

## TECHNOLOGICAL BEHAVIOUR OF A NEW 'NITROSAMINE SAFE' THIURAM DISULFIDE IN NATURAL RUBBER

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### ABSTRACT

*Thiuram class of ultra accelerators are widely used in the rubber industry to obtain high rate of cure and high cross-link densities in sulfur vulcanised rubbers. They are commonly used either as sulfur donors for heat resistance applications or as secondary accelerators in conjunction with sulfenamides. However, conventional thiurams have undesirable drawbacks due to their inherent toxicity and their ability to form regulated carcinogenic N-nitrosamines. The paper describes the technological behaviour of a new nitrosamine safe thiuram disulfide, tetraisononylthiuramdisulfide (TINTD), which has been derived from a safer secondary amine, di(3,5,5-trimethylhexyl) amine. It demonstrates the curing efficiency of TINTD, as a primary and secondary accelerator and also as a sulfur donor in black filled natural rubber. The unique features of TINTD and its vulcanisation breakdown product makes this thiuram disulfide highly attractive for use in soluble efficient vulcanisation systems and its use is described. The paper also discloses the accelerator action of TINTD in high ammonia natural rubber latex.*

### INTRODUCTION

Thiurams are a group of sulfur containing organic compounds which act as ultra-rubber accelerators, where only the disulfides and polysulfides also act as sulfur donors<sup>1</sup>. They are widely used in the rubber industry. The best known thiurams are tetramethylthiuramdisulfide (TMTD), tetramethylthiurammonosulfide (TMTM) and tetraethylthiuramdisulfide (TETD), which have been synthesised from short chain secondary amines where the alkyl chains are methyl or ethyl groups. Other common thiurams are dipentamethylenethiuramhexasulfide (DPTH) and tetrabutylthiuramdisulfide (TBTD), which are derived from piperidine and butylamine, respectively. Although these are most effective in cross-linking rubber, they all have limitations or concerns associated with them when used alone or in combination. They are highly toxic and can cause irritant dermatitis and Type IV allergic contact dermatitis<sup>2-6</sup>. During the vulcanisation reaction, they can also thermally breakdown to generate the parent secondary amine which, in the presence of oxides of nitrogen, produce regulated carcinogenic N-nitrosamines and nitrosatable substances<sup>7-9</sup>. Therefore, they are not very favourable for new compositions and should be avoided in formulation.

Due to various regulations<sup>10-14</sup>, there has been a push in all areas of the rubber industry to use safer accelerators. Some environmentally safer thiurams have

appeared on the market as a replacement for traditional thiurams for a number of reasons. They either do not produce N-nitrosamines that are restricted by the German TRGS 552 list, or the nitrosamines produced are reported to be less carcinogenic than those generated by the traditional thiurams. These thiurams are based on sterically bulky secondary amines such as diisobutylamine and dibenzylamine producing tetraisobutylthiuramdisulfide (TiBTD)<sup>15</sup>, and tetrabenzylthiuramdisulfide (TBZTD)<sup>16</sup>, respectively. Due to the sterically bulky alkyl or aryl groups on the secondary amines, these safer thiurams are slightly less effective, on weight to weight basis, during the vulcanisation reaction<sup>17</sup>.

The aim of the present paper is to demonstrate the technological performance of a recently developed nitrosamine safe thiuram disulfide, TINTD<sup>18</sup>, synthesised from diisononylamine, in natural rubber. It has been found that if diisononylamine, di(3,5,5-trimethylhexyl) amine, is nitrosated, its nitrosamine is involatile and also toxicologically much less hazardous in terms of both acute toxicity and metabolic activity. Genotoxic tests on N-nitrodiisononylamine (NDiNA) showed no evidence of mutagenic activity when tested through Ames test, either with or without metabolic activation<sup>19</sup>. In addition, no gene mutation effects were found when testing in vivo transgenic mammalian (HPRT mutation test), therefore NDiNA is not mutagenic<sup>20</sup>. These experimental findings show that there is no mechanism for carcinogenic activity from NDiNA. This implies that TINTD is a safer molecule with respect to N-nitrosamine concern and is an alternative safer thiuram to the traditional thiurams.

Traditional thiurams alone do not generally find application in latex mixtures<sup>21</sup>. However, in this paper, TINTD was evaluated as an accelerator in high ammonia natural rubber latex. It was also evaluated as a primary and secondary accelerator as well as a sulfur donor in black filled natural rubber. Furthermore, the replacement of TBTD by TINTD in soluble efficient vulcanisation (EV) cures was demonstrated.

