

# Characterization of additives in NR formulations by TLC-IR (UATR)

Lidia Mattos Silva Murakami<sup>1,2</sup>, Joyce Baracho Azevedo<sup>1,2</sup>, Milton Faria Diniz<sup>3</sup>, Leandro Mattos Silva<sup>4</sup> and Rita de Cássia Lazzarini Dutra<sup>1\*</sup>

<sup>1</sup>*Instituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brasil*

<sup>2</sup>*Tenneco Automotive Brasil, Cotia, SP, Brasil*

<sup>3</sup>*Divisão de Química – AQI, Instituto de Aeronáutica e Espaço – IAE, São José dos Campos, SP, Brasil*

<sup>4</sup>*Petroquímica Brasken S.A., Capuava, Santo André, SP, Brasil*

\*[ritacl@ita.br](mailto:ritacl@ita.br)

## Abstract

It is a well-established fact that rubber accelerator is essential to provide solution in different sectors. However, there is a reversal process which can reduce the material performance. Sulfur accelerators donors and organic peroxides have been presented as a solution to the problem. The methodology development that can separate or characterize those components is a challenge and still allows gaps, explained by the application of conventional technique to reach this goal. This study aimed at contributing to the use of off-line coupling of thin layer chromatography (TLC)/infrared spectroscopy (IR) by Universal Attenuated Total Reflection (UATR) for analysis of N-cyclohexyl-2-benzotiazolsulfenamide (CBS), tetraethylthiuram disulfide (TMTD) and dicumyl peroxide (DCP), in natural poly-cis-isoprene (NR) formulations, containing naphthenic oil. The best results were obtained for the plasticizer and DCP, in formulations that had a greater proportion of these compounds. The separation of CBS and TMTD was made with less effectiveness, due to bands overlapping.

**Keywords:** *additives, characterization, NR, TLC, UATR.*

## 1. Introduction

The competitive industrial environment has demanded of companies more agility in terms of response to the market. Companies have embraced some strategies to accomplish that specific objective and knowing better their own product substantially is one of them. Not only does this route lead to better process variable evaluation, but also it improves the employment of technology.

Products based on polymeric materials play a major role in Aerospace and Automotive Industry considering they can withstand harsh environments, reduces production costs and offers flexibility in processing. As a light solution, the polymers successfully replace metals and traditional compounds due to its mechanical resistance, corrosion resistance and ease in the manufacture of parts with narrower tolerance.

A vulcanized rubber is a widely applied polymer throughout several industrial areas. Its counterpart Natural rubber (NR) for instance, is applied in the automotive industry, like tires and hoses<sup>[1]</sup>, and in aerospace industry, as flexible joints<sup>[2]</sup>. It contains elastomer, vulcanization agent and accelerator, reinforcing filler, stabilizers, among other additives. This mixture is vulcanized after passing through thermal processes or after been exposed to high energy radiation<sup>[3]</sup>. Among these additives, it is possible to highlight the accelerators, which reduce the cure time and consequently the process costs. They are classified according to their chemical composition and / or their speed of action

in vulcanization. In Table 1, a list of the most common accelerators<sup>[4]</sup> is included.

Acknowledge the accelerators and vulcanizing agent of a formulation is paramount for new polymers development. Not only does it aid in reducing process costs, but also it increases the solution spectrum for industry. Taking this into account, the reversion problem is brought to our attention, when the polysulfide bond breaks causing reduction of crosslink density, changing the distribution of the bonds types and modification in main chain structure. These facts lead to reduced article performance.

Reversion resistance of rubber compounds has been obtained by controlling the sulfur content in the crosslink bonds, by applying sulfur donor accelerators and organic peroxides. In terms of thermal stability, their higher bond strength gives more stability than the carbon/sulfur/carbon bond and gives good properties for aging resistance<sup>[5]</sup>.

Study of sulfur vulcanization has been mentioned in the literature<sup>[6]</sup>. TMTD, among others accelerator polysulfides such as N,N-pentamethylenethiuram disulfide (CPTD) were employed and it was concluded that CPTD and its polysulfides are thermally less stable than is TMTD.

As reported by Joseph et al.<sup>[7]</sup>, among the various organic sulphur containing compounds, TMTD has been the most studied. Vulcanizates obtained using this compounds in combination with ZnO have superior thermal and oxidative

**Table 1.** Most usual accelerators and vulcanizing agent for elastomeric compositions.

Acronym / nomenclature	Acronym / nomenclature
MBT (2-mercaptobenzothiazole)	ZDBC (Dibutylthiocarbamate Zinc)
MBTS (benzothiazole disulfide)	ZDEC (zinc diethylthiocarbamate)
CBS (N-cyclohexyl-2-benzothiazolesulfenamide)	ZDMC (zinc dimethylthiocarbamate)
TBBS (N-tert-butyl-di (2-benzothiazolesulfenamide)	DPG (N, N'-diphenyl guanidine)
MBS (2- (4-Morpholiniothio) benzothiazole)	DOTG (Diortotolyguanidine)
TMTD (Tetramethylthiuram Disulfide)	DTDM (4,4'-dithiomorpholine)
TMTM (Tetramethylthiuram Monosulfide)	ETU (2-mercaptoimidazoline) / (ethylene thiourea)
TETD (tetraethylthiuram disulfide)	DCP (Dicumyl peroxide)

stability and negligible modulus reversion. According to radical mechanism, at vulcanization temperatures, interactive recombination will lead to the formation of accelerator polysulfides (TMTPs).

