



Distributed in the Interest  
of Product Development

# VANDERBILT

*Published Articles, Papers and Presentations*

## **Novel Accelerator Systems for Synthetic Polyisoprene**

By

Carrie Webster  
Waterborne Technologies  
R.T. Vanderbilt Company, Inc.

**R.T. Vanderbilt Company, Inc.**  
**30 Winfield Street, P.O. Box 5150, Norwalk, CT 06856-5150**  
**Telephone: (203) 853-1400**  
**Fax: (203) 853-1452, Web Site: [www.rtvanderbilt.com](http://www.rtvanderbilt.com)**

Before using, read, understand and comply with the information and precautions in the Material Safety Data Sheets, label and other product literature. The information presented herein, while not guaranteed, was prepared by technical personnel and, to the best of our knowledge and belief, is true and accurate as of the date hereof. No warranty, representation or guarantee, express or implied, is made regarding accuracy, performance, stability, reliability or use. This information is not intended to be all-inclusive, because the manner and conditions of use, handling, storage and other factors may involve other or additional safety or performance considerations. The user is responsible for determining the suitability of any material for a specific purpose and for adopting such safety precautions as may be required. R. T. Vanderbilt Company does not warrant the results to be obtained in using any material, and disclaims all liability with respect to the use, handling or further processing of any such material. No suggestion for use is intended as, and nothing herein shall be construed as, a recommendation to infringe any existing patent or to violate any federal, state or local law or regulation.



**R. T. Vanderbilt Company, Inc.**  
INDUSTRIAL MINERALS AND CHEMICALS

# **Novel Accelerator Systems for Synthetic Polyisoprene**

By

Carrie Webster  
Waterborne Technologies  
R.T. Vanderbilt Company, Inc.

Originally presented at the  
2004 International Latex Conference  
Akron, Ohio USA  
July 20-21, 2004

## Novel Accelerator Systems for Synthetic Polyisoprene Latex

### ABSTRACT

Synthetic polyisoprene latex is chemically very similar to natural rubber latex. However, the physical properties of synthetic vulcanized films have never equaled those of the natural product. Natural latex films can be cured quickly (in about 15 to 20 minutes) at low temperatures (~90 to 100°C) using a variety of accelerators that normally produce tensile strengths between 25 and 35 MPa. Unfortunately, synthetic polyisoprene latex could not be cured as easily because, until now, an accelerator system that promotes sulfur crosslinking has not been available to the latex industry at large. Regardless of the accelerator system, synthetic polyisoprene films rarely exceeded a tensile strength of 10 MPa. This paper describes several new accelerator systems that produce synthetic polyisoprene films with tensile strengths between 20 and 35 MPa at low curing temperature, and investigates different vulcanization systems to be used in the manufacture of the films. This paper will also examine the use of these new accelerator systems in natural rubber latex.

### INTRODUCTION

Scientists have for years been trying to develop a synthetic alternative to natural rubber latex (NRL). This has been a difficult process. Although isoprene was known to be the main component of NRL, the synthesis of "natural rubber" proved difficult, because the resulting elastomers consisted of a mixture of molecular configurations, unlike the stereo-regular *cis*-1, 4 polyisoprene (~99%) that makes up natural rubber. It was the discovery and development of new types of catalyst systems that finally allowed scientists to create the long sought after stereo-regular polyisoprene (IR). The two most common systems for the polymerization of isoprene are the Ziegler-Natta and the anionic system used by Kraton Polymers.<sup>1</sup>

**Table 1: Comparing Polymerization Process**

Emulsification Process	<i>cis</i> - 1,4 Density
Biosynthesis in trees (NRL)	>99%
Coordination Polymerization (Ziegler-Natta)	~96%
Anionic Polymerization	~90%

Unfortunately, these catalyst systems did not produce the exact ratio of *cis*-1, 4 bonds that are found in natural rubber. This meant that a more potent accelerator system was required to be developed. Since its first synthesis in the 1950s, synthetic polyisoprene has been used extensively in the dry rubber industry, but not until fairly recently was even an emulsion of this elastomer available to the latex industry. The discovery of a latex cure system for synthetic polyisoprene that produces superior films is a huge advance.<sup>2</sup>

R.T. Vanderbilt Company, Inc. (Vanderbilt) has developed several new cure systems for synthetic polyisoprene latex. The products described in this paper are the first synthetic polyisoprene accelerator systems developed for the latex industry at large. The other published synthetic polyisoprene accelerator systems are governed by patents owned by glove companies<sup>3</sup>, so that their use is restricted.

