

# The Behavior of Dithiocarbamate Derivative as Safety Accelerator of Natural Rubber Compounds

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**ABSTRACT:** A conventional vulcanization system containing tetrabutylammonium bis(4-methylphenyldithiocarbamate)zincate(II) (ZNIBU) was used for curing of natural rubber (NR) compounds. Rheometric ( $t_{s1}$ ,  $t_{90}$ , and CRI) and mechanical properties, such as tensile and tear strengths and modulus at 300%, were measured to evaluate the acceleration potential of ZNIBU. Commercial accelerators (TMTD, MBTS, and CBS) and a binary system CBS/ZNIBU were also tested for comparison purposes. It was observed that ZNIBU alone does not give either safe scorch time or cure rates appropriate for

industrial applications. Nevertheless, mechanical properties are comparable to those given by the other accelerators used. As for the binary system, positive synergistic effects can be found in tear strength and modulus of NR vulcanizates. Besides, ZNIBU does not contribute for the formation of nitrosamines in the vulcanization process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1938–1944, 2008

**Key words:** accelerator; natural rubber; mechanical properties

## INTRODUCTION

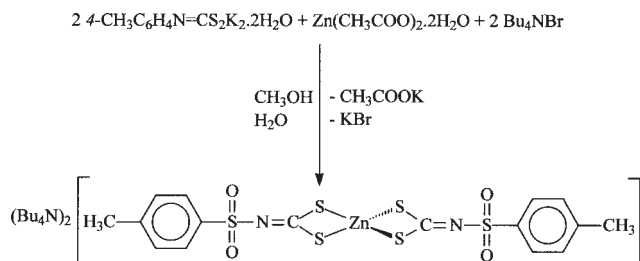
The discovery of the vulcanization process by Goodyear in 1839 marked the real beginning of the rubber industry. However, the widest use of the rubber products was not achieved until the discovery of organic accelerators, which not only increase the rate of vulcanization but also give vulcanizates with greatly improved physical properties. Organic amines, discovered by Oenslager and Hoffman and Gottlob, were the first organic accelerators.<sup>1,2</sup> Aniline was used extensively for several years. Dithiocarbamates were discovered in 1918. Thiuram disulfides were obtained by oxidation of the dithiocarbamates. Arylguanidines and thioureas were widely used during this period.<sup>3</sup> The effectiveness of zinc oxide and stearic acid as “activators” for dithiocarbamates and thiuram disulfides was also discovered.<sup>3</sup> A mile-

stone in the development of accelerators was the discovery by Bedford and Sebrell<sup>4</sup> and Bruni and Romani<sup>5</sup> of the usefulness of 2-mercaptobenzothiazole (MBT) as a vulcanization accelerator. This compound and its derivatives (sulfenamides) are presently the most widely used accelerators as they are relatively inexpensive, produce vulcanizates with good physical properties, and offer adequate levels of processing safety.

In spite of the evolution in the rubber industry, a considerable preoccupation has been devoted to the formation of nitrosamines associated with rubber processing and rubber products. Among the various human activities, the highest concentrations of nitrosamines have been found in the rubber industry. At present, experimental studies report that about 90% of the 300 tested nitrosamines have shown potential carcinogenic effects involving different organs of at least 39 different animal species. Predominant sites of tumor induction in animals include oral cavity, esophagus, stomach, urinary bladder, and brain.<sup>6–9</sup> Therefore, the introduction of “safe” amino components into traditional accelerator molecules could be an effective procedure to prevent formation of carcinogenic *N*-nitroso-compounds during rubbery goods production. About 20 new derivatives of the dithiocarbamate and sulfenamide class,

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**Scheme 1** Preparation and chemical structure for ZNIBU.

based on “safe” amines, were synthesized and shown to be suitable for industrial application.<sup>10</sup>

In this investigation, a new synthetic substance, tetrabutylammonium bis(4-methylphenyldithiocarbimate)zincate(II) (ZNIBU), was evaluated as a potential accelerator for NR compounds. ZNIBU (Scheme 1) does not contain amino groups, and hence will not contribute for nitrosamines formation in the vulcanization process. For comparison purposes, commercial accelerators were also employed and rheometric properties as well as tensile and tear strengths of NR compounds were measured.

