S1</sub> (minutes)	24.9	96.6	<b>81.8</b>
t <sub>S2</sub> (minutes)	50	115	<b>105</b>

\*Lanxess Therban® C 3446 HNBR

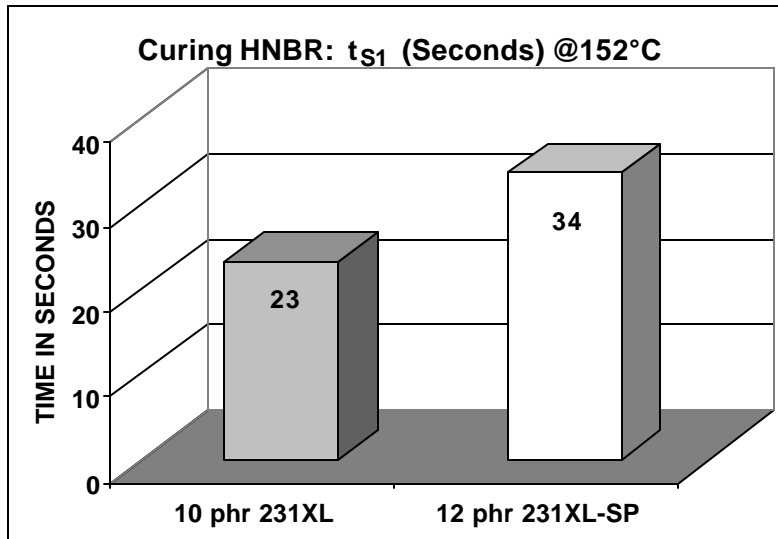
**Figure 15**

**Crosslinking HNBR with Luperox® 231XL-SP (M<sub>H</sub> – M<sub>L</sub>) at 152°C**



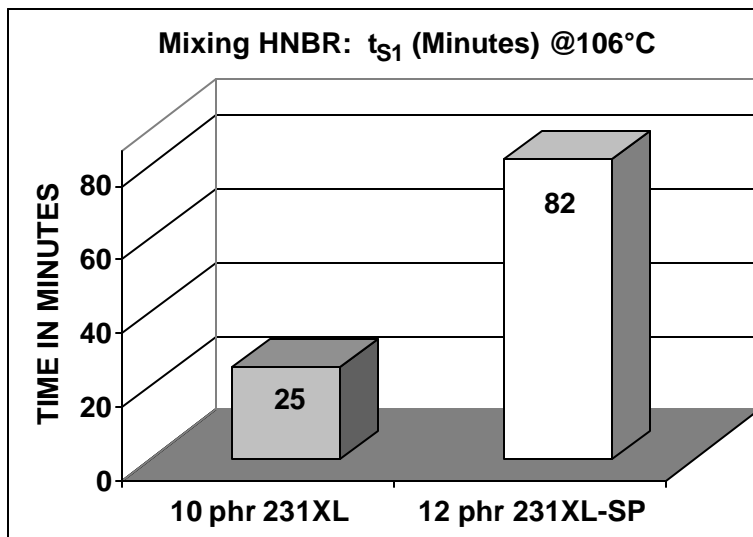
**Figure 16**

**Curing HNBR @152°C: 11 more Seconds for mold filling with 231XL-SP ( $t_{s1}$ )**



**Figure 17**

**Mixing HNBR @106°C: >3 Times Longer Mixing Time with 231XL-SP ( $t_{s1}$ )**



## **CPE: Increase Productivity with F40P-SP & Coagents**

### **Luperox® F40P-SP: Curing CPE for Cable Jacket**

When compounding and curing chlorinated polyethylene (CPE) for a wire and cable jacket, the goal is to increase productivity. To accomplish this, greater scorch protection is needed during the extrusion compounding, combined with the fastest cure rate possible in the continuous vulcanization (CV) tube, with no increase in the crosslinking temperature. Greater scorch protection is needed in the extruder to avoid premature crosslinking due to the higher extruder RPM required to make more ft/min of wire. The uncured cable jacket will pass through a steam heated (CV) tube. Tube length and steam temperature is limited so a more reactive crosslinking system is needed to increase productivity; otherwise, the cable jacket would be under-cured.

