



Distributed in the Interest
of Product Development

VANDERBILT

Published Articles, Papers and Presentations

Novel Accelerator Systems for Synthetic Polyisoprene

By

Carrie W. Burr
Waterborne Technologies



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

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

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

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, Inc. 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, trademark or copyright or to violate any federal, state or local law or regulation.

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.¹

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.²

R.T. Vanderbilt Company, Inc. (Vanderbilt) has developed several 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 companies³, so that their use is restricted.

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

Ingredient	Dry (PHR)	Wet (PHR)
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)	--	--

All the quantities shown in Table 3 are in Dry (PHR).

Table 3: Experimental and Commercial IR Accelerators

Accelerator/Compound	IR1	IR2	IR3	IR4	IR5	IR6
VANAX [®] PIC Dispersion			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. 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 (WB-8)	IR2 (WB-7)	IR3 (VANAX PIC)	IR4 (WB-5)	IR5 (WB-6)	IR6 (WB-6)
after mix	--	250	---	250	--	--
1 day	--	--	218	--	300	275
2 days	--	--	---	--	350	275
3 days	--	275	236	300	--	--
6 days	--	--	227	--	350	287.5
2 weeks	--	300	204	275	--	--

All the above accelerator systems showed excellent stability over time.

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
Tensile (MPa)	--	27.7	32.8	19.5	35.3	19.3
Ultimate Elongation (%)	--	830	900	840	860	1000