Influence of sulfenamide accelerators, such as CBS, on cure kinetics and properties of NR has been studied as well<sup>[8]</sup>. CBS accelerator shows the fastest sulfur vulcanization rate and the lowest activation energy ( $E_a$ ) because CBS accelerator produces higher level of basicity of amine species than other sulfenamide accelerators.

The effect of temperature and peroxide concentration has been studied<sup>[9]</sup>. DCP was evaluated among other peroxides. It was observed that DCP and di-tert-butyl peroxide (DTBP) showed lower amounts of decomposition products compared to other peroxides studied. DCP and DTBP were suggested as better curing agents for NR based rubber compounds at higher peroxide concentrations.

TMTD, CBS and DCP were the additives used in this current paper to be separated and characterized by reason of their chemical characteristics, good properties, including thermal stability and lower content decomposition products.

Fourier Transform Infrared Spectroscopy (FT-IR) is one of the techniques that has been largely applied for materials identification and characterization. However, due to the wide variety of products in the extracts of rubbers and the small concentration of additives contained, it is necessary to perform a separation step by thin layer chromatography (TLC). The association of Infrared Spectroscopy Technique (TLC/IR)<sup>[10,11]</sup> is required for chemical structure characterization, although it is hardly used in the literature.

In the TLC/ IR technique, using the KBr pyramids, the extract is dissolved in the solvent used for the extraction and applied on a suitable silica plate, which is developed in a closed chromatographic vat using a mobile phase (eluent). The plate is dried and the spots revealed, with specific product. The spots are grated and placed in a tube containing the KBr pyramids. A small amount of solvent used in the extraction is added to conduct the sample to the top of the pyramid. After solvent evaporation, this top is removed, scraped and pressed as a KBr disc for IR analysis. This technique was started in our laboratories, in the Brazilian Institute, Instituto de Aeronáutica e Espaço (IAE), in 1996<sup>[10]</sup> and it was used for additives analysis, in rubbers<sup>[12]</sup> as in paints, with positive results<sup>[11]</sup>.

Chauveau et al.<sup>[13]</sup> separated and identified several vulcanization agents (CBS, MBT, TMTM, DPG, MBT and TMTM) and antioxidants (IPPD and 6PPD) present in

hospital rubbers (synthetic polyisoprene-isoprene - IR and copolymer of butadiene and styrene - SBR), by means of the TLC technique. In parallel, the identification of additives by GLC coupled to a mass spectrometer (MS) method was made to confirm the presence or absence of additives.

The samples were extracted in acetone and two types of eluents were used: toluene/ethyl acetate/ammonia (100/5/1) to extract CBS, MBT, IPPD, 6PPD, TMTM and toluene/acetone/ammonia (45/65/1) to extract DPG, MBT, TMTM. UV fluorescent light was applied to reveal the eluted deposits. It was demonstrated that the TLC method was more efficient in the identification of additives, since it presented greater thermal stability, without degradation of it, during the extraction with acetone at 66°C. Despite of it, most additives were separated by TLC, even in small amounts of formulations analyzed. and by MS, through fragmented products, there were difficulties in separating some components, such as TMTM and CBS, under the conditions used.

Other recent studies, in IAE laboratories, were carried out to identify additives in polymers using the TLC/IR technique (off-line) and selective extraction. Among them is the Rodrigues et al.<sup>[11]</sup> publishing, where a painting formulation containing polyurethane (PU) and nitrocellulose (NC) was evaluated. In this study, three eluent systems were used: ethyl acetate/ethyl alcohol (70/35/30), pure toluene and toluene/ethyl acetate (70/30), applying Gibbs developer. Among the four additives of the formulation, it was possible to characterize two of them (ATBC plasticizer and oleamide slider) by UATR.

Damazio et al.<sup>[12]</sup> applied the same technique, TLC/IR technique (off-line), for the analysis of MBT, TMQ, TMTM and TMTD additives, in ethylene propylene diene monomer terpolymer based rubber (EPDM). Two types of EPDM were evaluated with two different kinds of eluent system: an eluent system with hexane, diethyl ether and acetic acid - 70: 30: 5, and Gibbs developer. The formulation studied contained more than one additive, and thus generated band overlap, but the characteristic absorptions of sulfide additives were revealed by UATR, even though they were in a lower proportion.

Other researches have been done to study rubber additives. For example, the potential of FT-IR analysis of gaseous pyrolyzates (PY-G/FT-IR) for characterization of EPDM additives has also been evaluated<sup>[14]</sup> TMTM, TMTD, and MBT were employed in this study. Results demonstrated that the PY-G/FT-IR technique can identify additives containing sulfur in concentrations as low as 1.4 phr (1.26%) in EPDM.

However, the method showed some limitation to detect TMTM and TMTD due to overlapping and to similarities of their PY-G/FT-IR spectra, which could not be distinguished from each other.

Although the quoted papers presented favorable results for rubber additives, formulations of NR containing peroxides were not analyzed in comparison with others containing sulfur accelerator or vulcanizing agent systems. There are also limitations for detecting of some sulfur additives. Then, in this paper, the applicability of the TLC/UATR technique was evaluated to characterization of TMTD, CBS and DCP, which are frequently found in NR and EPDM rubbers formulations, used in the industries mentioned earlier. In short, the interest of Automotive and Aerospace Companies in methodology development for problem solving and polymer article improvement is the same.