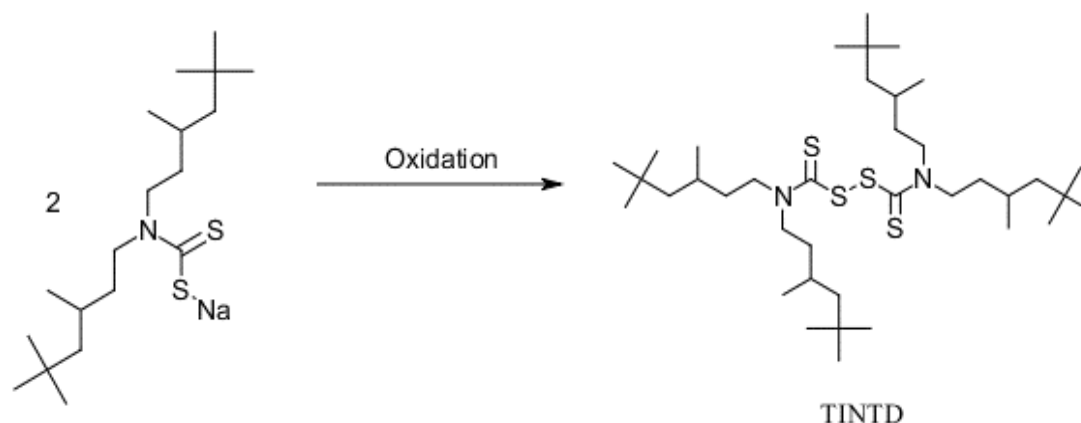
## EXPERIMENTAL

### Materials

Black filled natural rubber masterbatch (IOM 3 B012) was obtained from Clwyd Compounders, Wrexham, Wales. It contained Standard Malaysian Rubber CV 60 (100), carbon black FEF N550 (50), naphthenic oil (10), stearic acid (1) and antioxidant, octylated diphenylamine, ODP (1.5). Values given in brackets are phr. The black filled natural rubber masterbatch (LCR 50) for low creep rubbers for injection moulding was prepared at Robinson Brothers Limited in a BR Banbury mixer. The composition of this masterbatch was: SMR CV (100), carbon black N762 (30), zinc oxide PM 85 (5.89), zinc ethyl hexanoate (ZEH) 70% (1.43) and antioxidant TMQ (1.0). Unfilled natural rubber masterbatch (PC1) was prepared at Robinson Brothers Limited, on an open 2-roll mill, to assess the formation of nitrosamines and nitrosatable substances using the BS EN 71-12:2016. The composition of PC1 masterbatch was: pale crepe NR (100), stearic acid (0.6), active zinc oxide (0.6), sulfur (2.0), antioxidant Wingstay L (0.5).

CBS PM80, Sulfur PM80, ZnO PM85 and Wingstay L were obtained from Chemipat Ltd., Manchester. Commercial grade TBTD was produced at Robinson Brothers Limited.

High ammonia natural rubber latex (HA-NRL, LC212) was obtained commercially from Vita Liquid Polymers Limited, Manchester, UK. Compounding materials were obtained commercially from Aquaspersions, Halifax, UK and used either as dispersions, aqueous solutions or emulsions. TINTD was synthesised and emulsified at Robinson Brothers for testing in HA-NRL. Properties of TINTD are given in Appendix 1. Synthetic route from the sodium dithiocarbamate is given below.



## Equipment and Procedures

Two roll open mill with a friction ratio of 1:1.25 was used for mixing additives into the rubber masterbatch, completed within 15 minutes, utilising cooling water and steam heating for temperature control. Rheological study of all compounded rubber mixes was carried out at 160°C using Alpha Technologies (Monsanto) Moving Die Rheometer MDR2000E with an oscillating frequency of 1.667Hz and DAISY software version 8.60. Mooney viscosity determinations were carried out at 100°C by using a large rotor on an SPRI (Negretti Automation) pneumatically operated Mooney Viscometer. Appropriate test pieces were compression moulded for Tensile Strength, Hardness and Elongation evaluation, all to BS903 using an electrically heated hydraulic press. Tensile sheets were cured for T90 x 1.5 minutes. All tensile properties were determined to BS903: Part A2 Type 1 Dumb Bells (large) using an Instron 4302 Tensile testing machine with Blue Hill software. International Rubber Hardness Degree (IRHD) of samples was tested using the Wallace Rubber Hardness Tester. Thermal ageing studies were carried out in hot air using Wallace cell ovens at 70°C and 100°C to determine the influence of elevated temperature and time on tensile properties. Accelerated ageing and heat resistance tests were carried out in accordance with BS 903-A19:1998. The heat resistance test results are reported as the percentage change in the value of the property measured as calculated from the formula:  $\frac{X_a - X_0}{X_0} \times 100$  where  $X_0$  is the value of the property before ageing and  $X_a$  is the value of the property after ageing. Compression set determinations were carried out at either 70°C or 100°C using BS903 Part A6 (1992) method B (25% compression). Fatigue to failure tests were

carried out using the Monsanto Fatigue to Failure Tester. Averages are expressed in Japanese Industrial Standard (JIS) average using the highest four results from six used in every test. Other experimental techniques and latex study conditions are described in the appropriate sections. The cross-link densities were determined on black filled natural rubber vulcanisates using the Flory-Rehner equation<sup>22</sup>.

### Measurement of Cross-link Decomposition

The cross-link decomposition was evaluated from the reversion degree (R), using the following equation<sup>23</sup>.

$$R(\%) = \frac{M_H - M_{H+30}}{M_H} \times 100$$

Where  $M_H$  is the maximum torque and  $M_{H+30}$  is the torque after 30 minutes from the maximum torque. Also used, when appropriate, is  $M_{H+15}$  where the torque is 15 minutes from the maximum torque.