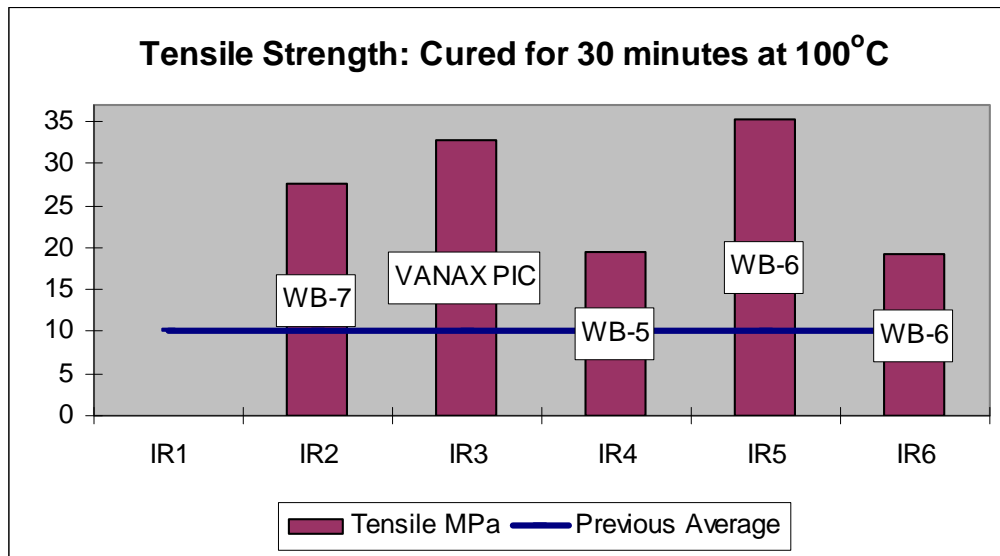


Figure 1: Tensile Strength Comparison

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

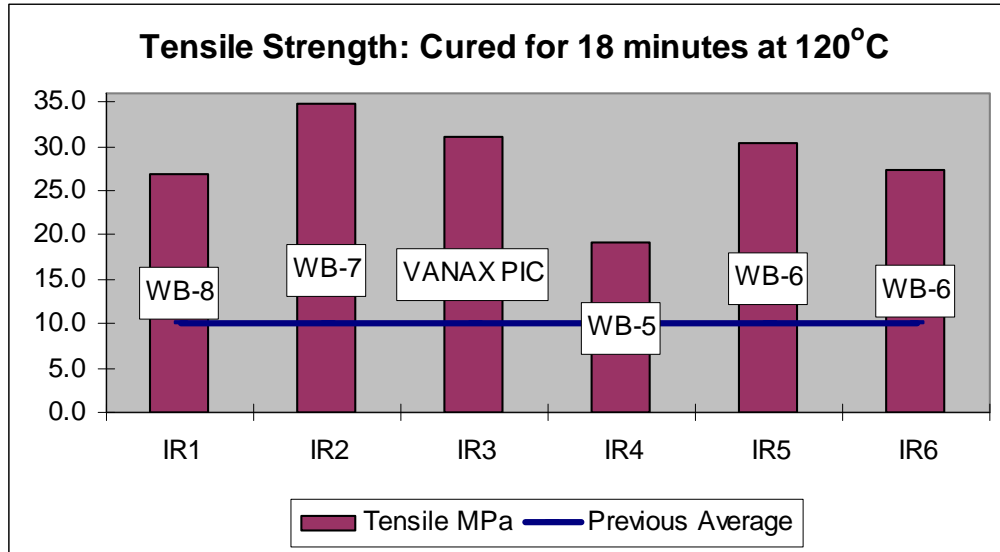


Figure 2: Tensile Strength Comparison

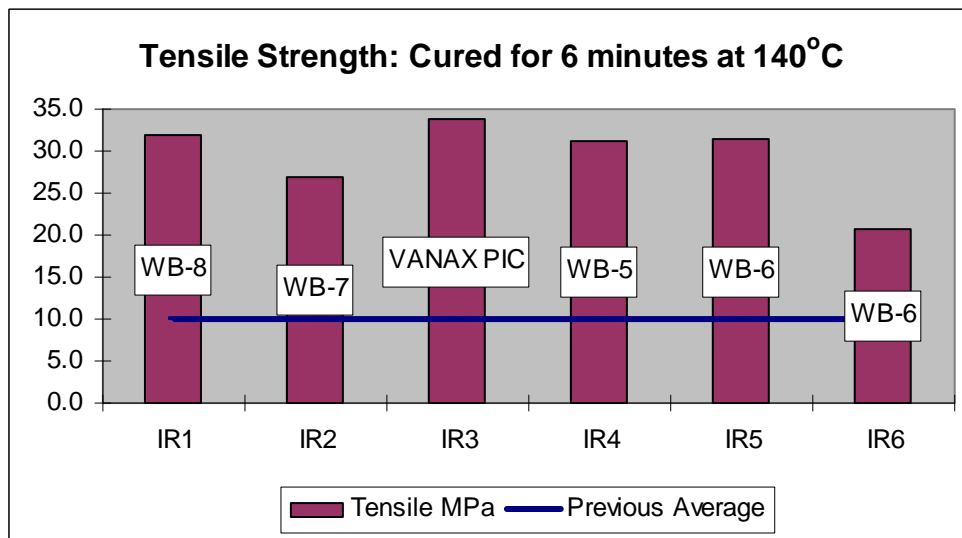


Figure 3: Tensile Strength Comparison

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

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

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

	NRL-1	NRL-2	NRL-3	NRL-4	NRL-5	NRL-6
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
Tensile, MPa	32.89	27.91	31.61	32.50	33.34	29.82
Elongation at break, %	755.06	768.11	756.24	773.07	777.79	763.84