## 2. Materials and Methods

### 2.1 Samples

The sample of NR was kindly provided by Tenneco Automotive. In Table 2, are presented the formulations developed for NR containing CBS or TMTD or DCP, named, respectively, NR (CBS), NR (TMTD) and NR (DCP).

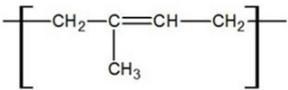
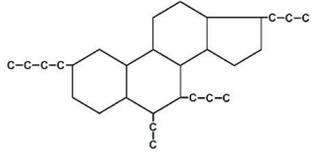
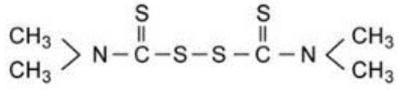
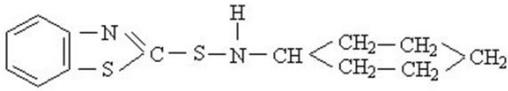
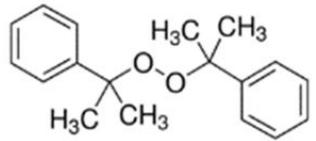
### 2.2 Rubbers preparation

The raw material was weighed on a precision scale and all components, except for accelerators (TMTD and CBS) and vulcanizing agent (DCP and Sulfur), were mixed in a laboratory banbury 2 liters for 240 sec., with a pylon pressure of 4 kgf/cm<sup>2</sup>, rotation of 70 rpm and initial temperature of 40°C, to produce the masterbatch. Then it was processed in a roller form six times in an open mill (laboratory cylinder), with rotation of 40 rpm. Later, the *masterbatch* was accelerated in *banbury*, with the rest of the weighted components (TMTD, CBS or DCP and sulfur) for 120 seconds, with 4 kgf/cm<sup>2</sup> pylon pressure, rotation of 70 rpm and initial temperature of 40°C. Eventually, the rubber was homogenized in roller form six times in an open mill (laboratory cylinder) with a rotation of 40 rpm and removed in blanked.

The rheometer curve interferes in the vulcanization temperature setting of a rubber part. High temperatures can promote a reversal process, where bonds breakage occurs, and consequently the degradation of the polymer<sup>[1]</sup>.

However, the vulcanization times obtained in rheometric tests should be performed at the same temperature as the part will be processed. The value of T90 should be the time to be used when the material thickness is between 1.5 and 2.5 mm<sup>[1]</sup>.

**Table 2.** NR System (phr).

Components	Functional Group / Structural Formula	NR (CBS)	NR (TMTD)	NR (PEROXIDE)
Natural Rubber (NR)		100	100	100
Naphthenic oil		7.7	5.4	5.4
Zinc oxide	ZnO	4.8	4.8	4.8
Stearic acid		1.6	1.6	1.6
Carbon Black N550	C	24	53	53
Sulfur	S	2.1	3.2	---
TMTD		---	1.1	---
CBS		1.1	---	---
DCP		---	---	6.4

In this current paper, the compounds vulcanization times were determined from the rheometric curves using a rheometer, from Alpha Technologies, model MDR 2000, at the same vulcanization temperature (T90@160°C), and the specimens thickness were 2.5 mm<sup>[1]</sup>.

For the preparation of vulcanized rubbers slabs, a hydraulic press with vulcanization time of 6 min., temperature in the plateaus of 160°C and 150 kgf/cm<sup>2</sup> of closing pressure was used.

### 2.3 Characterization equipment/conditions

For the TLC analysis, Merck glass chromatography plates, measuring 20 × 20 cm and covered with Silica Gel D60 and glass vat were applied. In the FT-IR analysis, a spectrometer FT-IR Spectrum One PerkinElmer (resolution 4 cm<sup>-1</sup>, gain 1, 4000 to 400 cm<sup>-1</sup>, 20 scans) was used. FT-IR spectra were obtained, by reflection technique, using the UATR accessory. It was used 20 scans for UATR analysis, based on other papers that they have successfully published for paint<sup>[11]</sup>, rubber<sup>[12]</sup> and oil analysis<sup>[15]</sup>. This scan number is a suitable to smooth noises in the FT-IR reflection techniques, such as UATR, diffuse reflectance (DRIFT) and attenuated total reflection (ATR).

### 2.4 Methodology

#### 2.4.1 Extraction and analysis by Infrared spectroscopy (IR) of rubbers and additives

Vulcanized rubber slabs were cut into small pieces, in sizes of approximately 3.0 x 3.0 x 3.0 mm and placed for extraction in acetone in Soxhlet extractor. The rubber

samples were prepared by pyrolysis (thermal degradation) and analyzed as liquids by transmission, by IR. The extracts containing the additives were analyzed by reflection, UATR.