## RESULTS AND DISCUSSION

### Demonstration of TINTD as a sulfur donor and as a primary accelerator for conventional, semi-EV and EV cure systems in natural rubber

In the following study, TINTD was evaluated as a sulfur donor and as an accelerator in the conventional (CV), semi- efficient (Semi-EV) and efficient (EV) cure systems using black filled NR masterbatch IOM 3 B012.

Four formulations, as given in Table 1, were studied. Comparative rheographs taken at 160°C are shown in Figure 1.

*Table 1*

Formulations for conventional, semi-EV, EV and sulfur donor cures with TINTD present at 2.5, 6.25, 20.5 and 16.5mmol, respectively. Weights given in grams.

	<b>Conventional</b>	<b>Semi-EV</b>	<b>EV</b>	<b>Sulfur Donor</b>
<b>Mix Number</b>	<b>Mix 1</b>	<b>Mix 2</b>	<b>Mix 3</b>	<b>Mix 4</b>
MB IOM 3 B012	162.5	162.5	162.5	162.5
ZnO	5	5	5	5
Sulfur	2.5	1.5	0.5	-
TINTD	1.72	4.3	14.1	11.0

The level of sulfur being decreased and the level of TINTD increased in ratios that are typical of conventional through Semi-EV to EV cure systems.

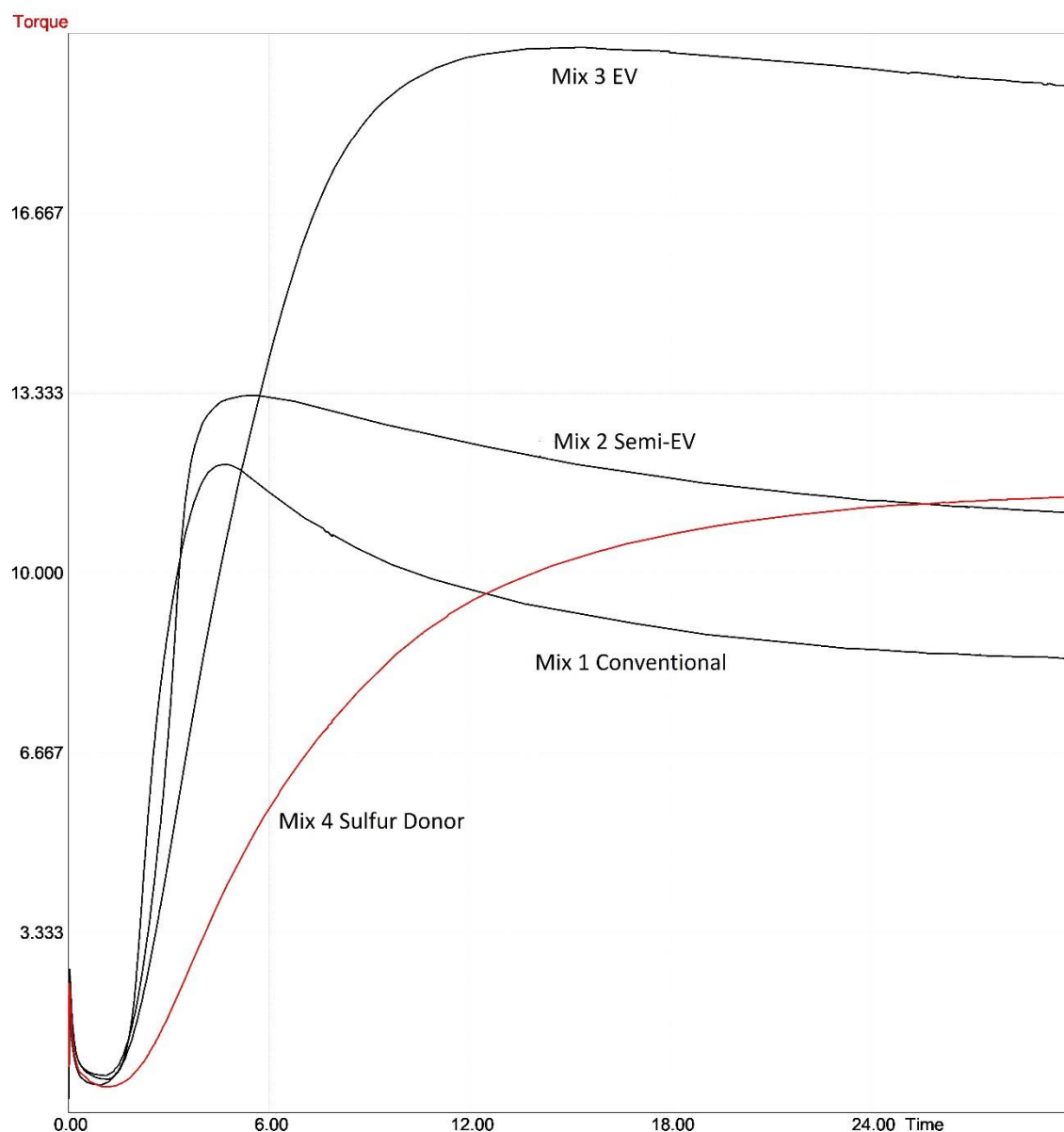


Fig.1 Rheographs of NR taken at 160°C using TINTD in conventional, semi-efficient (Semi-EV) and efficient (EV) cure systems and as a sulfur donor. TINTD present at 2.5, 6.25, 20.5 and 16.5 mmol, respectively.

