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VANDERBILT *Technical Data*

SETSIT[®]

Activated Liquid Dithiocarbamate Accelerators

by

Christopher Nola and Robert Dzikowicz

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**This version has been modified to include
R. T. Vanderbilt Company's SETSIT products that
were actually used in the study.**

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

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Introduction

Most people involved with latex are familiar with BUTYL NAMATE[®] (NaDBC), sodium dibutyldithiocarbamate or the sodium salt of dibutyldithiocarbamate. It is recognized as the liquid alternative to BUTYL ZIMATE[®] (ZnDBC), the zinc salt of dibutyldithiocarbamate, the latex industry's accelerator workhorse that is water-insoluble. Unfortunately, many latex chemists assume that it is the only alternative to BUTYL ZIMATE. It is not.

There is a whole world of chemistry that deals with activated liquid dithiocarbamate accelerators for latex. Obviously, sodium is not the only water-soluble/water-miscible salt that can be combined with the dithiocarbamate complex. Further, activators that have a pronounced and varied effect on the activity of the dithiocarbamate are as available as the different kinds of salts. These activators are sometimes referred to, especially with regard to dry rubber, as secondary accelerators.

As complicated as the chemistry may be, it is not the distinguishing characteristic among activated liquid accelerators. It is their performance in latex compounds that is strikingly flexible and innovative. Performance can be engineered into a latex compound by the proper selection of a liquid accelerator.

Activated liquid dithiocarbamate accelerators are:

- **Ultra Accelerators**

They promote rapid cures and excellent physical properties in latex films, both natural and synthetic. Rate and state of cure are comparable to those of BUTYL ZIMATE.

- **Designed for Specific Applications**

Activated liquid dithiocarbamates are available for general purpose use, for rapid room temperature cures, for resistance to precure, for rapid oven cures, for low nitrosamine generation to meet the German BGA requirements, for the reduction or elimination of the bitter taste of balloons and to comply with the ingredient requirements of rubber products for repeated use in contact with food (Title 21, Code of Federal Regulations, Part 177.2600.)

- **Water-Soluble or Water-Miscible**

- **Freeze/Thaw Stable**

- **Easy to use**
No **dispersing** or **emulsifying** is required. There is no intermediate step or additional manufacturing operation. There is no settling of solids to the bottom of the container. The liquid accelerators do not separate into layers as with emulsions. Therefore, no mixing or re-mixing is required. Housekeeping is minimal. Since all of the liquid accelerator is consumed, there are no effluent or container disposal considerations. The same vessel can be used repeatedly.
- **Very accurately weighed**
Can be done volumetrically by simply pouring the liquid into a transparent container up to the predetermined fill line. Adding the liquid to the latex virtually empties the container. There is no need to scrape the vessels to remove accelerator that has clung to the sides and bottom.

The Study

Because the various activated liquid dithiocarbamates were designed to have specific characteristics and are used for specific applications, their performance in latex is subtly different. When successful products have existed for long periods of time, we tend to forget that a multitude of compounding ingredients were screened and evaluated, their levels or dosages varied, and time and temperature conditions adjusted to achieve the desired properties in the finished product. Then, of course, a similar kind of deductive process takes place when the laboratory product is scaled up to plant production.

The Latex Chemist/Compounder

Without the latex chemist or compounder, there would be no discrimination in compounding ingredients. All formulas would be the same. Accelerators and antioxidants would be commodities sold only by price and not performance. That is not the case, however. It is the responsibility of the chemist/compounder to identify the most suitable ingredient in order to optimize the latex formula and compound.

In order to assist this latex chemist/compounder in the selection of the proper SETSIT liquid accelerator, we have compiled information that describe in detail the performance of our products in natural rubber latex. While the performance of the individual SETSITs are not the same in synthetic latexes, they are relative to each other.

Later in this paper, the SETSIT Profiles are described. Specific information can be obtained by calling the Waterborne Technologies Laboratory in Norwalk, CT.

The Compounds and Sample Preparation

Natural rubber latex was used to exhibit the performances of the activated liquid dithiocarbamates. Synthetic latexes, while generally slower to cure than natural rubber, are expected to respond to dithiocarbamate acceleration in a relative manner. Two base compounds were used: a high modulus compound and a low modulus compound.

THE BASE COMPOUNDS (phr)

	High Modulus	Low Modulus
	<u>WET</u>	<u>WET</u>
62% High Amm. Natural Rubber	161	161
10% Potassium Hydroxide	5	5
5% Potassium Caseinate	10	10
50% Sulfur Dispersion	2	1
50% Zinc Oxide Dispersion	6	1
50% Agerite[®] Stalite[®] S Dispersion	2.6	2.6
Accelerator	Variable	Variable

STALITE is a registered trademark of Noveon, Inc.

Notice that the difference in the high and low modulus compounds is the different levels of zinc oxide and sulfur. Also, note that the 100 parts formula is written in wet parts. Since the concentration of the activated liquid dithiocarbamates is proprietary, it was necessary to write the formula in “wet parts per hundred rubber” to be consistent.