The new systems, developed in Vanderbilt's Waterborne Technologies Laboratory, will be commercially available to all companies without license or royalty. This paper describes the new accelerator systems that are able to produce synthetic polyisoprene films with tensile strengths between 20 and 35 MPa at low curing temperature, and investigates different vulcanization systems to be used while making the films. This paper will also investigate the use of these new accelerator systems in natural rubber latex.

### Initial Experimentation: Synthetic Polyisoprene

This paper does not address the many compounds that were used in the development of these cure systems. Only those compounds which are part of an optimal cure system are discussed; these are shown in Tables 2 and 3.

**Table 2: IR Latex Masterbatch**

<b>Ingredient</b>	<b>Dry (PHR)</b>	<b>Wet (PHR)</b>
64% KRATON® IR-401 polymer	100.0	156.0
33% DARVAN® WAQ surfactant	0.3	0.8
33% Zinc Oxide Dispersion	0.5	1.5
50% Sulfur dispersion	1.5	3.0
50% VANOX® SPL Slurry	2.0	4.0
33% DARVAN SMO surfactant	0.5	1.5
Accelerator System (see Table 3)	--	--

Since these products are still experimental, with patents pending, the composition will not be disclosed at this time. All the quantities shown in Table 3 are in Dry (PHR).

**Table 3: Experimental and Commercial IR Accelerators**

<b>Accelerator/Compound</b>	<b>IR1</b>	<b>IR2</b>	<b>IR3</b>	<b>IR4</b>	<b>IR5</b>	<b>IR6</b>
VANAX® PIC Slurry			2.0			
WB-5				2.0		
WB-6					2.0	1.0
WB-7		2.0				
WB-8	2.0					

Films were coated using the above compounds and allowed to dry for 24 hours. The films were then vulcanized at 100°C for 30 minutes, 120°C for 18 minutes, and 140°C for 6 minutes, in an effort to determine the optimal cure time. The vulcanized films were then tested using a Monsanto T10 Tensometer. The different compounds were also tested for maturation using a Brookfield® Viscometer.

### Initial Results

When working with any polymer, balancing compound maturation and physical properties can be difficult. Products manufactured with pre-cured or matured compound tend to achieve superior physical properties and/or a faster rate of cure than compounds that are processed immediately after they are mixed. Latex compounds that continue to pre-cure to a point where the increasing viscosity renders them unusable are said to have exceeded their pot life. The novel cure systems described in this paper allow for the optimization of the maturation rate. As stated previously, the level of maturation was determined using a Brookfield Viscometer; the results are presented in Table 4.

**Table 4: Compounding Viscosities**

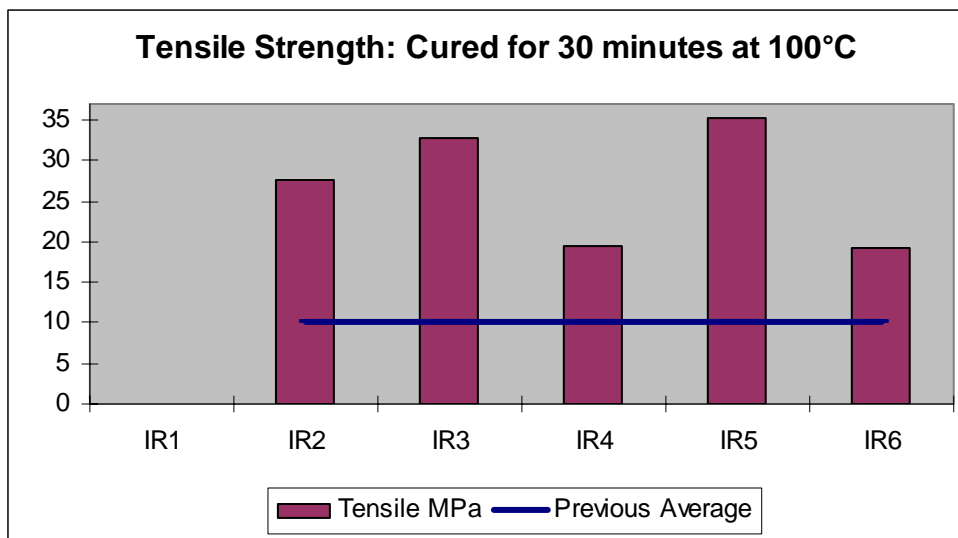
Viscosity, cps	IR1	IR2	IR3	IR4	IR5	IR6
after mix	--	250	250	250	--	--
1 day	--	--	--	--	300	275
2 days	--	--	--	--	350	275
3 days	--	275	400	300	--	--
6 days	--	--	--	--	350	287.5
2 weeks	--	300	2000	275	--	--