The rheological and Mooney data, reversion degree, tensile properties before and after thermal ageing (percentage heat resistance is given in brackets), hardness, compression set and fatigue to failure results for the conventional, Semi-EV, EV and sulfur donor cure systems are given in Table II.

*Table II*

Rheological properties of NR vulcanisates at 160°C using TINTD as a sulfur donor, and in conventional, semi-EV and EV cure systems. Mooney viscosity at 100°C, tensile properties before and after heat ageing, compression set and fatigue to failure.

	<b>Conventional Mix 1</b>	<b>Semi-EV Mix 2</b>	<b>EV Mix 3</b>	<b>Sulfur Donor Mix 4</b>
<b>Rheological Data at 160°C</b>				
TS1 (Minutes)	1.87	1.93	1.97	2.74
T10 (Minutes)	1.90	2.02	2.32	2.81
T90 (Minutes)	3.56	3.66	8.25	15.42
MH-ML (lb.in)	11.39	12.6	19.22	10.93
Rate (lb.in/minute)	8.60	9.62	3.70	1.44
Reversion degree (R) (%)	24.98	13.28	4.02	0.0
<b>Mooney Viscosity at 100°C</b>				
ML1+4 (100°C)	16.41	16.65	13.80	13.0
<b>Initial Tensile Properties</b>				
U.T.S (MPa)	17.8	19.8	17.9	16.2
Strain at Break (%)	599	545	406	570
100% Modulus (MPa)	1.48	1.66	2.17	1.0
200% Modulus (MPa)	3.67	4.41	6.33	2.77
300% Modulus (MPa)	6.98	8.43	11.81	5.65
500% Modulus (MPa)	14.86	17.77	-	13.3
Hardness (IRHD)	52	55	52	41
<b>Tensile Properties: Aged 7 days at 70°C</b>				
U.T.S (MPa)	14.2 (-20%)	18.6 (-6%)	15.2 (-15%)	16.9 (+4%)
Strain at Break (%)	345 (-42%)	361 (-34%)	294 (-28%)	525 (-8%)
100% Modulus (MPa)	2.77	3.29	3.12	1.21
200% Modulus (MPa)	7.13 (+94%)	8.75 (+113%)	8.95 (+41%)	3.56 (+28%)
300% Modulus (MPa)	12.48	15.06	-	7.12
Hardness (IRHD)	62	63	59	47
<b>% Compression Set: 22 hours at 100°C</b>				
	63.2	56.1	32.6	-
<b>Fatigue to Failure (100% extension, Cycles x 100)</b>				
	92	60	36	-

The curing efficiency of TINTD in black filled natural rubber is demonstrated in Figure 1 and Table II. It is clear from the above data that TINTD functions as an effective primary accelerator and as a sulfur donor to cure natural rubber.

Figure 1 and Table II also show that the conventional cure system exhibits more reversion, the calculated reversion degree being 25% compared to the EV system where it was only 4%. The Semi-EV cure system shows a compromise between the conventional and EV systems as indicated by the reversion degree being 13%. The reversion process reflects the cross-link degradation taking place in the vulcanisate. Conventional cured vulcanisates form mainly polysulfidic cross-link chains that are thermally unstable. The Semi-EV and EV cures produce mainly di and monosulfidic cross-links that are more thermally stable. Also, a higher cure torque curve, which is an indication of a higher state of cure, is given by the EV system with minimum

reversion taking place after optimum cure time. Sulfur donor based cure system does not show reversion, under similar vulcanisation conditions, for the same reasons as the EV cure. However, due to the lower loading of TINTD there is a lower amount of sulfur available from the sulfur donor resulting in lower rate and state of cure compared to the EV cure.

There is an increase in stress at 100%, 200%, 300% and 500% strain and a decrease in percentage elongation at break as the amount of TINTD is increased from conventional through semi-EV to the EV cure system. This is due to more efficient cross-linking taking place, although the amount of elemental sulfur in the cure system is decreasing from conventional to EV curing.

After one week's storage at room temperature, the EV cured vulcanisate started to bloom on the surface, which was identified as zinc diisononyldithiocarbamate (ZDNC) by UV spectrophotometric absorption technique. This indicates that the TINTD breaks down during the vulcanisation process, in the presence of zinc oxide, producing a more polar dithiocarbamate (ZDNC) that shows up as a bloom. It may be noted that the EV cure system contains a very large amount of TINTD, although highly soluble in the rubber matrix, its breakdown product which is also highly soluble in rubber matrix<sup>24</sup> exceeds its solubility in rubber from the EV cure. To avoid this bloom the level of TINTD was reduced in sulfur donor system.

The heat resistance properties of the vulcanisates, as measured by the change in ultimate tensile strength and elongation at break improve as the cure system is changed from conventional cure to semi-EV. However, the EV cured vulcanisates were expected to be thermally superior to the semi-EV system as the cross-links formed are largely monosulfidic. However, excess amount of TINTD caused blooming of the vulcanisate. This high level coupled with relatively low level of sulfur caused the vulcanisates to become too rigid. In all systems studied, there is a large change in vulcanisate properties upon ageing at 70°C, with respect to elongation at break and 200% modulus, as slow curing is still ongoing.