The Luperox F-CST formulation was optimized for EPDM to provide a long scorch time during compounding with a 20% faster cure rate without changing process temperatures. However, F-CST provided disappointing results. We do not recommend F-CST for this CPE application.

Referring to Table 6, a commonly used system for a CPE cable jacket is a blend of a scorch retarded acrylic type coagent with F40KEP. Acrylic coagents provide fast rates and the retarders help during compounding. This typical cure system is listed as our “Standard” in Table 6.

We evaluated Luperox F40P-SP (with the enhanced SP package developed for HNBR) along with several coagents. Our results are provided in Table 6 and in Figure 18, Figure 19 and Figure 20.

Table 6, Sample 2 provides the best overall result and is a blend of Vanax MBM and F40P-SP. The  $t_{C90}$  has been decreased 47% from 4.3 minutes to only 2.3 minutes, providing an 87% increase in cure productivity (nearly doubled productivity). Despite the fact that MBM is well known for scorch problems, the  $t_{S1}$  at 130°C was increased from 7.2 minutes to 47.8 minutes, a six-time factor increase in scorch time protection during the CPE compounding step.

Blends of peroxides can be used to change the rate of cure. In Table 6, Sample 3, we evaluated a 50-50 blend of 231XL-SP and F40P-SP with TAC coagent. This resulted in 43% increase in crosslinking productivity, but with an 18% loss of scorch time protection, based on the  $t_{S1}$  at 130°C. The 231XL-SP provided a fast cure, but also decreased the scorch time safety, relative to the much more thermally stable F40P-SP.

Table 6, Sample 1 (blend of TAC and F40P-SP) provided an 18% improvement in cure productivity with a six-time factor increase in scorch time during CPE compounding.

**Table 6**

**Crosslinking CPE with F40P-SP and Coagents for Wire & Cable Jacket**

	<i>Standard</i>	Sample 1	<b>Sample 2</b>	Sample 3
CPE	100	100	100	100
N-550	30	30	30	30
DIDP	30	30	30	30
CaCO3	125	125	125	125
MgO	5	5	5	5
SR-517	2	-	-	-
TAC	-	1.5	-	1.5
<b>MBM (HVA-2)</b>	-	-	<b>3</b>	-
<b>231-SP</b>	-	-	-	<b>4</b>
<i>F40KEP</i>	6	-	-	-
<b>F40P-SP</b>	-	<b>6</b>	<b>6</b>	<b>4</b>

<b>Crosslinking CPE: MDR @ 180 C</b>				
M <sub>H</sub> (dN-m)	33.07	35.52	32.42	33.40
M <sub>L</sub> (dN-m)	4.71	3.74	4.02	4.45
M <sub>H</sub> - M <sub>L</sub> (dN-m)	28.36	31.78	28.41	28.95
t <sub>C50</sub> (minutes)	1.2	1.4	0.9	0.7
<b>t<sub>C90</sub> (minutes)</b>	<b>4.3</b>	<b>3.6</b>	<b>2.3</b>	<b>3.0</b>
t <sub>S0.5</sub> (minutes)	0.4	0.4	0.4	0.2
t <sub>S1</sub> (minutes)	0.4	0.5	0.5	0.3
t <sub>S2</sub> (minutes)	0.5	0.6	0.5	0.3
t <sub>S5</sub> (minutes)	0.7	0.7	0.6	0.4
<b>% Decrease of t<sub>C90</sub></b>	<b>---</b>	<b>18%</b>	<b>47%</b>	<b>30%</b>