The compounds were mixed without the use of our favorite surfactants, DARVAN[®] WAQ and DARVAN SMO, because tensile strength was to be the parameter for cure activity and the cast films would not be leached. This is not a common practice in our laboratory, but we were determined to test for absolute

numbers rather than relative numbers. In most cases the tensile strengths are lower when surfactants are used but, for normal evaluation purposes, relative results are perfectly satisfactory.

The compounds were cast on glass plates, air dried, stripped, oven dried and cured in a circulating hot air oven for 20 min. @ 200°F. The films were then tested following the 24 hour ASTM waiting period.

Cure Parameter

We recognize that the terms **optimum cure** and **maximum cure** are not the same since most latex products are not cured to their maximum physical properties. They are cured to a percentage of their maximum properties for aging considerations. For instance, an **optimum cure** may develop 80% to 90% of the film's maximum physical properties. However, this study uses the terms interchangeably. We have chosen **tensile strength** as our cure parameter; therefore, **optimum cure** is achieved when **tensile strength** is **maximum**.

OPTIMUM CURE

The state of crosslinking when tensile strength is **maximum**.

OPTIMUM ACCELERATOR LEVEL

The level of accelerator that produces an **optimum cure**.

General Characteristics

Following the testing of each individual activated liquid dithiocarbamate and the controls, BUTYL NAMATE and BUTYL ZIMATE, we compiled the data into categories that compare all the dithiocarbamate accelerators with each other. We hope that this data will give the **latex chemist** a sharper perspective when choosing an activated liquid dithiocarbamate accelerator for a particular application.

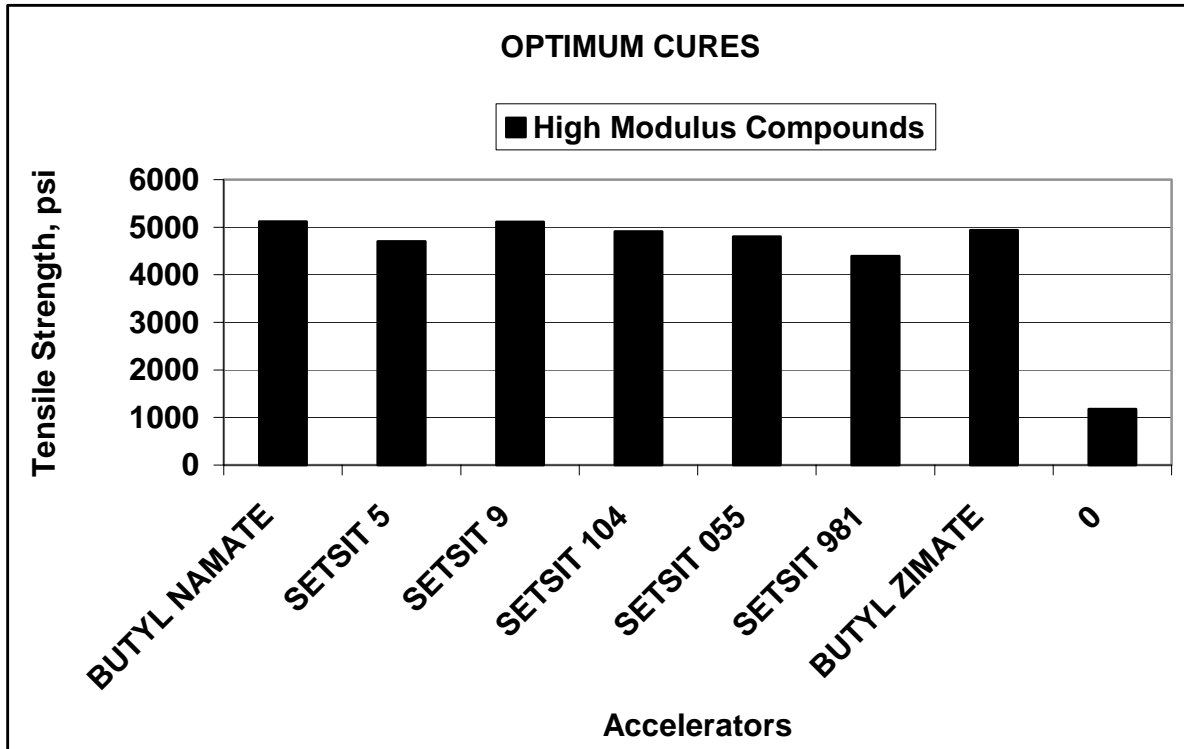
In the following discussion of the **general characteristics**, both high and low modulus compounds will be addressed but, only charts for the high modulus compounds will be displayed.

Optimum Accelerator Levels

For both the high and low modulus compounds, all the activated liquid dithiocarbamates deliver tensile strengths that are comparable to the tensile strength delivered by ZnDBC. The **optimum accelerator** levels of the low modulus compounds are greater than those of the high modulus compounds.

More accelerator is required to produce the high tensile strengths when the zinc oxide and the sulfur levels are minimal.

Figure 1:



On the chart above, tensile strengths were measured for cured NR latex films containing the optimum levels of accelerator. The controls are BUTYL NAMATE to the left and BUTYL ZIMATE to the right. The zero compound at the far right indicates that no accelerator was used and that, as a result, no significant tensile strength was developed.