## EXPERIMENTAL

### Materials

Natural rubber (NR) sample was supplied by Michelin Indústria e Comércio. Zinc oxide and stearic acid were standard reference materials. Sulfur was supplied by Intercuf, and accelerators by Bann Química. Aminox was supplied by Crompton. The compositions were prepared according to the formulation presented in Table I.

ZNIBU was synthesized<sup>10</sup> according to the reaction shown in Scheme 1. ZNIBU shows solubility in chloroform and dichloromethane, partial solubility in methanol and ethanol, and is insoluble in water.

### Preparation of mixtures, rheometric analysis, and preparation of test samples

Mixing was carried out on a two-roll mill at 70°C and 1 : 1.25 speed ratio, according to ASTM D3184-80. The batch weight was checked and recorded. If different from theoretical value by more than 0.5%, it was rejected. The sheeted compound was conditioned at 25°C ± 2°C for 24 h in a closed container before determination of the optimum cure time. This was obtained on a TI-100 Curometer at 150°C (ASTM D2084-81). For mechanical properties evaluation, test specimens were cut from vulcanized sheets prepared by compression molding in an electrically heated press at 150°C and 3.0 MPa. After condition-

**TABLE I**  
Typical Formulation

Material	Concentration (phr)
Natural rubber	100
Zinc oxide	3.5
Stearic acid	2.5
Accelerator <sup>a</sup>	0.8
Aminox <sup>b</sup>	2.0
Sulphur	2.5

<sup>a</sup> *N*-cyclohexyl-2-benzothiazole-2-sulphenamide (CBS), 2-bisbenzothiazole-2,2'-disulfide (MBTS), tetramethyl thiuram disulfide (TMTD) or tetrabutylammonium bis(4-methylphenyldithiocarbimate)zincate(II) (ZNIBU).

<sup>b</sup> Antioxidant—low temperature reaction product of diphenylamine and acetone.

ing for 24 h, the properties were measured along the grain direction.

### Physicomechanical testing of the samples

Stress-strain (ASTM D412-83) and tear strength (ASTM D624-86) data were determined on an Instron Universal Testing Machine, Model 101, on appropriate specimens.

### Analysis of variance

To evaluate ZNIBU as a potential accelerator for NR compounds, the analysis of variance by MINITAB 15<sup>TM</sup>® software was performed. Rheometric properties (scorch time,  $t_{s1}$ ; optimum cure time,  $t_{90}$ ; and cure rate index, CRI), and tensile and tear strengths were considered as a function of accelerator type. Accelerators used were CBS, MBTS, TMTD, and ZNIBU at 0.8 phr concentration. The specimens were randomly tested and the results were organized according to Tables II and III.<sup>11,12</sup>

The results were considered in view of the following hypotheses:

$$H_0: \tau_1 = \tau_2 = \dots = \tau_i = 0 \quad (1)$$

$$H_1 = \tau_i \neq 0 \text{ for at least one } i$$

If the first condition occurs then by changing the accelerator type no effect on the mean response will

**TABLE II**  
Typical Data for a Single-Factor Experiment

Treatment	Observations			Totals	Averages	
1	$Y_{11}$	$Y_{12}$	...	$Y_{1n}$	$Y_{1.}$	$\bar{Y}_{1.}$
2	$Y_{21}$	$Y_{22}$	...	$Y_{2n}$	$Y_{2.}$	$\bar{Y}_{2.}$
...	...	...	...	...	...	...
<i>a</i>	$Y_{a1}$	$Y_{a2}$	...	$Y_{an}$	$Y_{a.}$	$\bar{Y}_{a.}$
					$Y_{..}$	$\bar{Y}_{..}$

