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## Using Organic Peroxides in Open Air Systems to Cure Latex Articles

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### BIOGRAPHICAL NOTE

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### ABSTRACT

To cure a latex compound, a chemist would normally add sulfur, a metal oxide such as zinc oxide, and a combination of accelerators. Although this combination works extremely well, the continued use of some common accelerators has led to an increase in the incidence of delayed cutaneous hypersensitivity, also known as Type IV allergy. This type of allergy occurs when an antigen (residual chemical) interacts with specific T lymphocytes. The lymphocytes release inflammatory and toxic substances that can lead to a skin reaction<sup>1</sup>. Latex companies are trying to develop alternative cure systems that might help to reduce these allergic reactions.

This paper describes an alternative cure system for latex compounds. This new process (patent pending) uses organic peroxides instead of some of the more common accelerator systems, and is capable of producing films with tensile strengths between 20 and 25 MPa at relatively low curing temperatures. Latex compounds made with this system can be cured in either an open air environment or in closed systems, without exhibiting the surface tackiness that is often associated with the use of peroxides in an open air cure.

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## INTRODUCTION

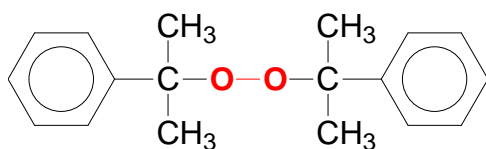
Crosslinking and/or vulcanization are defined as processes for converting a thermoplastic material or elastomer into a thermoset or vulcanizate.<sup>2</sup> This process converts unbound polymer chains into a single network which retains many desirable physical and chemical properties of the base polymer. The two major chemical processes by which crosslinking occurs in dry rubber systems are sulfur and peroxide cure systems. Until recently, only sulfur-based cure systems were available to the latex industry.

Although these systems work extremely well, in some cases the continued use of most common accelerators has led to an increase in delayed cutaneous hypersensitivity, also known as Type IV allergy. This type of allergy occurs when an antigen (in this case a residual chemical) interacts with specific T lymphocytes. The lymphocytes release inflammatory and toxic substances that can lead to a skin reaction.<sup>3</sup> Due to these potential issues latex companies are seeking to develop alternative cure systems that will reduce the incidence of allergic reactions.

This paper will outline one such alternative cure system. The new process (patent pending) uses organic peroxide emulsions instead of some of the more common accelerator systems, and is capable of producing films with tensile strengths between 20 and 25 MPa at relatively low curing temperatures. Latex compounds made with this system can be cured in either an open air environment or in closed systems, without exhibiting the surface tackiness that is often associated with peroxides in an open air cure. Additionally, this paper offers recommendations with regard to additional additives that further maximize the effectiveness of the cure system.

### Organic Peroxides

An organic peroxide is a molecule containing at least two oxygen atoms connected by a single bond to organic chemical groups, as depicted below:



Depending on the groups attached, the oxygen-oxygen bond is designed to break on heating, leaving one unpaired electron or free radical on each oxygen. These free radicals are able to promote certain chemical reactions, such as polymerization, the curing of thermosetting resins, and the crosslinking of elastomers. As organic peroxides decompose, they generate free radicals that in turn create an active site on the polymer backbone. The reactions between active sites produce strong carbon-carbon bonds between polymer chains, which in turn leads to a polymer network with desirable mechanical properties, in particular excellent resistance to heat.

When polymers are crosslinked by peroxides, carbon to carbon bonds are formed between individual polymer chains. The C-C bond is stronger and more thermally stable

than the S-S bond formed by elemental sulfur vulcanization. The use of a sulfur donor system will primarily form C-S type bonds, the thermal stability of which falls between that of S-S and C-C bonds. Due to the higher strength of the covalent C-C bond network, peroxide curing is the preferred crosslinking method to obtain optimum thermal stability.

**Table 1: A Comparison of Three Standard Cure Systems**

	<b>Elemental Sulfur</b>	<b>Sulfur Donor</b>	<b>Peroxide</b>
<b>Crosslink Bond Energy, kJ</b>	155-270 kJ	285 kJ	350 kJ

Decomposition rates of organic peroxides are reported in terms of half-life times and half-life temperatures. The half-life time of a peroxide at any specified temperature is the time in which 50% of the peroxide has decomposed. Correspondingly, the half-life temperature at any specified time is the temperature at which 50% of the peroxide has decomposed in the specified time. Table 2 shows how the number of half-lives correlates to the percentage of decomposed peroxide.