Table 1:

<u>Accelerator</u>	<u>Accelerator Level, phr</u>	
	Optimum Cure	Range
BUTYL NAMATE	1.0	0.5 – 2.0
SETSIT 5	1.5	1.0 – 4.0
SETSIT 9	2.5	1.25 – 5.0
SETSIT 104	1.5	0.25 – 4.0
SETSIT 055	1.5	0.5 – 3.0
SETSIT 981	2.0	1.0 – 6.0
BUTYL ZIMATE	2.0	0.5 – 3.0

The **range** of accelerator levels is defined as that amount, in wet parts per hundred, that will produce a tensile strength over 4000 psi or 27.6 MPa.

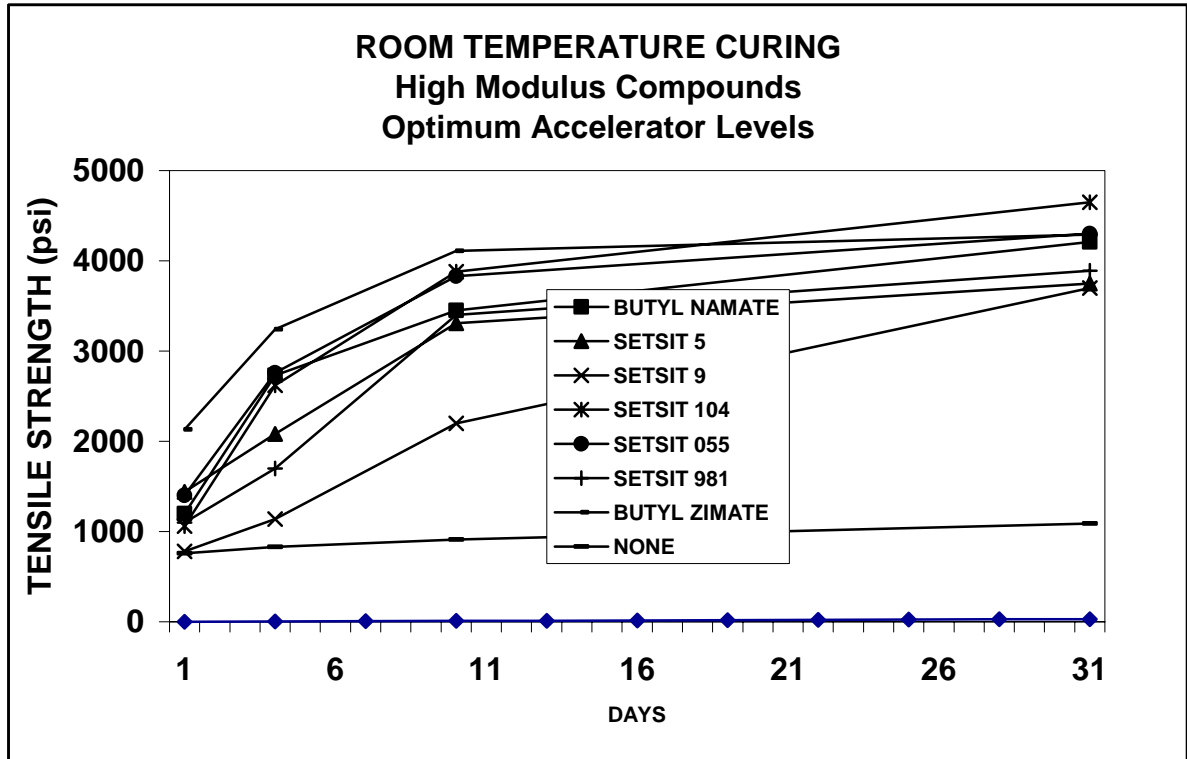
It is clear, then, that there is a workable range where tensile strengths can remain acceptable, while other physical properties like elongation and modulus can be adjusted.

Room Temperature Curing

Room temperature is generally recognized as 72°F. In this study it includes temperatures within 3°F of that bench mark. There was no intention to include January warehouse temperatures in Fargo, North Dakota or July temperatures in Key West, Florida.

Where room temperature curing is a consideration, it is clear from Figure 2 that choices exist. While pot life is not examined in this study, one could speculate that a plot of pot life in days against viscosity would rank the compounds in the same order. In other words, both graphs reveal the “hottest” accelerators.

Figure 2:



The Effect of the Liquid Accelerator on Modulus

The following two charts will show the effect of the level of zinc oxide and sulfur on the modulus of the compounds. Note that the type of **liquid dithiocarbamate accelerator** selected has an impact on the modulus as well.