#### 2.4.2 TLC analysis

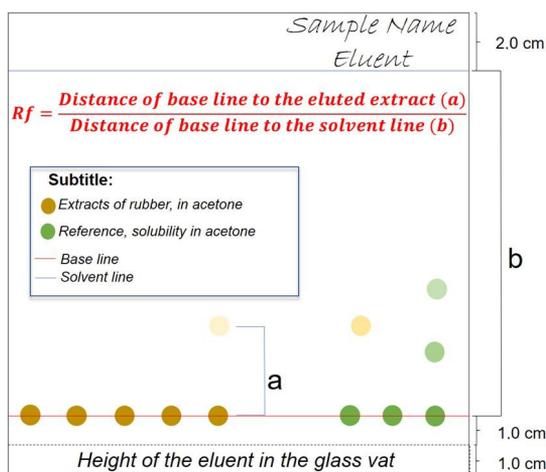
The TLC plates were labeled and identified with pencils and placed in an oven for 15 minutes at 105°C for activation, to remove moisture from the silica. With the aid of a micro syringe, approximately 15 µL of extract and pure additives were deposited, side by side, for use as a color reference and retention factor (Rf) on the TLC plate. The additives (TMTD, CBS and DCP), which were powders, were previously solubilized in acetone. The TLC plate was placed in the glass vat and the eluent was added until it reached the 1 cm mark. The run time of the eluent on the plate was timed until it reached the upper marking of 2 cm. Rf is the ratio of the distance traveled by the sample to the distance traveled by the eluent in the system (Figure 1).

After running the eluent, excess solvent from the plate was evaporated at room temperature in the exhaust hood, then eliminated in an oven for 15 minutes at 105°C. Four eluent systems were used, based on literature data: Toluene<sup>[16]</sup>; Toluene/Acetone (45/65) and Toluene/Ethyl Acetate (100/5)<sup>[13]</sup>, but in the last two cases ammonia was removed, due it is a product considered to be hazardous to health and the fluorescent developer replaced by the Gibbs reagent. The Toluene/Acetone system (65/45) was also used.

After oven dried and cooled to room temperature, the plates were revealed with a solution of 0.3g of the Gibbs reagent (2,6-dichloro-p-benzoquinone-4-chloroimine) in 30ml of ethyl alcohol. The Rf values and developed colors were noted for each eluted spot which was separated on the TLC plate from extract and pure additives.

#### 2.4.3 TLC/UATR analysis

The silica that contained the eluted deposits was scraped washed with 10 ml of acetone and filtered through filter paper on a watch glass. After the eluent evaporation, at room temperature to avoid degrade the material, the samples were analyzed by UATR (Figure 2).

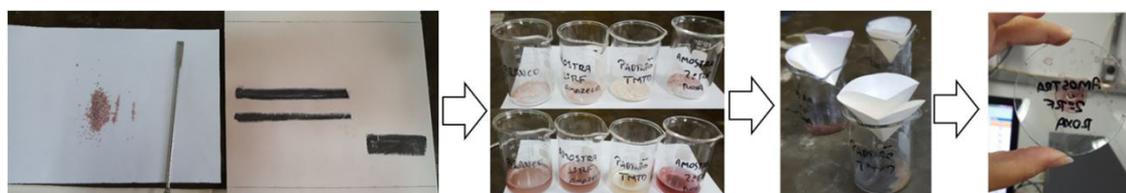


**Figure 1.** Preparation of the TLC plate for the deposition of the extracts and the RF marking.

## 3. Results and Discussion

### 3.1 UATR analysis of NR extracts, containing different additives

For the initial evaluation of the additives, extraction was carried out with the appropriate solvent, acetone<sup>[10]</sup>. The extracts were analyzed by UATR as casting films, to avoid the appearance of KBr moisture bands around 3300 and 1640 cm<sup>-1</sup>, as a result of solid sample pellets



**Figure 2.** Scraping process of the separated spots by the TLC plate and prepared for UATR analysis.

preparation, for transmission analysis, that could interfere on the observation of NH bands of CBS accelerator.

In Figure 3, it is included the UATR spectra of extracts, in acetone, from the vulcanized NR rubbers samples, compared to additives spectra, taken as references. The objective is verifying if by analyzing of the spectra of NR extracts, it is possible to indicate the different additives presence.

Although the extract spectrum of a rubber shows absorptions of all soluble additives in the used solvent, meaning there are overlapping bands of other formulation additives, it is possible to make some considerations:

- the spectra of Figures 3a, 3c and 3e are different, confirming that the formulations are not the same in terms of organic additives;
- a small number of the major CBS bands, approximately ( $\text{cm}^{-1}$ ), assigned to the following functional groups<sup>[17,18]</sup>: 3200 (NH) (very low-intensity band, better viewed when the extract spectrum was analyzed separately), 750 (ortho-substituted aromatic ring) and 730 ( $\text{CH}_2$ ), is present in the extract spectrum of NR (CBS). However, bands that should appear around 1500, related to benzothiazole<sup>[18]</sup>, were not visualized. There is also overlapping, in other regions, of naphthenic plasticizer bands, that have aliphatic CH groups, which absorb at 3000-2900, 1460-1400 and 700-750, and which is in greater proportion, relative to the formulation additives (see Table 2);
- a small number of bands ( $\text{cm}^{-1}$ ) around 1240 (C=S, C-S), 1140 (C-N), 560 (S-S) characterizes the presence of TMTD<sup>[12,17]</sup> in the NR (TMTD) extract spectrum. Despite of a greater similarity between NR extract (TMTD) and TMTD spectra that was observed in the fingerprint region, there were overlaps relative to  $\text{CH}_3$  groups bands between 3000-2900, 1400-1350, present in other additives;
- a small number of bands ( $\text{cm}^{-1}$ ) around 1250-1100, 980-870, of variable intensity, weak to strong, assigned to the C-O (stronger) and O-O (weaker) groups<sup>[18]</sup>, may serve as the basis for characterization of DCP presence. However, this typical intensity variation<sup>[12]</sup> makes their characterization difficult compared to other

additives. Due to other additives band interference in the formulation, it was decided to try to separate the additives, by TLC and TLC/UATR, from the others. It does not mean that the analysis of rubber extracts was already the first step in the methodology to evaluate the indication of different additives presence.