TINTD produces lower compression set in the EV cures but poor flex-fatigue properties due to the network being mainly monosulfidic. TINTD gives best fatigue to failure in the conventional cure system. This is due to the predominately polysulfidic network being formed and the high solubility of TINTD producing more flexibility in the network as a plasticiser.

Overall, the conventional cure system provides better flex and dynamic properties but poor thermal and reversion resistance. Bond dissociation energy is the underlying reason for the variation in the above properties of the different vulcanisates. The higher the number of sulfur atoms, the lower the bond dissociation energy of the linkage. Thus, the vulcanisates containing mainly mono or disulfidic linkages (EV and Semi-EV) have better heat stability and reversion resistance than those containing relatively high polysulfidic linkages, as in the conventional cures.

The above data clearly shows that TINTD functions as an accelerator in the conventional, Semi-EV and EV cure systems and as a sulfur donor in natural rubber. It produces lower compression set in the EV cures and gives good fatigue to failure performance in the conventional cure system.

### **Nitrosamines and Nitrosatable Substances**

Unfilled natural rubber masterbatch PC1 was compounded with 0.5phr TINTD and mixed on an open 2-roll mill, then press cured for 15 minutes at 150°C into a standard tensile sheet (approximately 2mm thick).

The vulcanised rubber sheet was tested at a UKAS accredited test laboratory (Tun Abdul Razak Research Centre, Hertford). It was tested for N-nitrosamines and N-nitrosatables in line with the BS EN71-12:2016 (four hours extraction in artificial saliva solution at 40°C), with analysis by GC-NCD (Gas Chromatography – Nitrogen Chemiluminescence Detector). The test method looks for all Nitrosamines and Nitrosatable substances including NDMA, NDEA, NDPA, NDBA, N-PIP, N-PYR, NDiNA, N-MOR and NDBzA.

The results from the rubber sample cured with TINTD showed that no N-nitrosamines nor N-nitrosatable substances were detected. Limit of detection being 1-2 µg/Kg.

### **Comparative study of TINTD and TBTD in soluble EV cures, as secondary accelerators, for low creep rubbers used in injection moulding**

TINTD is a viscous oily liquid, highly soluble in rubber and capable of functioning as a sulfur donor and a primary accelerator. During vulcanisation, in the presence of zinc oxide, its breakdown product is zinc diisononyldithiocarbamate; which is also very soluble in rubber. These features led to the investigation of TINTD performance in soluble EV cures using black filled NR masterbatch (LCR 50). The soluble EV cures reported<sup>25</sup> are used in low creep rubbers for injection moulding to produce rubber springs, mountings, couplings and brushes suitable for service at moderate to elevated temperatures. In the current study TINTD was evaluated against the most commonly used soluble EV accelerator, namely tetrabutylthiuramdisulfide (TBTD). The cure system reported was based on sulfur, MBS and TBTD giving vulcanisates with hardness (IRHD) of 50. Chemically MBS is N-oxydiethylene-2-benzothiazole sulfenamide.

Here, MBS was substituted by N-cyclohexyl-2-benzothiazole sulfenamide (CBS), because MBS is undesirable as it produces regulated N-nitrosomorpholine and CBS does not, because it is based on a primary amine. Note, MBS inherently gives a slightly longer processing safety compared to CBS<sup>26</sup>.

Table III shows the two formulations studied. Here TINTD is compared against the soluble EV accelerator TBTD in the presence of CBS and sulfur. Comparison of TINTD



and TBTD was carried out on molar equivalent basis. The rheological data are also given in the table and comparative rheographs, taken at 150°C and 190°C, are shown in Figure 2. The results show that the two mixes have similar rheological properties. At 150°C TINTD has a significantly longer processing safety compared to TBTD, as shown by TS1 and by Mooney data at 135°C. At 190°C both cures are almost identical and show reversion after maximum cure, the calculated reversion degree being 35.2% in both cases.

Table IV gives the tensile properties of the rubber sheets cured at 150°C before and after heat ageing. Results after ageing for 14 days at 70°C and for 3 days and 7 days at 100°C are given. Also shown are the compression set values and cross-link density of the vulcanisates.

The heat resistance properties of the vulcanisate cured with TINTD, as measured by the change in ultimate tensile strength, elongation at break and hardness, were found to be virtually identical to the results obtained by using the industry standard, namely TBTD. Furthermore, the compression set at 70°C and 100°C and cross-link density of the vulcanisate are comparable.

The above findings show that TINTD is a good substitute for TBTD as a secondary accelerator in low creep soluble EV systems. Furthermore, TINTD in combination with CBS does not have the inherent problems of TBTD combined with MBS, in terms of regulated carcinogenic nitrosamine generation.