All the above accelerator systems showed excellent stability. While the viscosity of the IR3 compound increased over the two weeks, it should be remembered that the latex compounds were prepared at 60% solids. Most dip operations use these compounds at half this concentration.

The first set of films was vulcanized at 100°C for 30 minutes. The results are presented in Table 5.

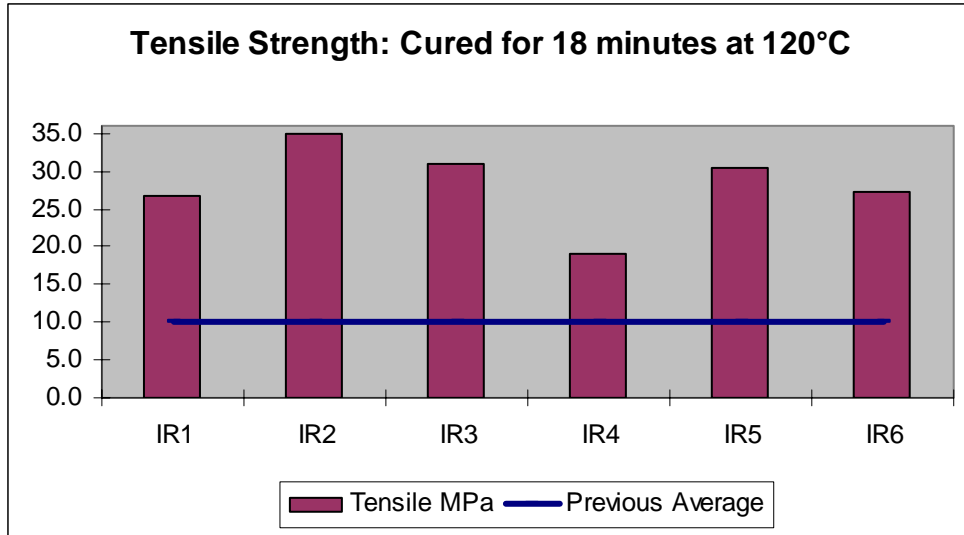
**Table 5: Original Physical Properties**

	IR1	IR2	IR3	IR4	IR5	IR6
<b>Tensile (MPa)</b>	--	<b>27.7</b>	<b>32.8</b>	<b>19.5</b>	<b>35.3</b>	<b>19.3</b>
Ultimate Elongation (%)	--	830	900	840	860	1000