<b>Compounding CPE: MDR @ 130 C</b>				
t <sub>S0.2</sub> (minutes)	4.9	30.6	35.8	4.1
t <sub>S0.4</sub> (minutes)	6.0	34.6	40.8	4.7
t <sub>S0.5</sub> (minutes)	6.2	36.4	42.4	4.9
t <sub>S0.6</sub> (minutes)	6.4	38.2	43.8	5.2
t <sub>S0.8</sub> (minutes)	6.8	41.5	46.0	5.7
<b>t<sub>S1</sub> (minutes)</b>	<b>7.2</b>	<b>44.6</b>	<b>47.8</b>	<b>6.1</b>
t <sub>S2</sub> (minutes)	11.7	58.6	54.6	8.2

CPE = Dow Tyrin® CM0136 CPE, 36% CI

DIDP = Diisododecylphthalate

MBM, HVA-2 = N, N'-phenylene-bismaleimide coagent

R. T. Vanderbilt Company, Inc., Vanax® MBM

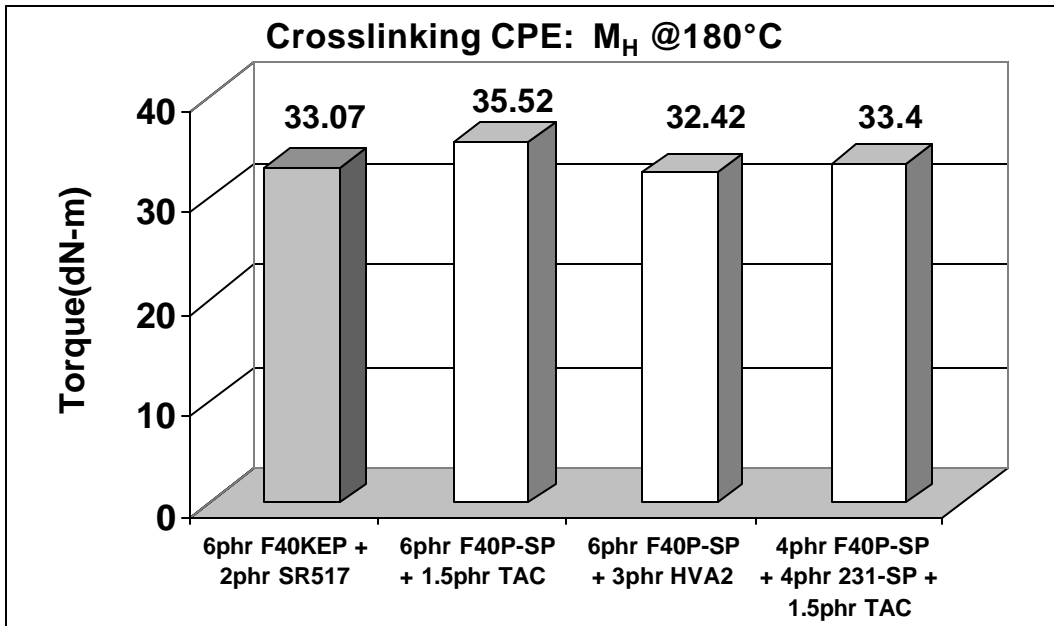
DuPont HVA-2

SR-517 = Sartomer Co. Saret® SR-517, a proprietary, scorch resistant acrylic coagent