**TABLE III**  
**The Analysis of Variance for a Single-Factor Experiment, Fixed-Effects Model**

Source of variation	Sum of squares (SS)	Degrees of freedom (DF)	Mean square (MS)	$F_o$
Treatments	$SS_{\text{Treatments}}$	$a - 1$	$MS_{\text{Treatments}}$	$MS_{\text{Treatments}}/MS_E$
Error	$SS_E$	$a(n - 1)$	$MS_E$	
Total	$SS_T$	$an - 1$		

$a$ , number of different levels of a single factor;  $n$ , number of observations;  $N$ , total number of observations ( $N = a*n$ ); if  $F_o > f_{\alpha, a-1, a(n-1)}$ , there is a real effect when the levels change.

$$SS_T = \sum_{i=1}^a \sum_{j=1}^n y_{ij}^2 - \frac{y_{..}^2}{N}; \quad SS_{\text{Treatments}} = \sum_{i=1}^a \frac{y_{i.}^2}{n} - \frac{y_{..}^2}{N}; \quad SS_E = SS_T - SS_{\text{Treatments}}.$$

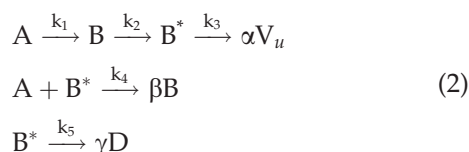
be observed (all  $N$  observations are taken from a normal distribution with mean  $\mu$  and variance  $\sigma^2$ ) and the ratio  $F_o$  will display an  $F$ -distribution with  $a - 1$  and  $a(n - 1)$  degrees of freedom.

## RESULTS AND DISCUSSION

The results of rheometric properties for NR compounds vulcanized with different accelerators are summarized in Table IV. The commercial accelerators (TMTD, MBTS, and CBS) behaved as expected. Scorch time ( $t_{s1}$ ) and optimum cure time ( $t_{90}$ ) for CBS and MBTS accelerators are very close. The CRI value, however, is higher for CBS than for MBTS. The TMTD-vulcanized compound exhibits a shorter  $t_{s1}$  value and a faster vulcanization when compared with the other commercial accelerators. ZNIBU shows a singular effect on the vulcanization process: the  $t_{s1}$  value is very small, only 1.5 min, but the time necessary for a complete cure is long, over 30 min.

An overall route for the vulcanization process is shown in Ref. 13. It is noticed that during the curing and network maturing periods, at least three reactions compete with each other, namely, crosslinking, desulfuration, and decomposition. The balance of reactions depends not only on the temperature but also on the accelerator type and concentration.

A simplified kinetic scheme for accelerated sulfur vulcanization based on the Coran model<sup>13</sup> is:



where, A is the accelerator and/or its reaction products (with sulfur,  $Zn^{2+}$ , etc.), B is a precursor to crosslinks, probably polymeric,  $B^*$  is an activated form of B, such as a polymeric polythiyl radical,  $V_u$  is a crosslink, D are inactive side products, and  $\alpha$ ,  $\beta$ ,

and  $\gamma$  are adjustable stoichiometric parameters. It was considered that if the reaction through  $k_4$  is much faster than through  $k_3$ , crosslink precursors  $B^*$  are rapidly quenched. Crosslink formation would be inhibited until A is substantially depleted. It is also considered that  $k_4$  and  $k_3$  are much greater than  $k_1$  and  $k_2$ . With these scheme and assumptions, under isothermal conditions, Coran<sup>13</sup> described the induction period kinetically rather than using an Arrhenius type relationship. The curing period was described separately by simple first-order kinetics. In this modified model, D represents inactive side products and it is useful to explain the change of maximum modulus with temperature, which is observed from the vulcanization of a styrene-butadiene rubber (SBR) compound.<sup>14</sup>