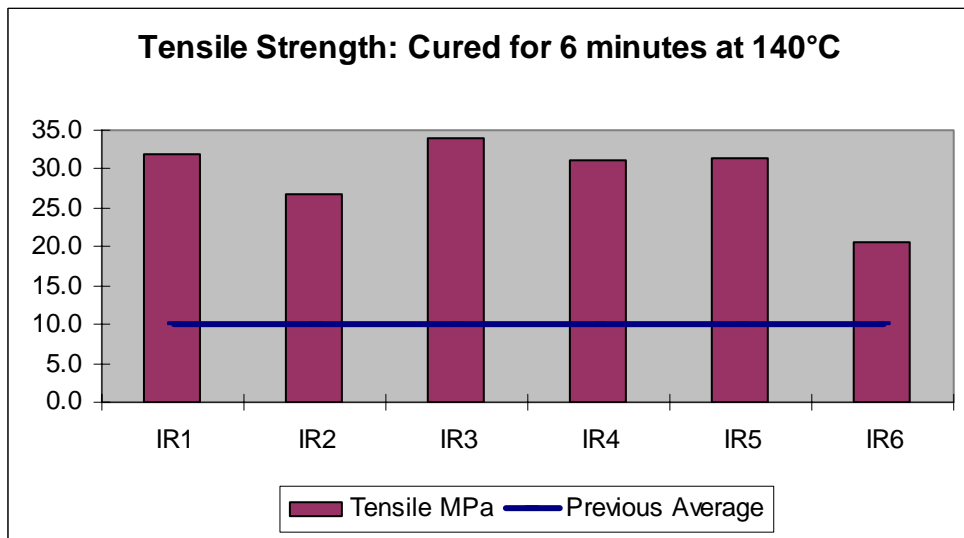


**Figure 1: Tensile Strength Comparison**

All films (Figure 1) showed a tensile strength well above the ~10 MPa that has been described in the literature.<sup>4</sup> As can be seen in Figures 2 and 3, the same is also true for the two other cure settings.



**Figure 2: Tensile Strength Comparison**



**Figure 3: Tensile Strength Comparison**

**Continued Experimentation**

Just as applications foster developments, developments for a single use frequently find multiple applications. In order to establish that these new accelerator systems have broader applicability, the experiments described above were replicated in Natural Rubber Latex (Tables 6 and 7).

**Table 6: NRL Masterbatch**

<b>Ingredient</b>	<b>Dry (PHR)</b>	<b>Wet (PHR)</b>
67% High-Ammonia NRL	100	149
10% Potassium Hydroxide	0.5	5.0
33% <b>DARVAN WAQ</b>	1.0	3.0
50% Sulfur Dispersion	1.0	2.0
50% <b>VANOX SPL Slurry</b>	2.0	4.0
33% <b>DARVAN SMO</b>	0.5	1.5
Accelerator System (variable)	--	--

The accelerators were then added, as shown in Table 7. All of the quantities are in Dry (PHR).

**Table 7: Accelerators in NRL**

<b>Accelerator/Compound</b>	<b>NRL1</b>	<b>NRL2</b>	<b>NRL3</b>	<b>NRL4</b>	<b>NRL5</b>	<b>NRL6</b>
<b>VANAX PIC Slurry</b>			<b>2.0</b>			<b>2.0</b>
WB-5				2.0		
WB-6					2.0	
WB-7		2.0				
WB-8	2.0					
<b>Zinc Oxide Dispersion</b>	0.5	0.5	0.5	0.5	0.5	

The films were coated on glass plates and allowed to dry for 24 hours, after which they were placed in the oven for vulcanization. The oven was allowed to rise to temperature for 4 minutes. The films were cured for 20 minutes at 100°C or 120°C. They were then tested for unaged modulus, tensile, and ultimate elongation, using an Instron® 3366 Universal Testing Machine.

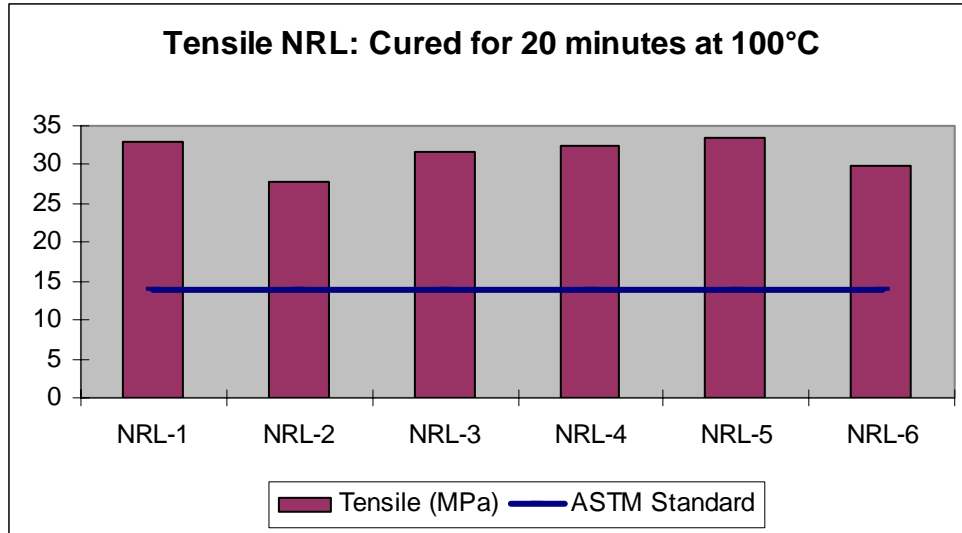
## Results

The optimization of the uses of these experimental products is ongoing; the initial results of the investigation are presented below.