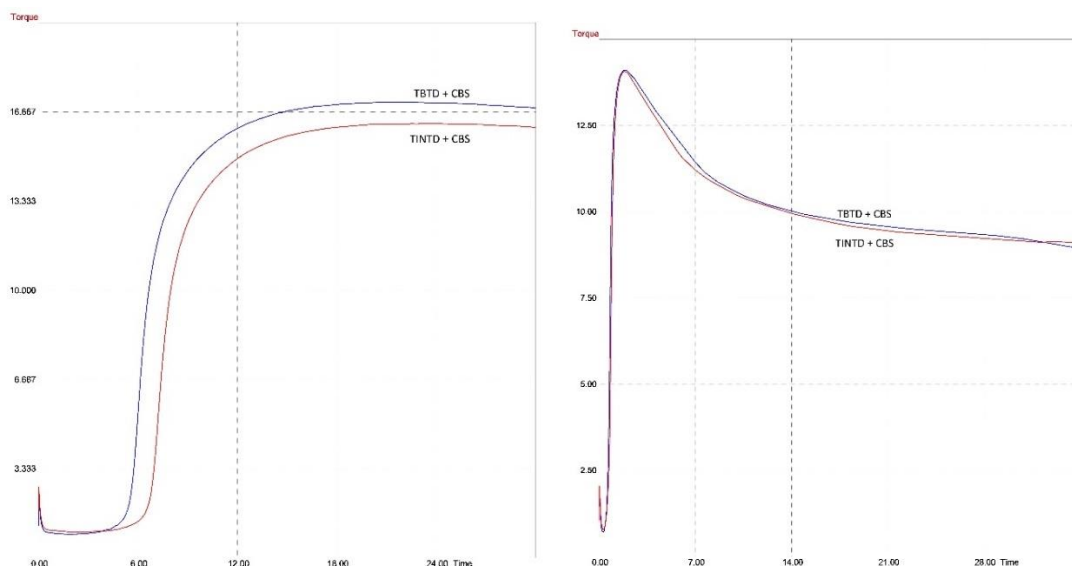


Fig.2 Rheographs of NR taken at 150°C and 190°C comparing TINTD and TBTD in the presence of a sulfenamide, CBS.

Table III

Formulation details and rheological properties of NR vulcanisates at 150°C and 190°C

<b>Formulation Mix</b>	<b>Mix 7 (TBTD)</b>	<b>Mix 8 (TINTD)</b>
Rubber masterbatch (LCR 50)	137	137
CBS (phr)	1.7	1.7
Sulfur (phr)	0.7	0.7
TBTD (phr)	0.7*	-
TINTD (phr)	-	1.18*
<b>Rheological Data at 150°C</b>		
TS1 (Minutes)	5.42	6.62
T90 (Minutes)	10.49	11.56
MH (lb.in)	17.04	16.24
Rate (lb.in/minute)	8.87	8.22
<b>Rheological Data at 190°C</b>		
TS1 (Minutes)	0.49	0.63
T90 (Minutes)	1.12	1.18
MH (lb.in)	14.10	14.07
MH-ML (lb.in)	13.39	13.29
Rate (lb.in/minute)	32.21	30.65
Reversion degree (R) (%)	35.2	35.2
<b>Mooney Data</b>		
ML1+4 (100°C)	23.0	24.0
ML1+4 (135°C)	14.5	15.5
Cure Index at 135°C	1.9	2.2

\*Both TBTD and TINTD loading = 1.71mmol

Table IV

Miscellaneous and tensile properties before and after heat ageing

	<b>Mix 7 (TBTD)</b>	<b>Mix 8 (TINTD)</b>
<b>Initial tensile properties</b>		
Hardness (IRHD)	52	51
Ultimate tensile strength (MPa)	26.8	27.0
Strain at break (%)	659	683
Stress at 100% strain (MPa)	1.09	1.02
Stress at 200% strain (MPa)	2.39	2.23
Stress at 300% strain (MPa)	4.90	4.59
<b>After ageing for 3 days at 100°C</b>		
Hardness (IRHD)	58 (+6)	58 (+7)
Ultimate tensile strength (MPa)	21.9 (-18%)*	23.5 (-13%)
Strain at break (%)	463 (-30%)	487 (-29%)
Stress at 100% strain (MPa)	1.78	1.71

Stress at 200% strain (MPa)	4.48	4.33
Stress at 300% strain (MPa)	9.08	8.83
<b>After ageing for 7 days at 100°C</b>		
Hardness (IRHD)	62 (+10)	60 (+9)
Ultimate tensile strength (MPa)	18.7 (-30%)	19.3 (-29%)
Strain at break (%)	402 (-39%)	415 (-39%)
Stress at 100% strain (MPa)	1.99	1.94
Stress at 200% strain (MPa)	5.19	5.08
Stress at 300% strain (MPa)	10.64	10.37
<b>After ageing for 14 days at 70°C</b>		
Hardness (IRHD)	61 (+9)	60 (+9)
Ultimate tensile strength (MPa)	24.3 (-9%)	25.2 (-7%)
Strain at break (%)	500 (-24%)	514 (-25%)
Stress at 100% strain (MPa)	1.67	1.64
Stress at 200% strain (MPa)	4.13	4.08
Stress at 300% strain (MPa)	8.59	8.47
<b>Miscellaneous properties</b>		
<b>Compression set</b>		
1 day at 70°C	24	24
1 day at 100°C	50	52
3 days at 100°C	61	63
<b>Cross-link density (mol cm<sup>-3</sup>)</b>		
	2.42 x 10 <sup>-4</sup>	2.32 x 10 <sup>-4</sup>

\* Percentage heat resistance is given in brackets.