**Table 2: Half-Lives vs. Percentage of Decomposed Peroxide**

<b>Number of Half-Lives</b>	<b>Percentage of Decomposed Peroxide</b>
0	0
1	50
2	75
3	87.5
4	93.75
5	96.9
6	98.4
7	99.2
8	99.6
9	99.8
10	99.9

Since crosslinking is directly related to the amount of decomposed peroxide, at least 6 to 10 half-lives of peroxide decomposition are recommended for crosslinking operations.

### **Peroxide Emulsion Development**

Prior to beginning work on a peroxide cure system for latex, it was necessary to find a way to incorporate the insoluble peroxides in a water-based system. It was found that the best way to do this was to prepare an emulsion using 1,1-bis(t-butylperoxy) 3,3,5-trimethylcyclohexane (**VAROX® 231**) and water. This peroxide was chosen because it has a good time/temperature profile which is suitable for latex compounding. An emulsion made from 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (**VAROX DBPH**) was also prepared at this time. This product was chosen because it complies with the requirements of FDA 21 CFR Section 177.2600 for rubber articles intended for repeated use. The disadvantage of this peroxide in latex is its higher activation temperature.

An emulsion is a two-phase system consisting of fine droplets of one liquid (usually an oil) suspended in another (usually water with which the oil is immiscible).<sup>4</sup> Salad dressing is an example of this type of emulsion. These emulsions can now be easily added to the water-based latex system.

## EXPERIMENTATION<sup>5,6</sup>

Since this system is new to the latex industry, much trial and error was involved in order to achieve the goal of producing samples with minimum amounts of tackiness that met the requirements of all relevant ASTM standards. The time and temperature required to cure films with the peroxides had to be determined first. The compounds listed in Tables 2 and 3 were used to begin this process.

**Table 2: NRL Masterbatch 1**

Ingredient	Dry (phr)	Wet (phr)
Natural Rubber Latex	100.0	161.3
Potassium Hydroxide	0.5	5.0
<b>DARVAN<sup>®</sup> WAQ</b> surfactant	1.0	3.0
<b>DARVAN<sup>®</sup> SMO</b> surfactant	0.5	1.5
<b>VANOX<sup>®</sup> SPL Slurry</b> antioxidant	2.0	4.0

For the purposes of this paper, a fifty percent emulsion of **VAROX 231** will be referred to as WB-11. All quantities in Table 3 are in Dry (PHR).