The first set of films was vulcanized at 100°C for 20 minutes.

**Table 8: Original Physical Properties**

	<b>NRL-1</b>	<b>NRL-2</b>	<b>NRL-3</b>	<b>NRL-4</b>	<b>NRL-5</b>	<b>NRL-6</b>
300% Modulus, MPa	1.54	1.39	1.56	1.50	1.67	1.59
500% Modulus, MPa	4.22	3.48	3.80	4.02	3.54	3.53
<b>Tensile, MPa</b>	<b>32.89</b>	<b>27.91</b>	<b>31.61</b>	<b>32.50</b>	<b>33.34</b>	<b>29.82</b>
Elongation at break, %	755.06	768.11	756.24	773.07	777.79	763.84



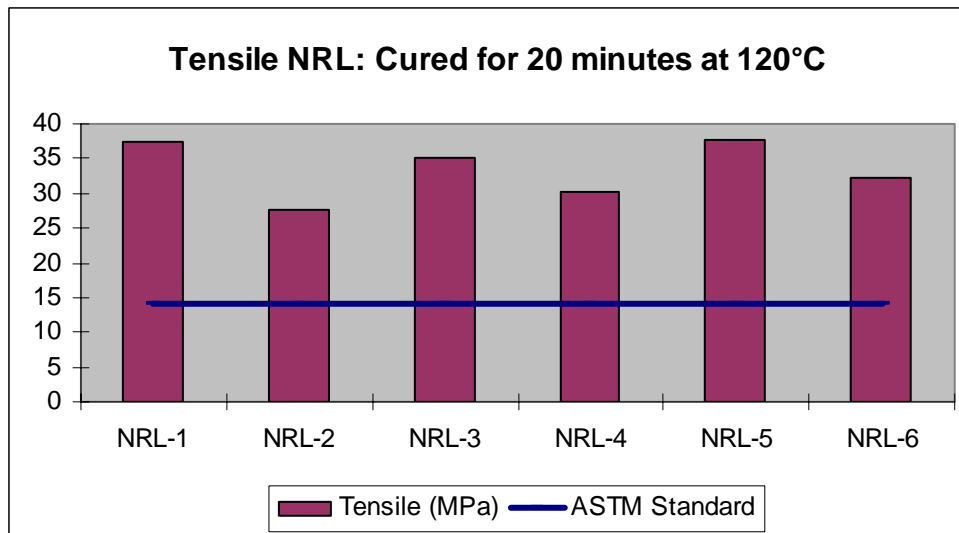
**Figure 4: Tensile Strength Comparison**

The tensile strength of all of the Natural Rubber Latex compounds is excellent, well above ASTM standard D 3578. Of particular note are the excellent results for compound NRL-6, which was produced without Zinc Oxide Dispersion. Experimentation with regard to accelerator systems without Zinc Oxide is ongoing (patent pending).

The second set of films was vulcanized at 120°C for 20 minutes.

**Table 9: Original Physical Properties**

	<b>NRL-1</b>	<b>NRL-2</b>	<b>NRL-3</b>	<b>NRL-4</b>	<b>NRL-5</b>	<b>NRL-6</b>
300% Modulus, MPa	1.77	1.75	1.70	1.71	1.80	1.59
500% Modulus, MPa	4.01	4.20	3.66	3.78	3.76	2.78
<b>Tensile, MPa</b>	<b>37.27</b>	<b>27.6</b>	<b>34.97</b>	<b>30.11</b>	<b>37.75</b>	<b>32.09</b>
Elongation at break, %	784.02	728.8	767.99	769.90	768.06	815.85



**Figure 5: Tensile Strength Comparison**

The results in Tables 8 and 9 confirm that these accelerator systems work equally well in both IR and NRL.