### 3.2 TLC analysis of NR extracts and the different additives

Four eluent systems were used: A) toluene, already used in research on the antioxidant N-phenyl-N'-isopropyl-p-phenylenediamine (IPPD) in NR<sup>[10]</sup>, B) toluene/acetone (65/45), C) toluene/acetone (45/65) and D) toluene/ethyl acetate (100/5); B, C and D systems being used in our laboratories and in research of different accelerators and antioxidants of NR or poly (cis-isoprene) rubber (IR)<sup>[13]</sup>. Gibbs reagent, already used in other NR research<sup>[10]</sup>, was the developer.

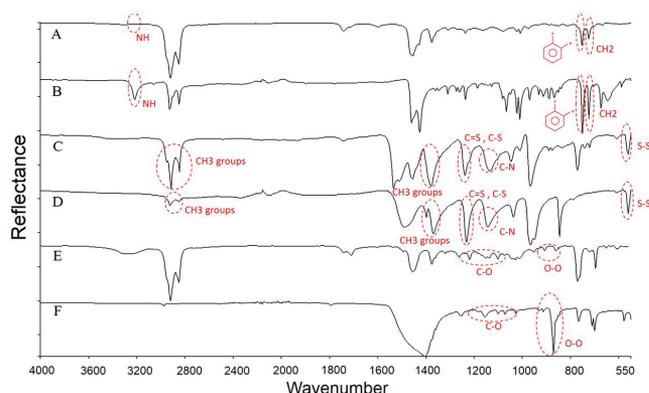
### 3.3 NR (CBS)

In Table 3, TLC data for NR (CBS) rubber are included, using toluene, toluene / acetone (65/45), toluene / acetone (45/65), toluene/ethyl acetate (100/5), as eluents, and Gibbs reagent as developer, which will respectively be referred to as: NR(CBS) – Toluene/Gibbs, NR(CBS) – Toluene/acetone (65/45)/Gibbs, NR(CBS) – Toluene/acetone (45/65) / Gibbs and NR(CBS) – Toluene / ethyl acetate (100/5)/Gibbs.

In relation to TLC analysis, only the Toluene/Acetone (45/65) / Gibbs system indicated a possible CBS separation. The other systems did not show efficiency for this procedure, since the colors of deposits and/or RF were different from those observed for respective accelerator. It is apparently caused by the greater plasticizer content and the presence of different products concentrations in the formulation<sup>[10]</sup> (Table 2, already shown).

### 3.4 NR (TMTD)

In Table 4, is included TLC data for NR(TMTD) rubber, using toluene, toluene/acetone (65/45), toluene/acetone (45/65), and toluene / ethyl acetate (100/5) as eluents and Gibbs reagent as developer, that will be, respectively, referred to as systems: NR (TMTD) – Toluene / Gibbs, NR (TMTD) -



**Figure 3.** UATR spectra of the acetone extracts of the vulcanized NR, containing additives and references additives: (A) NR (CBS); (B) CBS; (C) NR (TMTD); (D) TMTD; (E) NR (DCP); (F) DCP.

**Table 3.** TLC data for NR(CBS) Systems.

Sample Eluent/Developer Running time (h: min: sec)	Eluted deposit - Color of eluted deposit	Distance traveled by the eluent (cm)	Rf
NR (CBS)	CBS extract – Purple	8.6	0.54
Toluene/Gibbs	NR (CBS) extract 1°Rf – Grey	2.4	0.15
1:04:13	NR (CBS) extract 2°Rf - Light yellow	3.0	0.19
NR (CBS)	NR (CBS) extract 3°Rf - Yellow	15.0	0.94
Toluene/Acetone (65/45)/Gibbs	CBS extract – Purple	14.6	0.91
0:53:25	NR (CBS) extract 1°Rf - Yellow	14.0	0.88
NR (CBS)	CBS extract - Yellow	15.6	0.98
Toluene/Acetone (45/65)/Gibbs	NR (CBS) extract 1°Rf - Light yellow	15.5	0.97
0:48:06	CBS extract - Purple	10.1	0.67
NR (CBS)	NR (CBS) extract 1°Rf - Light yellow	2.4	0.15
Toluene/Ethyl Acetate (100/5)/Gibbs	NR (CBS) extract 2°Rf - Light brown	7.0	0.44
1:02:00	NR (CBS) extract 3°Rf - Strong yellow	7.6	0.48
	NR (CBS) extract 4°Rf - Light grey	14.5	0.91

**Table 4.** TLC data for the NR (TMTD) system.

Sample Eluent/Developer Running time (h: min: sec)	Eluted deposit (Color of eluted deposit)	Distance traveled by the eluent (cm)	Rf
NR (TMTD)	TMTD extract - Dark yellow	3.6	0.23
Toluene / Gibbs	NR (TMTD) extract 1°Rf - Light yellow	6.6	0.41
1:12:44	NR (TMTD) extract 2°Rf - Light purple	8.7	0.54
NR (TMTD)	TMTD extract - Dark purple	13.0	0.81
Toluene/Acetone (65/45)/Gibbs	NR (TMTD) extract 1°Rf - Light purple	14.0	0.87
0:46:45	TMTD extract - Yellow	14.3	0.89
NR (TMTD)	NR (TMTD) extract 1°Rf - Light yellow	15.0	0.94
Toluene/Acetone (45/65)/Gibbs	NR (TMTD) extract 2°Rf - Light yellow	15.9	0.99
0:48:06	TMTD extract - Dark purple	8.9	0.56
NR (TMTD)	NR (TMTD) extract 1°Rf - Light purple	8.9	0.56
Toluene/Ethyl Acetate (100/5)/Gibbs	NR (TMTD) extract 2°Rf - Light purple	12.0	0.75
1:00:00			