2-Bisbenzothiazole-2,2'-disulfide (MBTS)-accelerated sulfur vulcanization of rubber has been studied by various authors.<sup>15-18</sup> Gradwell and McGill<sup>19</sup> investigated the sulfur vulcanization of polyisoprene accelerated by MBTS. According to the authors, MBTS reacts readily with sulfur, and the polysulfidic accelerator complexes react with the rubber chain to form pendent groups. This benzothiazole pendent group then abstracts a hydrogen from a neighboring chain giving rise to the formation of a crosslink. It has been shown that MBTS does not react with ZnO and that the higher crosslink densities obtained when ZnO is present are attributed to ZnO aiding the abstraction of the benzothiazole pendent group to give zinc mercaptobenzothiazole.

**TABLE IV**  
**Rheometric Properties for NR Compounds Vulcanized with Different Accelerators**

Accelerator	Scorch time ( $t_{s1}$ , min)	Optimum cure time ( $t_{90}$ , min)	Cure rate index (CRI)
TMTD	$2.3 \pm 0.1$	$4.6 \pm 0.3$	$43.9 \pm 3.1$
CBS	$5.7 \pm 0.4$	$11.5 \pm 0.2$	$17.2 \pm 0.6$
MBTS	$4.2 \pm 0.8$	$12.1 \pm 0.1$	$12.9 \pm 1.4$
ZNIBU	$1.5 \pm 0.4$	$32.4 \pm 4.2$	$3.3 \pm 0.4$