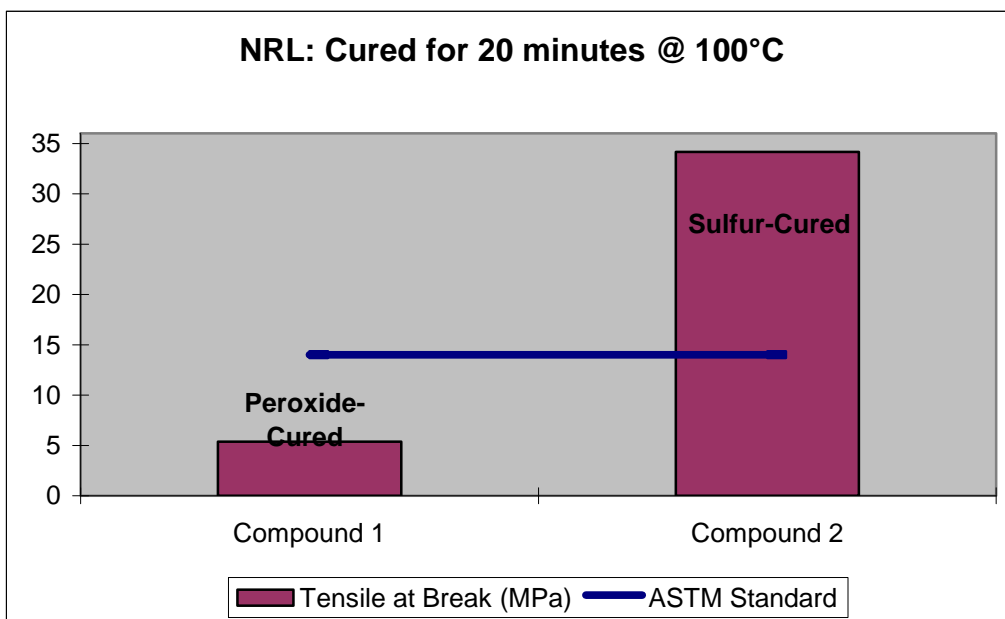
**Table 3: NRL Variables 1**

Ingredient / Compound	1	2 (control)
<b>WB-11 peroxide emulsion</b>	1.0	---
Sulfur Dispersion	---	1.0
<b>Zinc Oxide Dispersion</b>	---	0.5
<b>BUTYL ZIMATE<sup>®</sup></b> accelerator	---	1.0

Films made from these compounds were coated on glass plates and allowed to dry for 24 hours. They were then vulcanized at either 100°C for 20 minutes or 150°C for 10 minutes in order to determine the optimal cure time and temperature. The vulcanized films were then tested for unaged modulus, tensile, and elongation using an Instron<sup>®</sup> 3366 Universal Testing Machine.

### *Results*

The first set of films was cured for 20 minutes at 100°C. This is a typical cure cycle for natural rubber latex.



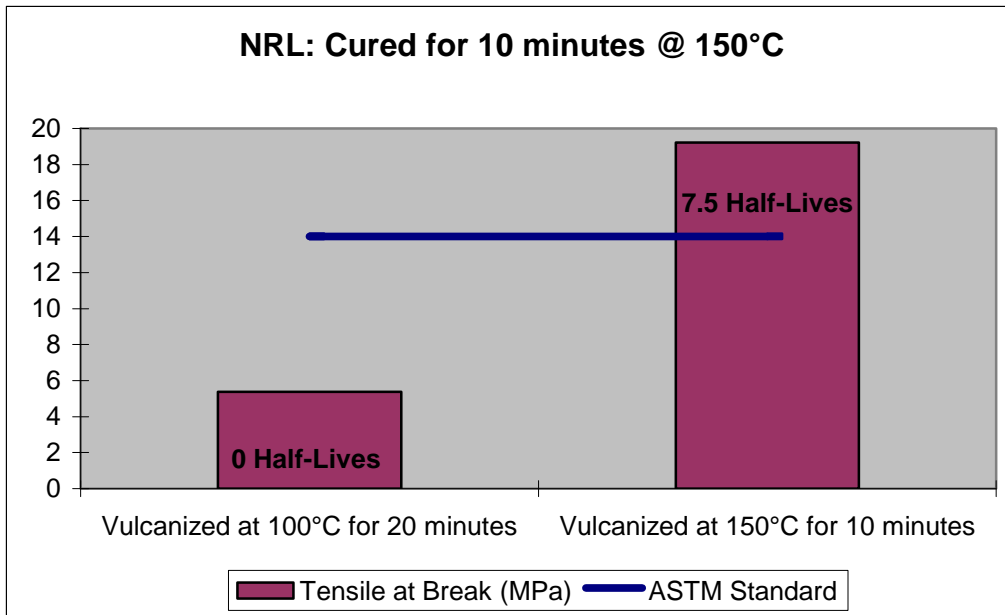
**Figure 1: Compound 1 vs. Compound 2**

The films made from Compound 1 have physical properties that are noticeably inferior to those of the films made from Compound 2. Additionally, the tensile strength of the film does not meet the requirements of current ASTM Standards for gloves made of NRL. Using a half-life calculator, it was determined that at 150°C, WB-11 goes through one half-life every 1.31 minutes<sup>7</sup>. Since the crosslinking density is directly related to the amount of peroxide decomposed, at least 6 to 10 half-lives are recommended to achieve the necessary physical properties.

**Table 4: Half-Life Comparison WB-11**

Temperature (°C)	Half-Life Time (min)
100	376.45
110	107.91
120	32.96
130	10.68
140	3.65
<b>150</b>	<b>1.31</b>
160	0.50

Using the information in Table 4, it was determined that at 150°C, WB-11 would have 7.5 half-lives in 10 minutes.



**Figure 2: Time and Temperature Comparison**

By increasing the cure temperature to ensure that the peroxide is allowed at least 6 half-lives of decomposition, the physical properties of the film were greatly improved.