Toluene/acetone (65/45)/Gibbs, NR (TMTD) - Toluene/acetone (45/65)/Gibbs and NR (TMTD) - Toluene/ethyl acetate (100/5)/Gibbs. TLC analysis suggested that is possible to separate this accelerator, especially, by the toluene/ethyl acetate (100/5)/Gibbs (1°Rf) system.

### 3.5 NR (DCP)

In Table 5, are included TLC data for NR(DCP) rubber, using toluene, toluene/acetone (65/45), toluene/acetone (45/65), and toluene/ethyl acetate (100/5), as eluents, and Gibbs reagent as developer, that will be referred to, respectively, as systems: NR (DCP) - Toluene/Gibbs, NR (DCP) - Toluene/acetone (65/45)/Gibbs, NR (DCP) - Toluene/acetone (45/65)/Gibbs. By the TLC analysis, all the eluent systems showed RF closer to those observed for DCP, although some colors presented differences, possibly because of plasticizer presence, which suggests that the separation is feasible to the accelerator by these eluent systems, with higher accuracy for the Toluene/Acetone (45/65)/Gibbs and NR (DCP) - Toluene/ethyl acetate/Gibbs.

## 4. TLC/UATR analysis

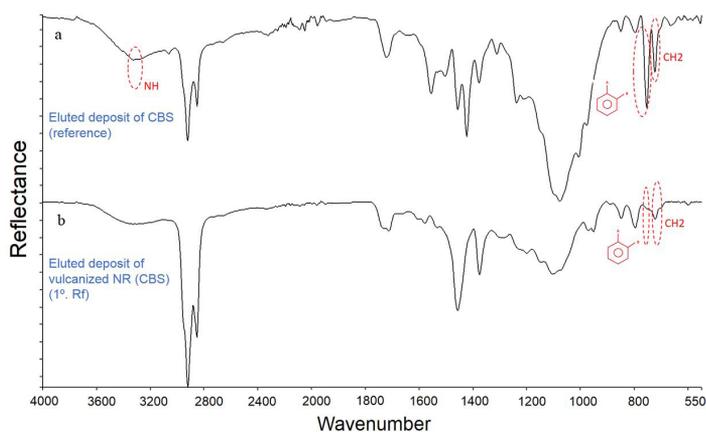
### 4.1 NR(CBS)

By the IR spectra analysis, the separation of CBS presumably did not occur, due to the greater presence of plasticizer (see Table 2). There are only indications of separation beside the evaluation of the spectrum referring to the extract in toluene/acetone (45/65), through bands in ( $\text{cm}^{-1}$ ), most likely assigned<sup>[17]</sup> to the groups: 3329 (NH), 2922, 2853 and 722 ( $\text{CH}_2$ ) and 755 (C-H ortho substitution) (Figure 4).

An interesting fact is under conditions (toluene/Gibbs) for similar formulations of NR<sup>[6]</sup>, the rubber extract usually produces an eluted deposit, in higher RF and yellow color, which is essentially the plasticizer. Thus, the analysis of the 3°RF deposition in toluene was made to characterize the naphthenic plasticizer in the formulation, succeeding in the applied methodology (Figure 5), since that the separated product spectrum (3°Rf) showed the same absorptions of referred additive.

**Table 5.** TLC data for the NR (DCP) system.

Sample - Eluent/Developer	Eluted deposit - Color of eluted deposit	Distance traveled by the eluent (cm)	Rf
<b>Running time (h: min: sec)</b>			
<b>TLC Plate</b>			
NR (DCP)	DCP extract - Purple	14.6	0.91
Toluene / Gibbs	NR(DCP) extract 1°Rf - Yellow	14.7	0.92
1:04:13			
NR (DCP)	DCP extract - White	15.0	0.94
Toluene/Acetone (65/45)/Gibbs	NR(DCP) extract 1°Rf - Yellow	14.4	0.90
0:53:45			
NR (DCP)	DCP extract		1.00
Toluene/Acetone (45/65)/Gibbs	NR(DCP) extract 1° Rf - Light yellow	16.0	1.00
0:48:06			
NR (DCP)	DCP extract - White	12.9	0.81
Toluene/Ethyl Acetate (100/5)/Gibbs	NR(DCP) extract 1°Rf - White	2.4	0.15
0:54:51	NR(DCP) extract 2°Rf - Light yellow	4.7	0.29
	NR(DCP) extract 3°Rf - Yellow	12.4	0.78

**Figure 4.** UATR spectra (after TLC, in toluene/acetone (45/65): (a) Eluted deposit of CBS (reference); (b) eluted deposit of vulcanized NR (CBS) (1° Rf).