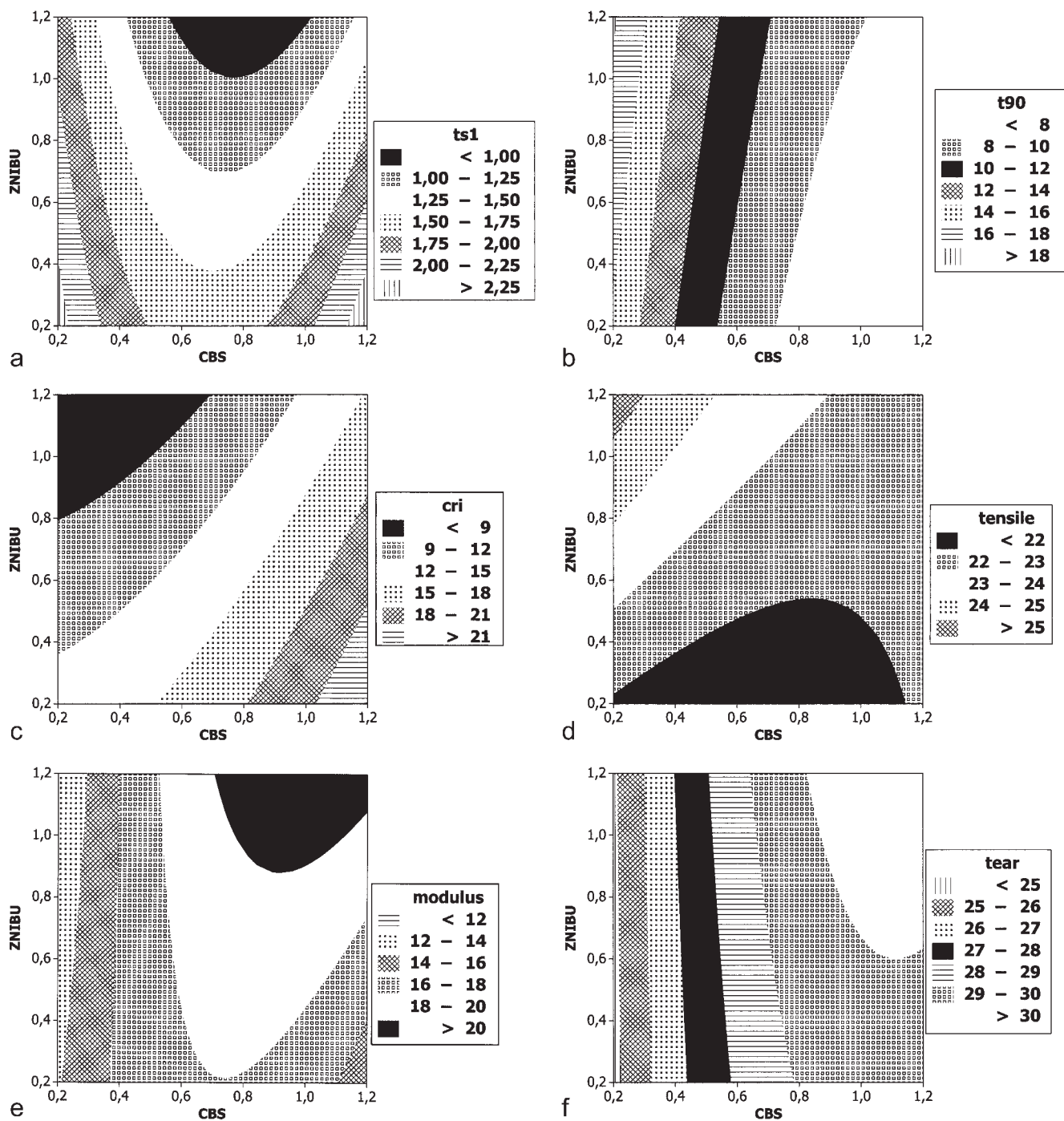


Figure 1 Contour plots for the second-order model—relationship between property and proportion of accelerators.

In other investigation, Gradwell and McGill<sup>20</sup> observed the sulfur vulcanization of polyisoprene accelerated by CBS. The delayed action of CBS accelerator is explained in terms of an exchange reaction between benzothiazole terminated polysulfidic pendent groups on the polymer chain and CBS to yield unreactive amine terminated pendent groups and 2-bisbenzothiazole-2,2'-disulfide (MBTS). The formed MBTS reacts with sulfur to form 2-bisbenzothiazole-2,2'-polysulfides (MBTPs), which also form pendent

groups. Crosslinking does not commence until all of the CBS has been consumed and pendent groups are no longer deactivated. During crosslinking, MBT is released. Zinc oxide does not react with CBS, and its role in increasing the crosslink density is attributed to its promoting crosslinking reactions between pendent groups and neighboring chains rather than intramolecular reactions, which would lead to cyclization.

From overall route for the vulcanization process<sup>13</sup> and the results obtained by Gradwell and



**TABLE V**  
Analysis of Variance for Rheometric Properties of NR Compositions Containing Different Accelerators

Source of variation	$F_o^a$		
	Scorch time ( $t_{s1}$ )	Optimum cure time ( $t_{90}$ )	Cure rate index (CRI)
Accelerator type	26.23	63.54	197.67

<sup>a</sup>  $f_{0.05, 3, 4} = 6.59$ , for 95% of significance level.

McGill,<sup>19,20</sup> it can be concluded that either MBTS or CBS exhibit a safe scorch time ( $t_{s1}$ ) because of the existence of an induction period. Therefore, only when A (the accelerator and/or its reaction products) is completely depleted and B\* concentration is appreciable, the crosslink process begins. Then, as soon as crosslink begins, the optimum cure time ( $t_{90}$ ) is rapidly reached.

With regard to TMTD, polysulfide type accelerators are generally acknowledged to act as sulfurating agents for accelerated vulcanization in the absence of ZnO.<sup>21,22</sup> In tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization, interaction of tetramethylthiuram polysulfides (TMTP) with the polymer chain via a concerted reaction<sup>21–24</sup> leads to the formation of thiuram-terminated pendent groups and dimethyldithiocarbamic acid (Hdmtc).<sup>21–26</sup> Crosslinking is said to result from the interaction between pendent groups or from a reaction between a pendent group and a neighboring polymer chain.<sup>27,28</sup> Zinc oxide acts as a catalyst, and its presence turns the crosslinking process faster. Therefore, TMTD in the NR vulcanization leads to small scorch time and high cure rate index.