### General discussion on the properties and behaviour of TINTD in black filled natural rubber

It has been demonstrated that TINTD functions as an accelerator in the conventional, Semi-EV and EV cure systems and as a sulfur donor in natural rubber. It produces low compression set in the EV cures and gives good fatigue to failure performance in the conventional cure system.

The longer branched alkyl chains on the nitrogen of thiuram disulfide, TINTD, and zinc dialkyldithiocarbamate, ZDNC, are responsible for the high solubility of the compounds in the rubber. Neither TINTD nor ZDNC readily produce diisnonylamine. Furthermore, diisnonylamine does not nitrosate easily, due to presence of branched chains in the molecule. ZDNC, also commercially known as Robac Arbestab Z, has been established as a nitrosamine safe accelerator.

Nitrosamine safe means that either the high molecular weight and bulkiness of the nitrosatable substances dramatically decreases their accessibility, thus restricting nitrosation or limiting the availability of their nitrosated amines and their related alkylating substances, as in the case of N-nitrosodiisnonylamine (NDiNA). Or safe due to the chemical nature of the related nitrosamines, which can only produce a

stable carbenium ion, these being weak alkylating substances and so unable to damage RNA and DNA to the extent of causing carcinogenesis. As a result, their toxicology is non-carcinogenic<sup>13</sup>.

Due to the high solubility of TINTD and ZDNC in natural rubber, TINTD has the characteristics to replace TBTD. Which, as stated above, is a highly effective soluble thiuram disulfide for soluble EV cure systems but produces a regulated carcinogenic N-nitrosodibutylamine. It was shown that TINTD can replace TBTD as a secondary accelerator in the presence of a sulfenamide, for example CBS in black filled natural rubber. TINTD had similar rheological and physical properties and cross-link density compared to TBTD in the vulcanisates, including percentage reversion, compression set and heat resistance at elevated temperatures.

### Effectiveness of TINTD as an accelerator in natural rubber latex

TINTD was tested in high ammonia natural rubber latex by first converting it into an aqueous emulsion, using potassium laurate as the emulsifier with high speed stirring using a Silverson high shear mixer.

The cross-linking efficiency of the TINTD emulsion was evaluated by compounding it into HA-NR latex with other ingredients and then pre-vulcanising it for 6 hours at 65°C. Comparison was done against a blank containing no accelerator. The compounding recipes used are given in Table V.

*Table V*  
Compounding formulations in high ammonia natural rubber latex

<b>Concentration (%<sub>w/w</sub>)</b>	<b>Ingredients</b>	<b>DRY WEIGHTS, (g)</b>	
		<b>Mix 5</b>	<b>Mix 6</b>
60	High Ammonia NR latex	100.2	100.2
30	Potassium Caprylate	0.5	0.5
5	Potassium Hydroxide	0.5	0.5
50	Zinc Oxide	0.5	0.5
50	Phenolic Antioxidant	0.5	0.5
60	Sulfur	1.0	1.0
50	TINTD	-	0.8

The total solids during compounding were adjusted to 50% with deionised water. The cross-link density measurements during pre-vulcanisation study were carried out using a modified solvent swell test<sup>27</sup>, a test that measures percentage linear swell in toluene. After the pre-vulcanisation period it was found that the percentage linear swell for the blank was 172% and that for TINTD was 122% clearly indicating that TINTD had functioned as an accelerator during pre-vulcanisation of natural rubber latex.

Brookfield viscosity measurements of the pre-vulcanised latex at room temperature,  $20 \pm 2^\circ\text{C}$ , over the four weeks storage period, Figure 3, showed that the TINTD caused the latex to thicken slightly. However, as the latex was not stirred continually this may not be a true reflection of pot life.

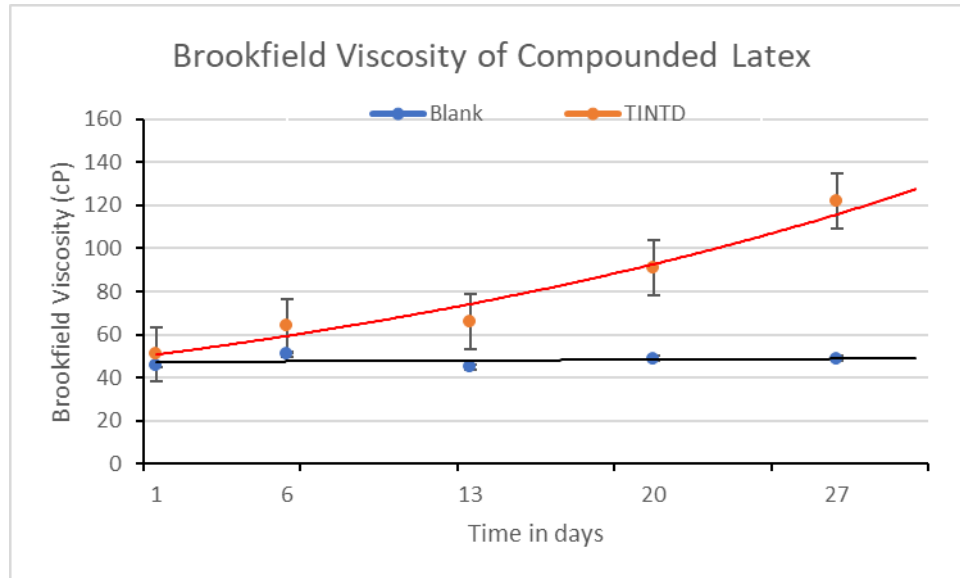


Fig.3 Viscosity measurements of compounded latex at  $20 \pm 2^\circ\text{C}$ .