*Experimentation Continued*

The next step in the optimization of this cure system required the reduction of surface tack. One of the difficulties of working with peroxides in latex is the fact that peroxide-cured films are typically limited to closed air systems. This is because oxygen, when it contacts the film surfaces, reacts with the peroxy catalyst to form hydroperoxy radicals. These radicals hinder vulcanization and degrade the film through a process called chain scission. This can cause the film to become extremely sticky or tacky, which can make the film unusable. In peroxide-cured dry rubber parts such as o-rings, “tack” occurs only at the surface of the part. By adding a combination of surfactants and other chemicals including coagents, the issues with surface tack should be minimized.

**Table 5: NRL Masterbatch 2**

<b>Ingredient</b>	<b>Dry (phr)</b>	<b>Wet (phr)</b>
Natural Rubber Latex	100.0	161.3
Potassium Hydroxide	0.5	5.0
<b>WB-11 Peroxide Emulsion</b>	1.0	2.0
<b>DARVAN WAQ</b>	1.0	3.0
<b>DARVAN SMO</b>	0.5	1.5
<b>VANOX SPL Slurry</b>	2.0	4.0

All quantities in Table 5 are in Dry (PHR).

**Table 6: NRL Variables 2**

<b>Ingredient/Compound</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Sulfur Dispersion	---	---	---	0.1
<b>DARVAN L</b>	0.5	0.5	0.5	---
<b>DARVAN SMO</b>	0.5	---	0.5	0.5
<b>VANOX ZMTI</b>	---	1.0	1.0	1.0

Films made from these compounds were coated on glass plates and allowed to dry for 24 hours. They were then vulcanized at 150°C for 10 minutes. The vulcanized films were then tested for unaged modulus, tensile, and elongation using an Instron® 3366 Universal Testing Machine.

### *Results*

There is no ASTM test available to evaluate the degree of film tackiness in latex, so it was necessary to develop a method to evaluate the degree of film surface tack. It was decided to rate the tackiness of each film on a scale of 1 to 5, with 1 indicating an absence of tack and 5 indicating a level of surface tackiness rendering the film unusable. It is important to note that this is a completely subjective test, and should be considered only as a guide.

**Table 7: Degree of Tack on NRL Films**

<b>Compound</b>	<b>Degree of Surface Tack</b>
1	5
2 (control)	1
3	3
4	3
5	3
6	3

Although the addition of **DARVAN L**, **DARVAN SMO**, and **VANOX ZMTI** helps to decrease the amount of surface tack in peroxide-cured NRL films, it has still not completely eliminated the problem, and experimentation is ongoing.

### Experimentation Continued

After determining which of the formulations produced films with the lowest levels of surface tack, it was time to ascertain how these formulations performed in other latexes.

**Table 8: CR Masterbatch**

<b>Ingredient</b>	<b>Dry (phr)</b>	<b>Wet (phr)</b>
<b>Neoprene 750</b>	100.0	200.0
Potassium Hydroxide	1.0	10.0
<b>WB-11 Emulsion</b>	1.0	2.0
<b>DARVAN WAQ</b>	1.0	3.0
<b>DARVAN SMO</b>	0.5	1.5
Sulfur Dispersion	0.1	0.2
<b>VANOX SPL Slurry</b>	2.0	4.0
<b>VANOX ZMTI Slurry</b>	1.0	2.0
Sodium Polyacrylate Thickener	0.3	2.3