With regard to ZNIBU, a singular behavior is found. ZNIBU gives a small scorch time, similar to TMTD, but the optimum cure time and cure rate index for the two compounds are completely different. The molecule of ZNIBU shows a complex structure (Fig. 1) with the presence of bulky chemical groups. Therefore, if a rapid formation of B (precursor to crosslinks, probably polymeric) does occur, according to overall route for the vulcanization process and the modified Coran model,<sup>13</sup> this would explain the small  $t_{s1}$  value; however, as B is available to interact with the rubber for the formation of B\* (activated form of B), there must be some deleterious effect occasioned by ZNIBU bulky structure, which would lead to the delay in the crosslink formation, in such a way that a final vulcanizate network would only be formed after long cure times.

In Table V, the analysis of variance for rheometric properties of NR compositions containing different accelerators is shown. If  $F_o > f_{\alpha, a-1, a(n-1)}$ , where  $\alpha$  is a significance level,  $H_o$  is rejected and accelerator

**TABLE VI**  
Mechanical Properties for NR Compositions Containing Different Accelerators

Accelerator	Tensile strength (MPa)	Tear strength (kN/m)	Modulus at 300% (MPa)
TMTD	19.3 ± 2.9	38.4 ± 1.4	4.5 ± 0.6
CBS	21.8 ± 0.9	39.1 ± 4.1	3.9 ± 0.4
MBTS	21.4 ± 1.1	33.7 ± 2.4	2.2 ± 0.3
ZNIBU	22.2 ± 4.9	36.7 ± 2.9	3.4 ± 0.3

type in the NR composition significantly affects rheometric properties, tensile or tear strength of the NR compounds. All rheometric properties present  $F_o$  value greater than the  $f$  value fixed at 95% of significance level. This is an indication that the change in the accelerator type promotes remarkable modification on the vulcanization process, as discussed previously.

Table VI summarizes the mechanical properties for NR compositions containing different accelerators. It can be observed that there are no significant differences imparted by the accelerators upon NR vulcanizates. Although ZNIBU presented poor performance concerning vulcanization parameters (short scorch time and long cure time), NR compounds vulcanized with ZNIBU showed tensile and tear strengths and modulus at 300% in the same order of magnitude as the commercial accelerators. Analysis of variance for mechanical properties in Table VII confirms this statement. All mechanical properties present  $F_o$  value inferior to the  $f$  value fixed at 95% of significance level. This indicates that by changing the accelerator type no appreciable modification in the properties of NR vulcanizates is observed or, in other words, that the final networks probably exhibit similar crosslink density despite the accelerator used.

Combinations of accelerators are frequently used in the rubber industry. When a binary system is used, any of the following three situations can be expected: (i) synergistic system; (ii) systems in which the activity of the pair does not exceed that of the most active accelerator; and (iii) systems with an

**TABLE VII**  
Analysis of Variance for Mechanical Properties of NR Compositions Containing Different Accelerators

Source of variation	$F_o^a$		
	Tensile strength (MPa)	Tear strength (kN/m)	Modulus at 300% (MPa)
Accelerator type	0.25	1.27	0.80

<sup>a</sup>  $f_{0.05, 3, 4} = 6.59$ , for 95% of significance level.