TAC = Triallyl Cyanurate coagent

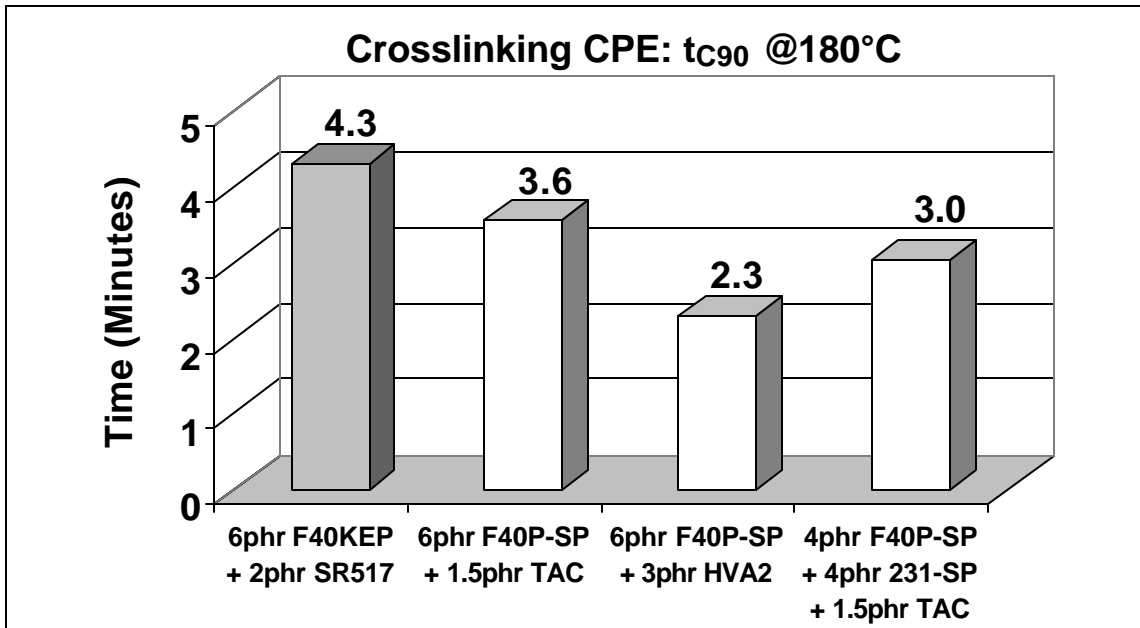
**Figure 18**

**Equal State of Cure using F40P-SP in CPE with TAC, HVA-2 or 231-SP as Secondary Peroxide for Crosslinking CPE Wire & Cable Jacket**



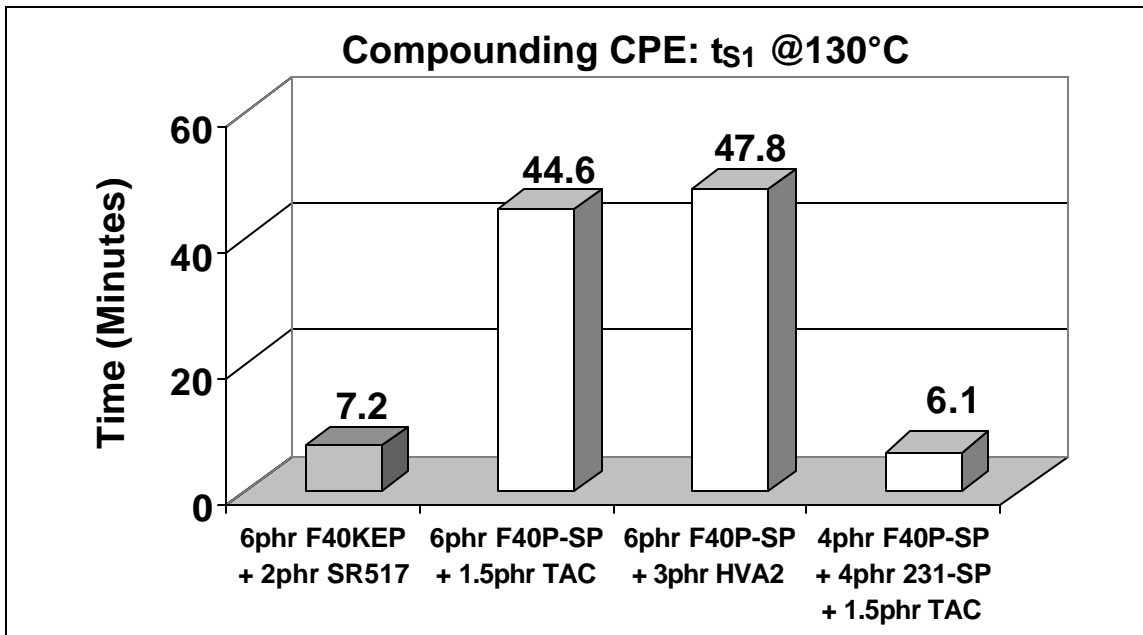
**Figure 19**

**Shorter Cure Times using F40P-SP in CPE with TAC, HVA-2 or 231-SP as Secondary Peroxide for Crosslinking CPE Wire & Cable Jacket**