Figure 3:

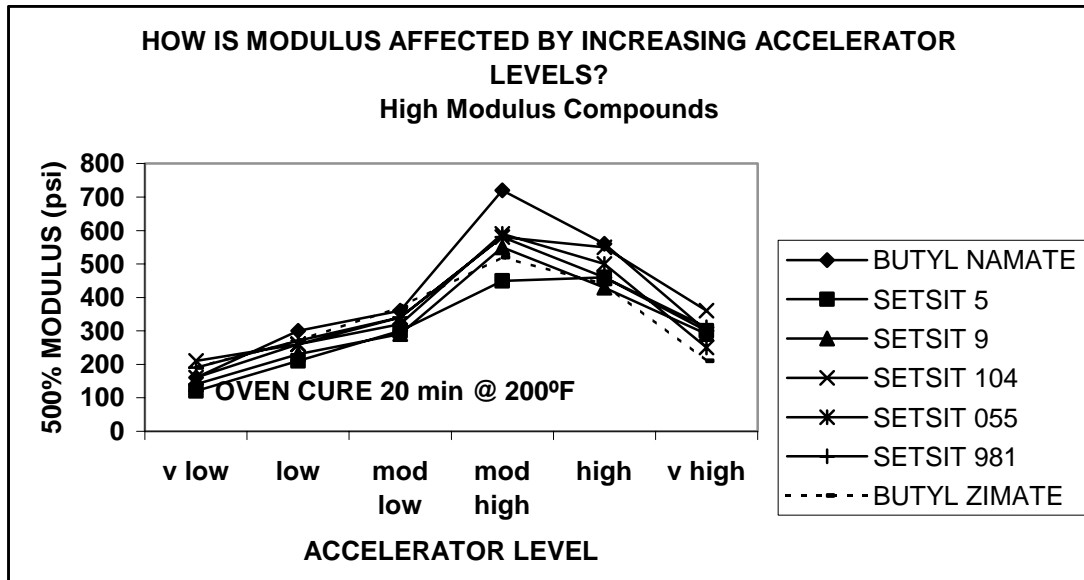


Figure 4:

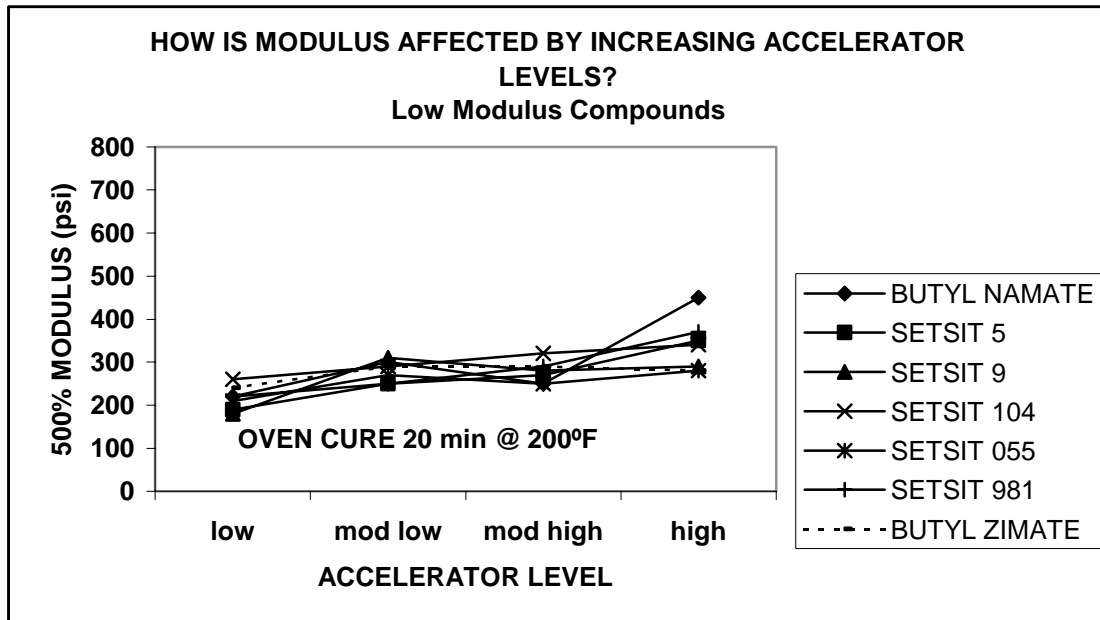


Figure 3 shows that there is an accelerator level above which the modulus no longer increases but decreases. We would expect compound properties, most notably aging and high temperature resistance, to drop off at this point. Simply put, more is not necessarily better. Also, at this level the difference in 500% modulus values is approximately 400 psi: the values range from 300 psi to 700 psi, depending on the type of **liquid accelerator** used.