After pre-vulcanising and cooling the latex, it was flowed into glass moulds and dried in humid atmosphere at room temperature for 72 hours to obtain latex rubber sheets for testing. This was followed by leaching in still water for two hours and drying at room temperature. These sheets were then post cured for 40 minutes at  $100^\circ\text{C}$  and tested for tensile properties. Samples were also heat aged at  $70^\circ\text{C}$  and  $100^\circ\text{C}$  in moving air oven and their tensile properties measured. Table VI shows the tensile properties of the dried rubber sheets.

Table VI

Tensile properties of latex rubber sheets before and after heat ageing

<i>Properties tested</i>	<i>Blank, Mix 5</i>	<i>TINTD, Mix 6</i>
<b>Initial data</b>		
Ultimate tensile strength (MPa)	6.0	25.9
Strain at break (%)	1020	957
Stress at 300% strain (MPa)	0.57	0.86
<b>Aged 22 hours at <math>100^\circ\text{C}</math></b>		
Ultimate tensile strength (MPa)	4.9	27.9
Strain at break (%)	1134	1025
Stress at 300% strain (MPa)	0.52	1.03
<b>Aged 7 Days at <math>70^\circ\text{C}</math></b>		
Ultimate tensile strength (MPa)	6.0	20.9
Strain at break (%)	1050	900
Stress at 300% strain (MPa)	0.54	1.13

It can be seen from Table VI that the blank had no useful tensile properties. Whilst the blown film produced from using TINTD had good tensile properties even after heat ageing.

Although not optimised, either in terms of emulsion stability or concentration of accelerator used, TINTD was found to act as an accelerator in high ammonia natural rubber latex.

## CONCLUSION

The new nitrosamine safe thiuram disulfide, TINTD, has been shown to function as a sulfur donor and a primary or secondary accelerator for curing natural rubber. The long-branched alkyl chains on the nitrogen of TINTD makes it more soluble in the elastomer. Furthermore, ZDNC formed during the vulcanisation reaction, is also highly soluble, due to the long-branched alkyl chains on the nitrogen of the dithiocarbamate. The high solubility of TINTD and ZDNC in rubber, similar to traditional TBTD and ZDBC, coupled with the safer nature of TINTD and ZDNC makes the use of TINTD highly attractive for soluble-EV systems, especially where carcinogenic nitrosamine and nitrosatable substance formation and also accelerator toxicity, irritant dermatitis and Type IV allergy is of concern. Furthermore, if any N-nitrosodiisononylamine is produced, from the breakdown of TINTD or ZDNC to diisononylamine, the lower volatility of this N-nitrosamine results in a reduced airborne workplace exposure. However, due to the higher molar mass of TINTD, in which only 26.2% is active thiuram and the increased steric hindrance from the alkyl chains, there is a need to add higher amounts of accelerator to obtain similar technological properties in the rubber. Since TINTD is a viscous liquid, the addition of higher loading has a plasticising effect on the compound, thus making the rubber softer whilst maintaining a similar cross link density. This can be used to advantage by reducing or omitting the addition of oils or plasticiser in the rubber compound.

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**APPENDIX 1**

## Properties of TINTD

Chemical name	Bis(3,5,5-trimethylhexyl) carbamothiosulfanyl-N, N-bis (3,5,5-trimethylhexyl) carbamodithiote
Synonyms name	Tetraisononylthiuramdisulfide
Empirical formula	C <sub>38</sub> H <sub>76</sub> N <sub>2</sub> S <sub>4</sub>
Relative molar mass	688
Appearance	Yellow to light brown viscous oil
Solubility	Insoluble in water. Soluble in toluene and other non-polar solvents
Thermal stability	Thermally stable up to 150°C

## List of Abbreviations used in the main text

TMTD	Tetramethylthiuramdisulfide	NDMA	N-nitrosodimethylamine
TETD	Tetraethylthiuramdisulfide	NDEA	N-nitrosodiethylamine
DPTH	Dipentamethylenethiuramhexasulfide	NDBzA	N- nitrosodibenzylamine
TBTD	Tetrabutylthiuramdisulfide	NDBA	N-nitrosodibutylamine
TMTM	Tetramethylthiurammonosulfide	N-PYR	N-nitrosopyrrolidine
TBZTD	Tetrabenzylthiuramdisulfide	NMOR	N-nitrosomorpholine
TiBTD	Tetraisobutylthiuramdisulfide	NPIP	N-nitrosopiperidine
ZDNC	Zinc diisononyldithiocarbamate	NDiNA	N-nitrosodiisononylamine
CBS	N-cyclohexyl-2-benzothiazolesulfenamide	ZEH	Zinc 2-ethylhexanoate