#### 4.2 NR (TMTD)

Despite the fact there would be loss of material and spectral resolution in the TLC/IR technique, perhaps caused by the conditions applied, mainly due to transmission/pellet technique<sup>[8]</sup> application, Figure 6 shows that in the UATR spectrum of extract, in toluene, of TMTD after TLC, there are very similar absorptions to the reference TMTD UATR spectrum, also to the UATR spectrum of the extract, in toluene/acetone (45/65), which does not happen with the TMTD spectra, obtained in other eluent/developer systems. The Figure suggests that in the analysis of NR spectra, in TLC/UATR technique, the reference spectrum of analyzed accelerator should be used, under the same conditions as the TLC analysis.

By TLC analysis, toluene/ethyl acetate (100:5)/Gibbs that would be used to separate the TMTD, and this can be better visualized by comparing NR(TMTD) (1°Rf) and TMTD spectra, after TLC, in this system (Figure 7), and with discussion of the spectra being made according to data found in the literature<sup>[12]</sup>.

In recent paper<sup>[12]</sup>, it was evaluated the additives separation, including TMTD, in ethylene propylene diene monomer terpolymer (EPDM), with other eluent systems. It was mentioned that despite the fact there was some overlap of bands, it was possible to indicate in spectra obtained after TLC, in conditions (70% of hexane / 30% of ethyl ether and 5% of acetic acid), two absorptions in 1240 cm<sup>-1</sup> (C=S, C-S) and 560 cm<sup>-1</sup> (S-S) of TMTD, also associated to the bands shape of sulfur compounds, even in a small proportion in the formulation (also around 1phr, as in current paper).

In Figure 7, albeit there is also overlap, notably in the region of 3000-2800 and 1400-1460 cm<sup>-1</sup>, of CH<sub>2</sub> and CH<sub>3</sub> groups, the C-N band, around 1140 cm<sup>-1</sup>, common bands to other additives, the absorptions of geminated methyl group, between 1380-1350 cm<sup>-1</sup> and around 560 cm<sup>-1</sup> (S-S), of TMTD<sup>[12,17]</sup>, as well as their shape, are better visualized in the rubber extract spectra, in comparison with the TMTD spectrum, after TLC, suggesting that the used conditions, toluene / ethyl acetate (100:5) / Gibbs, are suitable for the NR rubber, for this purpose. In addition, the TLC analysis

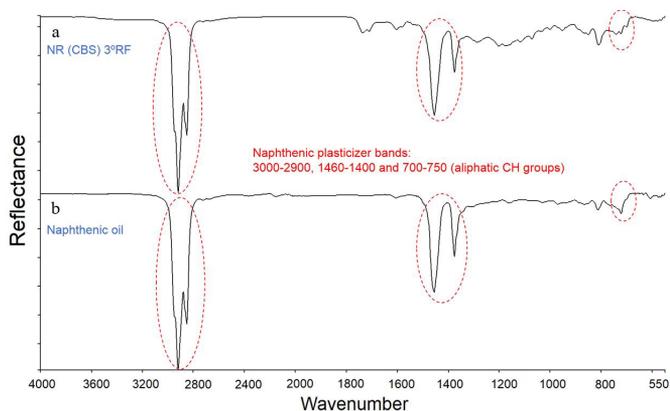


Figure 5. UATR spectra (after TLC): (a) Eluted deposit, in toluene, of vulcanized NR (CBS) (3° Rf); (b) naphthenic oil.

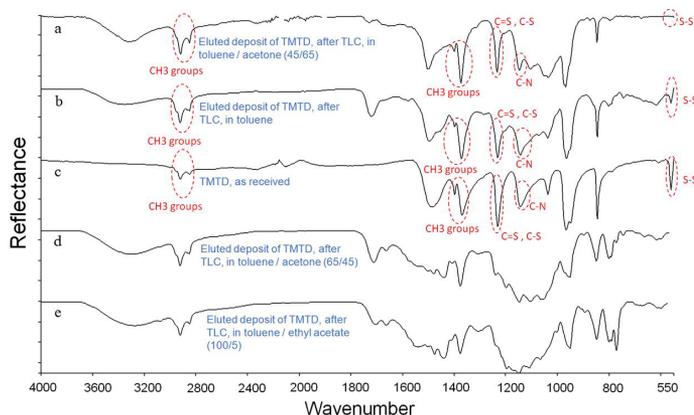


Figure 6. UATR spectra: (a) Eluted deposit of TMTD, after TLC, in toluene/acetone (45/65); (b) Eluted deposit of TMTD, after TLC, in toluene; (c) TMTD, as received; (d) Eluted deposit of TMTD, after TLC, in toluene/acetone (65/45); (e) Eluted deposit of TMTD, after TLC, in toluene/ethyl acetate (100/5).