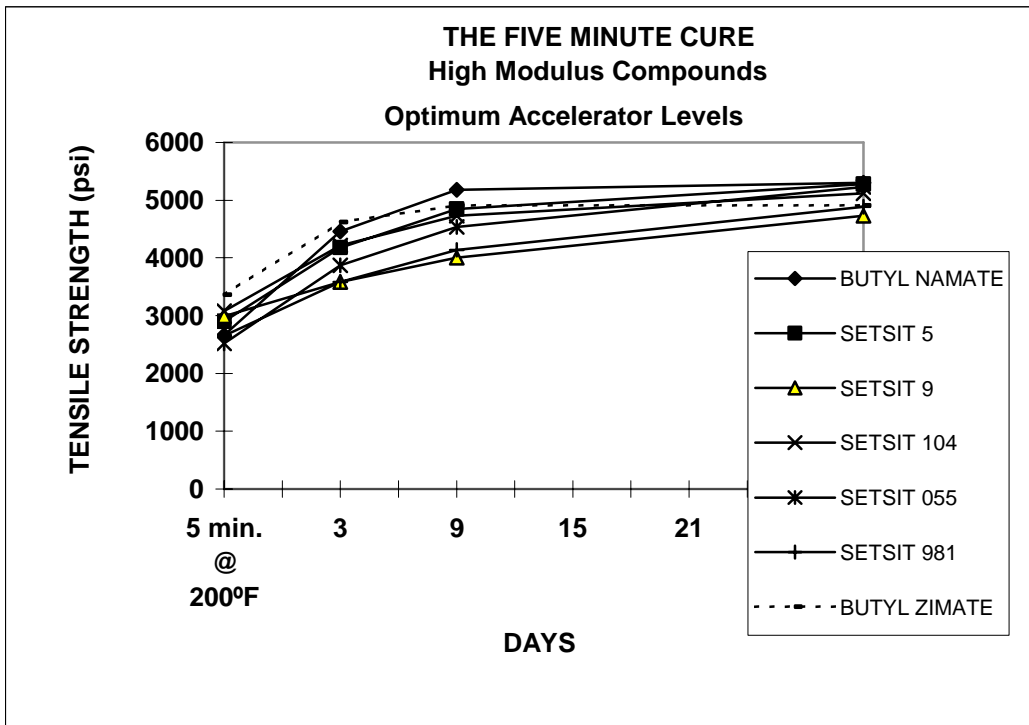
Except for the BUTYL NAMATE, the low modulus compounds displayed in Figure 4 are not affected by the selection of liquid accelerator. In both figures, though, it is the BUTYL NAMATE that appears to have runaway modulus.

The Five Minute Cure

We have shown that BUTYL ZIMATE and some activated liquid dithiocarbamates will cure a latex film at room temperature. Vulcanization, then, cannot be a static condition. We can determine the ideal conditions for a maximum or optimum cure in a circulating hot air oven. An obvious question will occur to a resourceful latex chemist: can these two methods of vulcanization be used to advantage?

We devised the **five minute cure** to answer this question. Instead of curing the latex films for 20 minutes at 200°F, we cured them for 5 minutes at 200°F. Then we tested the physical properties periodically to note any increase in the state of cure over time.

Figure 5:



Note, in Figure 5, that the **five minute cure** gives us the best of both worlds. After only 3 days at room temperature we have achieved the same degree of cure as in curing at room temperature for 30 days (see Figure 2). Also, after 9 days, the degree of cure is comparable to a full oven cure of 20 minutes at 200°F (see Figure 1).

R. T. Vanderbilt Company is not a manufacturer of latex products, and we are not suggesting any new plant procedures. However, the use of activated liquid dithiocarbamates can add a great degree of flexibility to plant processing methods.

Once again, only the high modulus compounds are displayed. The low modulus compounds react similarly, except that the ultimate tensile strengths are slightly lower but still very respectable. They average approximately 4500 psi after 9 days following a **five minute cure**.

Profiles

We have made no attempts in the preceding to distinguish between the types of SETSITs. Rather, we presented the general characteristics of all by compiling the data for a single vulcanizing phenomenon. It is clear from observing the highs and lows of the tensile strengths and moduli that each activated liquid dithiocarbamate reveals its own cure personality in latex films. The differences might seem inconsequential to the layman but they are the kind of data that a latex chemist can appreciate.