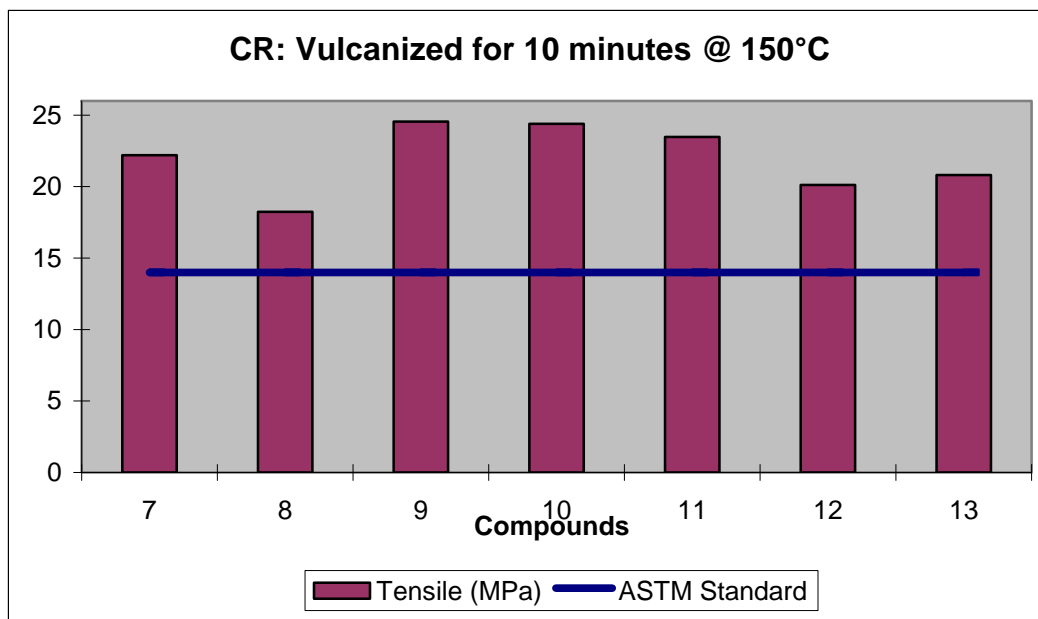
**Table 9: CR Variables**

<b>Ingredient</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>
<b>DARVAN L</b>		0.5					
<b>DARVAN SMO</b>	0.5		0.5	0.5	0.5	0.5	0.5
<b>DIAK<sup>®</sup> 7</b>			0.25	0.50	0.75	1.00	1.50

Films made from these compounds were coated on glass plates and allowed to dry for 24 hours. They were then vulcanized at 150°C for 10 minutes. The vulcanized films were then tested for unaged modulus, tensile, and elongation using an Instron<sup>®</sup> 3366 Universal Testing Machine.

### Results

All the compounds listed above were cured for 10 minutes at 150°C.



**Figure 3: CR Tensile Results**

The films made using the formulations in Tables 8 and 9 all show superior levels of tensile strength. All far exceed the ASTM standard of 14 MPa. Additionally, the films made with coagents confirm the theory that increasing the concentration of coagent improves the state of cure up to a certain point, after which it decreases or stabilizes. Additional research is currently being conducted on the use of coagents in latex.

It was also important to evaluate the surface tack levels of these films. As before, a score of 1 indicates no surface tack.

**Table 10: Degree of Tack on CR Films**

Compound	Degree of Surface Tack
7	1
8	1
9	1
10	1
11	1
12	1
13	1

The data in Table 10 supports the theory that coagents are useful in minimizing chain - scission reactions that lead to increased levels of surface tack due to film degradation. Coagents react with and stabilize the polymer radicals, which are likely to participate in crosslinking. This in turn minimizes the level of surface tack present on the films.

## CONCLUSION

This paper has presented a crosslinking system that was developed in the R.T. Vanderbilt Company's Waterborne Technologies Laboratory. The system uses organic peroxide emulsions in combination with surfactants and coagents to crosslink latex articles. Since the original publication of these developments, additional work has been done to minimize the surface tack in natural rubber latex.

Additionally, Vanderbilt has recently commercialized an emulsion of VAROX® DBPH. While not discussed in this paper, this product can also be used to crosslink latex articles both in open and closed air systems. If you are interested of a sample of this material or additional information on our open-air peroxide cure system, please contact R.T. Vanderbilt Company, Inc.

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## Notes

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<sup>1</sup> Plambeck, A. (2005, Jan. 4). Type I Versus Type IV Allergic Reactions: How do they differ?. *The Alert*, 10(3).

<sup>2</sup>Chemical Curing of Elastomers and Crosslinking of Thermoplastics. Elf Atochem, April, 1993.

<sup>3</sup> Plambeck, A. (2005, Jan. 4). Type I Versus Type IV Allergic Reactions: How do they differ?. *The Alert*, 10(3).

<sup>4</sup> Mausser, R.F. (Ed.) (1987). *The Vanderbilt Latex Handbook*. Connecticut: R.T. Vanderbilt Company, Inc.

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<sup>7</sup> Peroxide Half-life calculator