### Conclusion

This paper has examined new accelerator systems developed in Vanderbilt's Waterborne Technologies Laboratory. Based on the experimentation at Vanderbilt, these accelerator systems have been shown to effectively cure synthetic polyisoprene at temperatures as low as 90°C to as high as 140°C. The optimal time and temperature vary with oven temperature and curing time; however, acceptable films can be obtained by curing at the relatively low temperature range of 100°C to 120°C for 18 to 30 minutes. At higher temperatures (130°C to 140°C), satisfactory cures can be obtained in less than 10 minutes.

Although these novel cure systems have been designed specifically for use in synthetic polyisoprene, they also show excellent results in natural rubber latex. As the results indicate, an excellent film can be achieved by using these systems. By using the same accelerator system in both IR and NRL, manufacturing facilities will be able to significantly reduce their raw material requirements and inventories. Finally, it has been shown that these accelerators are capable of curing without the use of zinc oxide, which is a significant development. Additional experimentation with regard to the replacement of zinc oxide with VANOX ZMTI is ongoing (patent pending).

# Samples of VANAX<sup>®</sup> PIC Slurry are now available.

## Please contact R.T. Vanderbilt Company, Inc. for more information.

### Notes

- Synthetic Polyisoprene: Kraton Polymers Group -- IR 401 Synthetic Polyisoprene
- Natural Rubber Latex: Getahindus, Sdn Bhd, Malaysia – LATZ
- WB-5, WB-6, WB-7, WB-8: R.T. Vanderbilt Company, Inc. – experimental products which are currently available for sampling.

KRATON is a registered trademark of Kraton Polymers Group.

DARVAN, VANAX and VANOX are registered trademarks of R.T. Vanderbilt Company, Inc.

Instron is a registered trademark of Instron Corporation.

Brookfield is a registered trademark of Brookfield Engineering Laboratories, Inc.

---

<sup>1</sup> Henderson, P. (2001, Dec.). From Isoprene Monomer to Synthetic Polyisoprene Latex and its Uses. Retrieved June 15, 2004 from [www.kraton.com](http://www.kraton.com).

<sup>2</sup> Valin, K. (1990). Synthetic Polyisoprene. *The Vanderbilt Rubber Handbook* (13<sup>th</sup> Ed.). Norwalk, CT: R.T. Vanderbilt Company, Inc.

<sup>3</sup> Patent Application Number 20020173563: Allegiance Corporation, filed March 12, 2002.

Patent Number 6,618,861: Microflex Corporation, issued September 16, 2003.

Patent Application Number 20030161975: filed August 28, 2003.

<sup>4</sup> Dipped Goods from KRATON Polymers Latex and Solutions. (2000, June). Retrieved June 1, 2004 from [http://www.kraton.com/tl\\_warehouse/technical\\_literature/docs/K0028\\_FSb-00E.pdf](http://www.kraton.com/tl_warehouse/technical_literature/docs/K0028_FSb-00E.pdf).

When using any chemical product, obtain and comply with the precautions and warnings on the Material Safety Data Sheet, label and [other documentation], and utilize good industrial handling procedures.

The information presented herein, while not guaranteed, was prepared by technical personnel and, to the best of our knowledge and belief, is true and accurate as of the date hereof. No warranty, representation or guarantee, expressed or implied, is made regarding accuracy, performance, stability, reliability or use. This information is not intended to be all-inclusive, because the manner and conditions of use, handling, storage, and other factors may involve other or additional safety or performance considerations. The user is responsible for determining the suitability of any material for a specific purpose and for adopting such safety precautions as may be required. R.T. Vanderbilt Company does not warrant the results to be obtained in using any material, and disclaims all liability with respect to the use, handling, or further processing of any such material. No suggestion for use is intended as, and nothing herein should be construed as, a recommendation to infringe any existing patent or to violate any federal, state, local law or regulation.

8/05

**For additional information regarding our  
high quality minerals and chemicals,  
please visit our website:**

**[www.rtvanderbilt.com](http://www.rtvanderbilt.com)**

- Technical data sheets
- MSDS information
- Sample requests
- Specifications
- Product brochures
- Articles
- Presentations
- Reports