**Figure 20**

**Longer Scorch Time during Compounding of CPE using F40P-SP with TAC, HVA-2 or 231-SP as Secondary Peroxide for CPE Wire & Cable Jacket**



## SUMMARY

Arkema Inc., has commercialized two new grades of organic peroxide, specifically designed for use in compounding and crosslinking EPDM elastomers:

- **Luperox® F40M-SP**
- **Luperox® F-CST**

The F40M-SP provides scorch protection during compounding and cure.

The F-CST provides similar scorch protection, plus a 20% faster cure rate without increasing the original cure temperature. These two products are being sold commercially via the R. T. Vanderbilt Company, Inc. under the Varox tradename:

- **Varox® 802SP-40MB**
- **Varox® 802-40CST**

In this newest paper, we introduced three new, developmental SP peroxide grades. These two grades below have been optimized for use in EPDM and HNBR, compounding and crosslinking. Luperox 231XL40-SP can be used as a co-curing peroxide in combination with Luperox F40M-SP for curing CPE.

- **Luperox® 231XL40-SP**
- **Luperox® 230XL40-SP**

The third new, developmental SP peroxide grade: Luperox F40P-SP was designed specifically for compounding and crosslinking HNBR, to provide enhanced scorch time protection. This peroxide also provides excellent performance in CPE crosslinking when used with select monomeric crosslinking coagents like Vanax MBM (from R. T. Vanderbilt Company, Inc.) and triallyl cyanurate.

- **Luperox® F40P-SP**

## ACKNOWLEDGEMENTS

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Finally, the authors must thank James Feorino, Peter Callais, and Jerome Raphanaud of Arkema Inc. & Arkema S.A. for their valuable contributions, guidance and expert leadership, which created the “bridge” between research and the customer.

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<sup>1</sup> Fabien DEBAUD, Alfredo DEFRANCISCI and Leonard PALYS, Technical Paper "SP and CST Technologies – A new generation of cost saving curatives in rubber processing." Presented at a Meeting of the Rubber Division, American Chemical Society, Columbus, OH, October 5-8, 2004, Paper No. 9.

<sup>2</sup> Fabien DEBAUD, Alfredo DEFRANCISCI and Leonard PALYS, "A new generation of cost-saving curatives.", RubberWorld, Volume 232, No. 2, pages 39-42, 56, May 2005.

<sup>3</sup> Vanax and Varox are trade names of the R. T. Vanderbilt Company, Inc.; 30 Winfield Street Norwalk, CT 06855; telephone 800-243-6064; See website: <http://www.rtvanderbilt.com/vnews>

<sup>4</sup> Jennifer Fogue, Courtland Handy and Ray Cash, R. T. Vanderbilt Company, Inc. Project R-1823; Varox 802 CST and SP Spider Flow Test. April 08, 2005

<sup>5</sup> Technical publication and computer diskette, "Half-life – Peroxide Selection Based on Half-life", Arkema, Inc., 2000 Market Street, Philadelphia, PA 19103, USA, Telephone: (215) 419-7000. Also available at the Peroxides web-site of Arkema: [www.Luperox.com](http://www.Luperox.com)

<sup>6</sup> Jennifer Fogue, Courtland Handy and Ray Cash, R. T. Vanderbilt Company, Inc. Project R-1834; Performance Evaluation of Varox 230XL-SP and Varox 231XL-SP. May 27, 2005

<sup>7</sup> Private Communications.

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