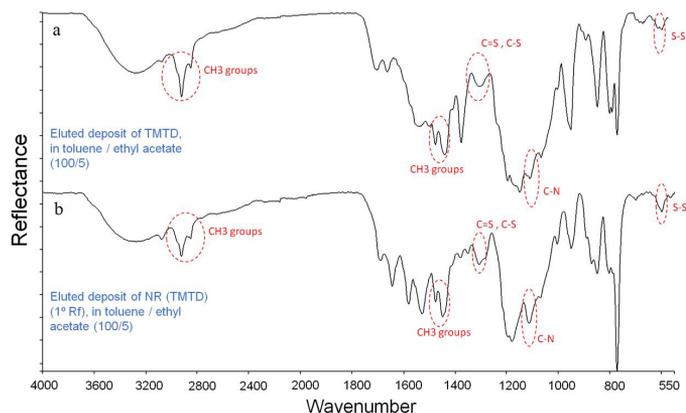
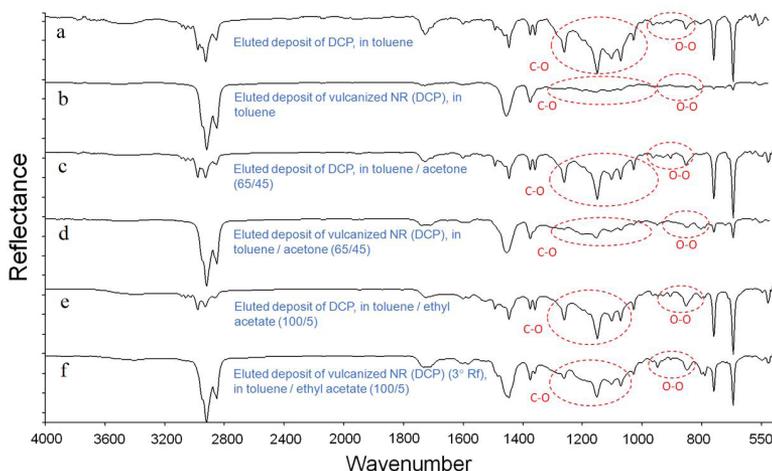


Figure 7. UATR (after TLC) spectra: (a) eluted deposit of TMTD, in toluene/ethyl acetate (100/5); (b) eluted deposit of vulcanized NR (TMTD) (1° Rf), in toluene/ethyl acetate (100/5).

showed Rf of the NR(TMTD) rubber extract equal to that observed for the TMTD (reference), indicating the TLC/UATR coupling was effective, as an indication of this accelerator in the formulation.

### 4.3 NR (DCP)

By the TLC analysis, all eluent systems used were efficient for the separation of DCP, with better result for Toluene / Ethyl Acetate (100/5) / Gibbs, 3°Rf. This is also



**Figure 8.** UATR spectra: (a) eluted deposit of DCP, in toluene; (b) eluted deposit of vulcanized NR (DCP), in toluene; (c) eluted deposit of DCP, in toluene/acetone (65/45); (d) eluted deposit of vulcanized NR (DCP), in toluene/acetone (65/45); (e) eluted deposit of DCP, in toluene/ethyl acetate (100/5); (f) eluted deposit of vulcanized NR (DCP) (3° Rf), in toluene/ethyl acetate (100/5).

demonstrated by the UATR analysis, Figure 8. In this figure, the similarity of the spectra can be noted as well and, with the bands ( $\text{cm}^{-1}$ ) being around 1250-1100, 980-870, of variable intensity, weak to strong, assigned to the C-O (stronger) and O-O (weaker) groups<sup>[12]</sup>, that may fit as reference in the characterization of the DCP presence, which can be better observed, meeting the TLC data.

After these results, the TLC-IR(UATR) analysis applied to separate and characterize NR additives such as CBS, TMTD and DCP, was considered available to rubber quality control in laboratories because is faster and simpler than methodologies involving other coupling types such as TG/IR<sup>[19]</sup>. In this study<sup>[19]</sup>, although good results were reached for sulfur additives such as MBT and TMTM, they were characterized by a complex methodology of its degradation products. Plasticizer was not detected, whereas in the TLC/UATR showed in this current paper, naphthenic oil was separated and characterized. Degradation studies are not necessary too. However, such methods can be considered complementary, if it necessary wide characterization of rubber additives.

## 5. Conclusion

UATR analysis of acetone NR extracts showed some differences in the formulations, the TMTD presence were better demonstrated. However, there are overlaps of bands of other additives. Therefore, it is necessary a separation/identification step, such as TLC/IR.

By TLC and TLC/UATR analysis, it was only evidenced the CBS separation/identification using the toluene/acetone system (45/65). By TLC/UATR analysis, it was possible to characterize the naphthenic oil presence, with the system (toluene/Gibbs). Perhaps, this separation/identification has been facilitated by this additive, paraffinic oil, being present in a higher proportion in the formulation (7.7 phr) than the other accelerators like CBS and TMTD (5.4 phr) in their specific formulations.

TLC analysis suggested that is achievable to separate TMTD, specifically by the toluene/ethyl acetate (100/5) / Gibbs (1° Rf) system. TLC/UATR analysis confirmed this indication, despite of some bands overlaps, which was once registered in EPDM rubber formulations, apparently because of the small TMTD amount in referred formulations.

By the TLC/UATR analysis, all eluent systems used were efficient for the separation of DCP, predominantly the Toluene/Ethyl Acetate (100/5)/Gibbs, 3° Rf, constituting the best methodology result in terms of characterization (TLC) and identification (UATR). It may be explained by the higher quantity of the additive (6.4 phr) in relation to the others (1.1 phr), in the specific formulations.

The decision to use the same curing time for all formulations did not affect the analysis because the results showed the additives separation by TLC and their identification by FT-IR (UATR), by characteristics bands of DCP (Figure 8) and TMTD (Figure 7). The unambiguous separation and identification of CBS may have been impaired due to the higher content of plasticizer in its formulation, which may have been the factor that facilitated the separation and identification of naphthenic oil (Figure 5).

In short, it was concluded that the developed TLC/UATR methodology for studying the additives not only has it contributed to the potential of formulations characterization in the automotive industry, but also could be applied in the aerospace area. The reason is related to these compounds that can be present in NR and EPDM formulations. It is a multiplier effect of acquired technical knowledge, being extremely useful to predict specific properties for different applications.

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