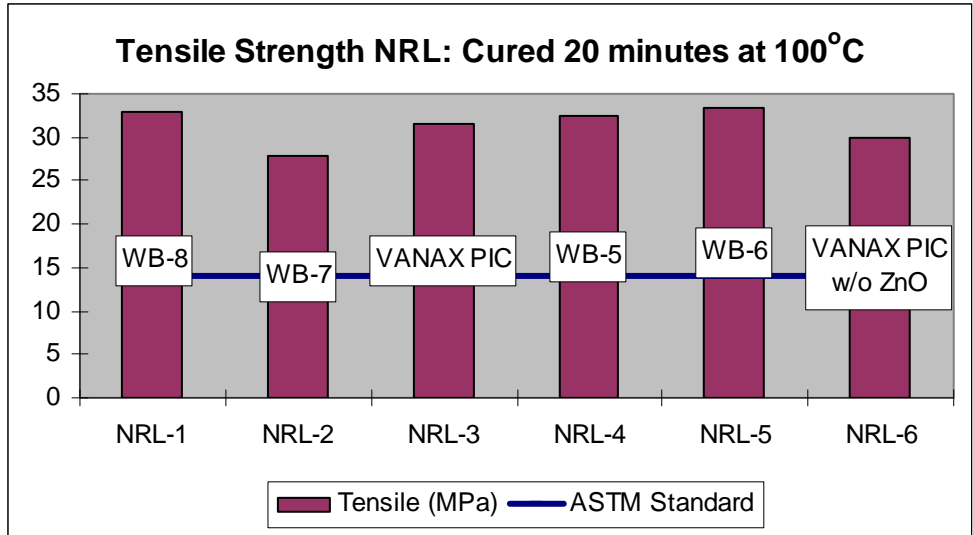


Figure 4: Tensile Strength Comparison

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 the use of zinc oxide.

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

Table 9: Original Physical Properties

	NRL-1	NRL-2	NRL-3	NRL-4	NRL-5	NRL-6
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
Tensile, MPa	37.27	27.6	34.97	30.11	37.75	32.09
Elongation at break, %	784.02	728.8	767.99	769.90	768.06	815.85

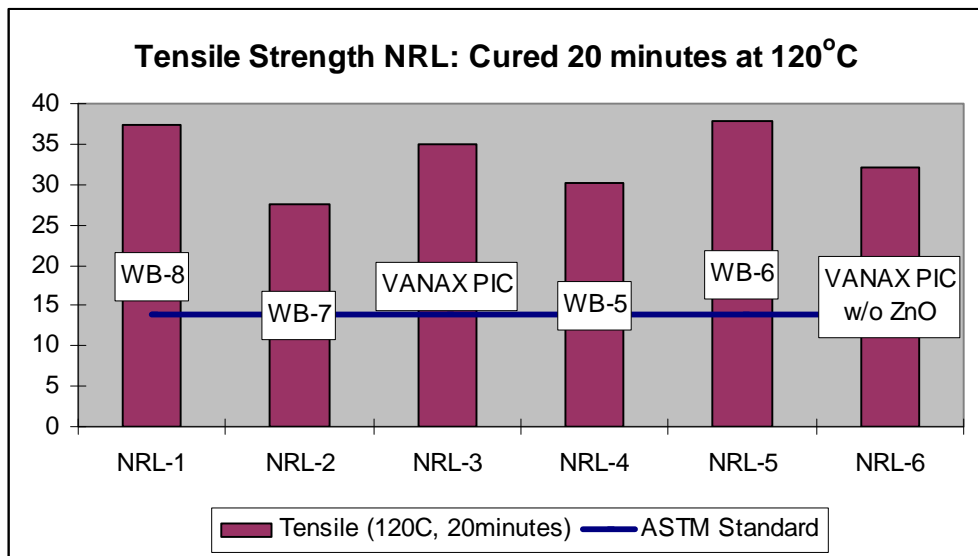


Figure 5: Tensile Strength Comparison

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 accelerator systems developed in Vanderbilt's Waterborne Technologies Laboratory for use in synthetic polyisoprene. 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 information on using **VANOX ZMTI** in place of zinc oxide can be found in TDS No. 1217, "**VANOX ZMTI Slurry and SETSIT[®] Liquid Accelerator: A Low Zinc Compound.**"

Notes

- 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.

Instron is a registered trademark of Instron Corporation.

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

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

¹ Henderson, P. (2001, Dec.). From Isoprene Monomer to Synthetic Polyisoprene Latex and its Uses. Retrieved June 15, 2004 from www.kraton.com.

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

³ 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.

⁴ 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.

Please contact R.T. Vanderbilt Company, Inc. for more information or samples of VANAX[®] PIC Dispersion or the other Novel Accelerators outlined in this paper.