TABLE VIII  
Proportions of the Binary System CBS/ZNIBU  
for NR Vulcanization

Mixture	1	2	3	4	5
CBS (phr)	1.2	0.2	1.2	0.2	0.7
ZNIBU (phr)	0.2	0.2	1.2	1.2	0.7

additive functionality of the accelerators. Originally, the higher activity of binary accelerator systems was explained by the formation of either eutectic mixes or salt-forming compounds that possess better solubility in rubber and greater chemical reactivity.<sup>22</sup> Therefore, as an attempt to overcome the poor performance of ZNIBU concerning the rheometric parameters, CBS and ZNIBU were combined in proportions as shown in Table VIII. The aim was to create a possible synergistic system where negatives effects of ZNIBU upon  $t_{s1}$  and  $t_{90}$  could be corrected and mechanical properties improved.

For better interpretation of results, response surface methodology (RSM) has been used. RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. It also has important applications in the design, development, and formulation of new products, as well as in the improvement of existing products designs.<sup>29</sup> In our case, the results from Table VIII have been approximated to the true response by a second-order model as described by the equation:

$$\eta = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \beta_{ij} x_i x_j \quad (3)$$

Figure 1 presents the results for the binary system CBS/ZNIBU, where a theoretical response surface shows the relationship between property (rheometric or mechanical) and the contents of accelerators in the binary system.

From Figure 1, it can be observed that for rheometric properties ( $t_{s1}$ ,  $t_{90}$ , and cure rate index or CRI) a synergistic effect is found only for the scorch time. The contour plot shows that vulcanization of NR compounds through a high scorch time can only be achieved if one of the following conditions is fulfilled, concerning the CBS/ZNIBU mixture: either CBS is present in a much higher proportion than ZNIBU or the accelerators are both present in small quantities. If none of these conditions is met, the ZNIBU present in the composition will impart a still shorter  $t_{s1}$ , resulting from its combined effect with CBS—the black and white regions in the contour plot, in which  $t_{s1}$  is lower than 1.25 min.

As for optimum cure time ( $t_{90}$ ), CBS/ZNIBU mixture behaves as a system in which the activity of the pair does not exceed that of the most active accelera-

tor, in other words, CBS must be always present in high quantity, at least 0.8 phr, as the black region in the contour plot suggests. For CRI values as well as  $t_{90}$ , similar behavior was found for binary accelerator system. Therefore, it can be concluded that ZNIBU must be used only in very small quantities if both safety and high reaction rates for the NR vulcanization are desirable.

For mechanical properties, Figure 1 shows that tensile strength values above 25 MPa are only reached when ZNIBU is present in amounts higher than 1.0 phr together with small percentage of CBS (region with squares in contour plot), however, this condition is not satisfactory for processing for tear strength and modulus at 300%, better performance is obtained, at first, when CBS/ZNIBU mixtures contain both accelerators in the same percentage around 1.0 phr.

## CONCLUSIONS

Rheometric and mechanical properties of NR compounds vulcanized with a new substance named ZNIBU, or tetrabutylammonium bis(4-methylphenyl-dithiocarbimate)zincate(II), were evaluated. Commercial accelerators such as TMTD, MBTS and CBS, and a binary system CBS/ZNIBU were also tested. From the results, it can be concluded that the performance of ZNIBU as accelerator is not adequate with regard to scorch and optimum cure time. As for the mechanical properties, the results found for these NR compounds vulcanized either with ZNIBU or the commercial accelerator were of the same magnitude.

A possible binary system, CBS/ZNIBU, did not completely solve processing problems although for tear strength and modulus at 300% some synergistic effect could be found.

The mode of action of ZNIBU might be similar to those presented by correlated dithiocarbamates. Nevertheless, it is important to note that the small structural differences between dithiocarbimides and dithiocarbamates shall determine significant differences in their chemistry and physicochemical properties. For example, their solubility in the reaction medium will not be the same for the zinc dithiocarbimate is necessarily a dianionic complex. Studies on the mechanism of the rubber vulcanization with ZNIBU and the positive synergistic effects of ZNIBU and CBS binary systems are on their way, and the results of these investigations will be published in due course.

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