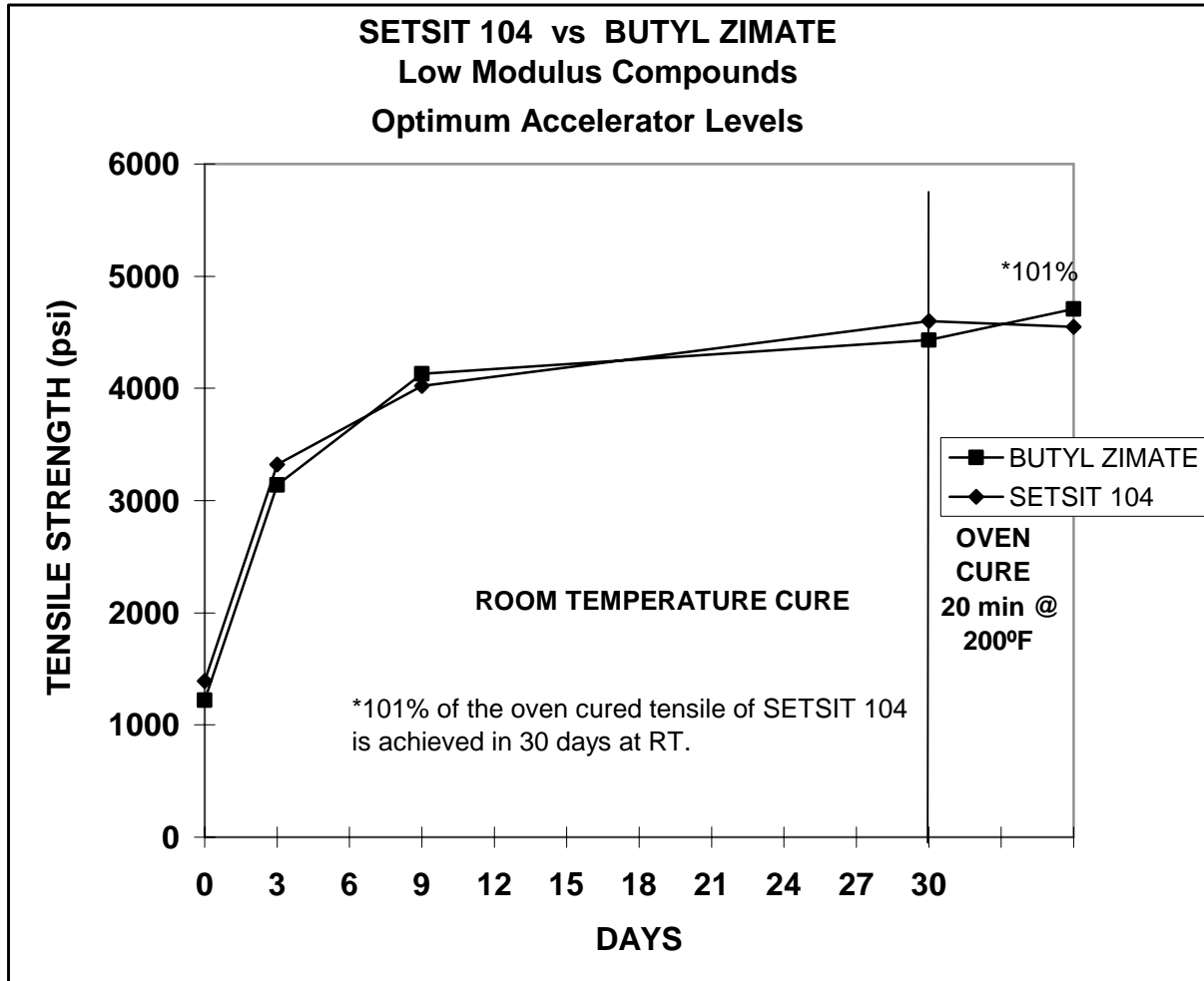
Once a SETSIT is selected for activity, pot life, low nitrosamines, FDA component listing, balloon taste or combinations of these, it is important to isolate the latex film vulcanization data for subsequent plant processing. We have done this for each of the activated liquid dithiocarbamates, and for both high and low modulus compounds.

These “profiles” answer the questions:

1. How does the activity compare with BUTYL ZIMATE?
2. What is the activity at various accelerator levels?
3. What is the effect of accelerator level on tensile strength and modulus together?
4. What are the room temperature characteristics?
5. What are the 5 minute cure characteristics?
6. How does room temperature aging with and without a five minute cure compare with optimum oven curing?

Since we displayed the high modulus compounds for preceding examples, we will exhibit the activity of one of the SETSITs in a low modulus compound in order to illustrate the profile.

Figure 6:



Note: While the chart lines in Figure 6 continue from the room temperature data to the oven cure data on the far right, it is only a convention. The data for the oven cure were derived independently. That is, the films were tested after 24 hrs following an oven cure according to ASTM standards.

Figure 6 shows that there is very little difference between the activity of SETSIT 104 and BUTYL ZIMATE in either room temperature curing or oven curing. It is virtually identical. Another reason therefore exists for selecting one over the other.

Figure 7:

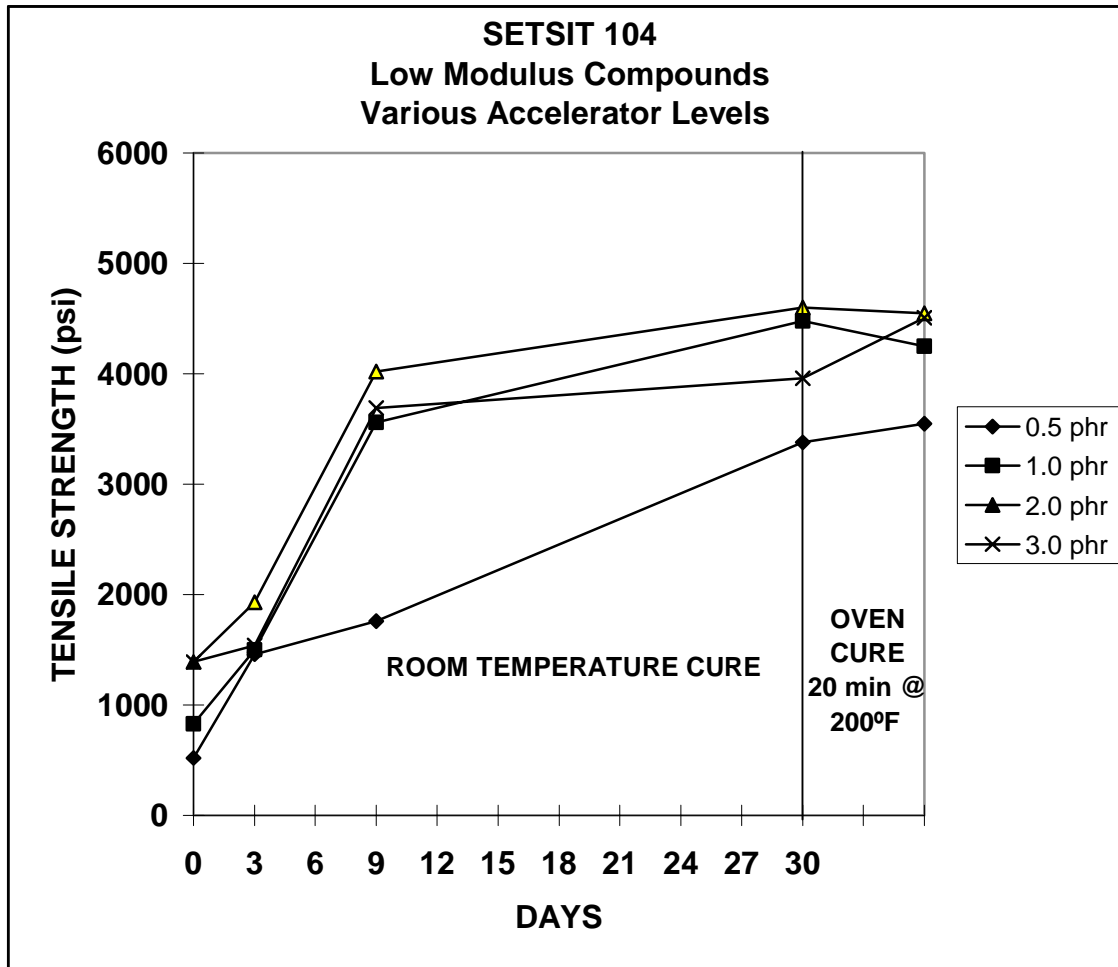


Figure 7 shows that a half part of SETSIT 104 is too little to produce a 4000 psi tensile in a low modulus compound when curing either at room temperature or in a high temperature oven. Once again, more is not necessarily better. Equal or superior properties are produced with either 2 or 3 phr of SETSIT 104.

Figure 8:

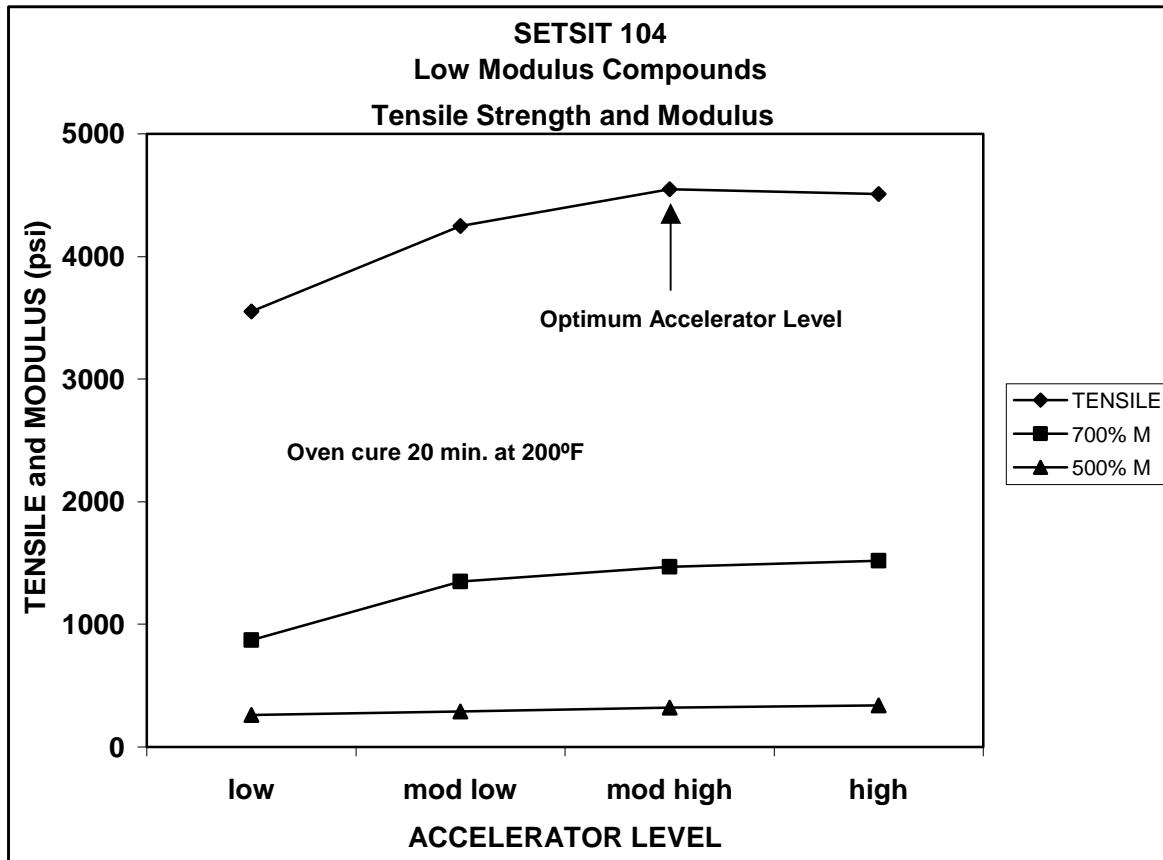
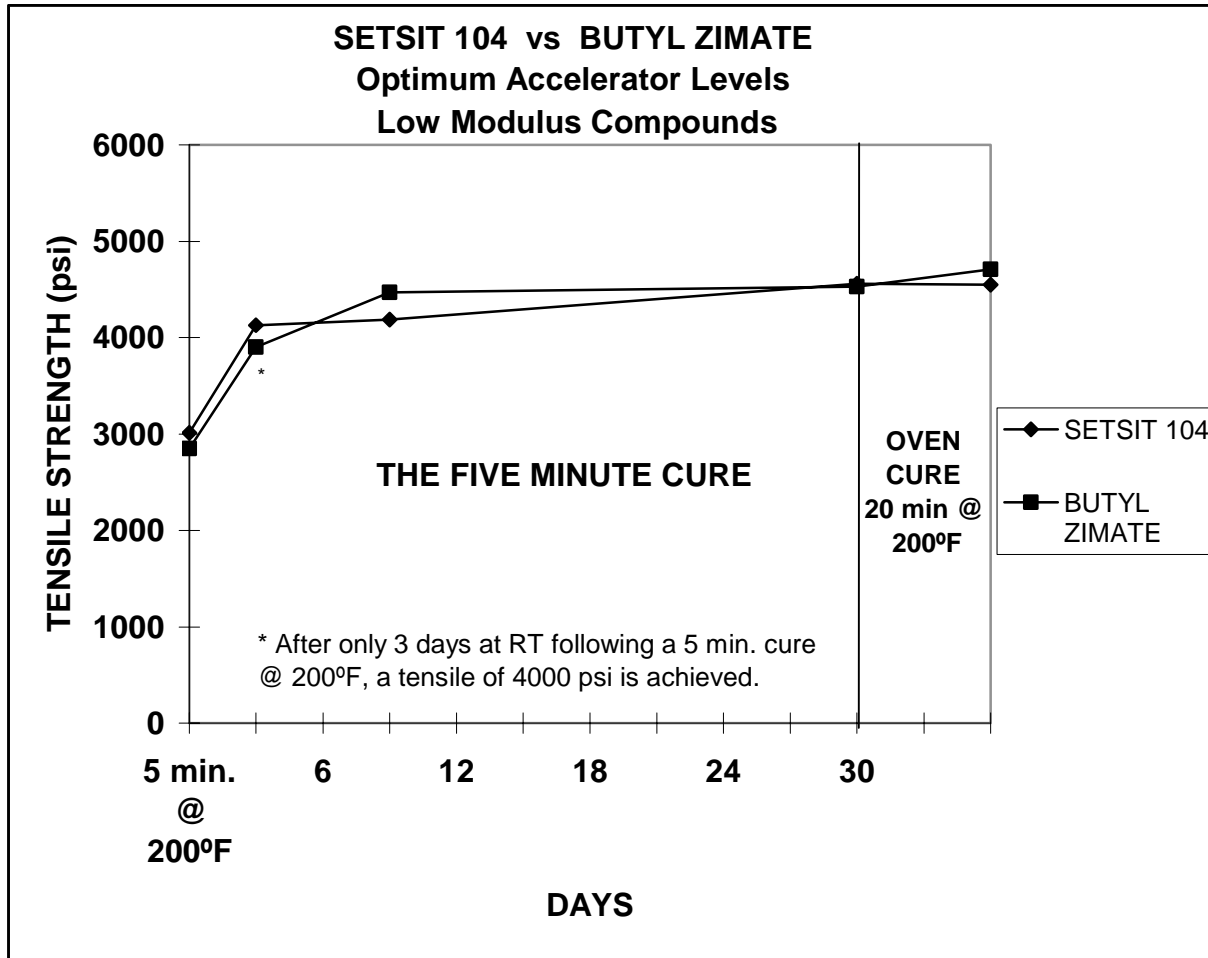


Figure 8 verifies our conclusion from Figure 7. For an oven cure, going from 2 phr to 3 phr of accelerator gives no advantage in tensile strength.

The 500% modulus is virtually independent of the accelerator level.

Figure 9:



Lastly, the 5 minute cure offers some insight into the pros and cons of an undercure compared to BUTYL ZIMATE. Once again, the cure characteristics of SETSIT 104 are very similar to those of BUTYL ZIMATE.

Review

We are especially pleased to have introduced activated liquid dithiocarbamates to those of you who were not previously familiar with them.

We also recommend that latex chemists and compounders take advantage of our detailed study and individual profiles on the activity and characteristics of these liquid accelerators to develop new latex products.

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