

# **Spectroscopic Studies of Ultrathin Microtomed Sections of Polymers. Part III. Rapid Characterization of Antioxidants in Cured Black-Loaded Rubbers from Ultraviolet Spectra of Extracts of Sections**

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## **INTRODUCTION**

Previous papers<sup>1,2</sup> have described the use of ultrathin microtomed sections (ca. 2  $\mu$  thick) and scale expansion for identifying polymer in a black-loaded cured rubber, and both polymer and filler in a cured rubber containing inorganic filler. Sections were cut, initially, with the use of petroleum naphtha, toluene, or acetone, depending upon which was needed to swell the rubber.

The use of an ultraviolet-transparent liquid to swell the rubber, which would enable sections to be cut, should also lead to a very fast extraction of antioxidants and, possibly, accelerator residues. This would obviate the need for cutting the sample with scissors and extracting with cold solvent, which is the normal, somewhat lengthy technique for the treatment of vulcanizates in these laboratories.<sup>3</sup>

A UV-transparent cutting liquid, methyl cyclohexane, has been found, and thus the identification of antioxidant in certain cured black-loaded rubbers may be carried out, in addition to the characterization of rubber and filler.

## **EXPERIMENTAL**

UV spectra were run on a Beckman DK.2 Spectrometer under the following operating conditions: Scanning time, 5; scale expansion, 2X; Time constant, 0.2; sensitivity, 12.

Some UV-transparent solvents, such as isooctane and isopropyl alcohol (both had been chromatographed and distilled), were tried as cutting liquids for natural rubber but were found unsuitable as they did not swell the rubber sufficiently. Carbon tetrachloride was partially successful for natural rubber: sections were obtained plus an extract which showed evidence, in its UV spectrum, of antioxidant content. However, carbon te-

TABLE I  
UV Spectra of Methyl Cyclohexane Extracts of Microtomed Sections of Cured Black-Loaded Rubbers

Sample	Extraction time, hr.	Antioxidant in mix	Accelerator in mix	Main Maxima, $m\mu$	Assignments	Identity of compounds in extract
Natural rubber (carbon tetrachloride extract)	1	Nonox HFN (1 phr) <sup>b</sup>	Santocure <sup>b</sup>	320-300 (broad, flat) 280-270	PBN? PBN	Phenyl- $\beta$ -naphthylamine (PBN)
Natural rubber	1 and 24	Nonox HFN (1 phr)	Santocure	309 298 272 231, 236 (shoulders)	PBN ? PBN PBN	PBN + decomposition products
Krylene (butadiene styrene copolymer)	1 and 24	Nonox HFN (0.75 phr)	Santocure	310-290 (very broad and flattish)	PBN	PBN + Dresinate + BLE
GRS 1502 and also photoinitiated GRS (butadiene/styrene copolymers)	1 and 24	Santoflex AW (0.75 phr)	Santocure	273 256, 262 (weak)	PBN Dresinate?	
		Nonox HFN (0.75 phr) Santoflex AW (0.75 phr)	Santocure	308 282 (weak)	PBN Dresinate or BLE? PBN	PBN + decomposition products
Butyl rubber	1	—	MBTS TMT	282 (weak) 268 and 265 (weak, shoulders) 260 (weakish) 255 (weak, shoulder, ?)	ZMC ? ZMC ?	Zinc dimethyl dithiocarbamate (ZMC) + other decomposition products

trachloride has a disadvantageous "cut-off" in the UV at ca. 260  $m\mu$ , missing most of the short wavelength end of the UV spectrum.

A small sample of a good swelling agent for natural rubber,<sup>4</sup> methyl cyclohexane (Hopkin and Williams Ltd., Chadwell Heath, Essex, England), was found to be UV-transparent and also successful for sectioning and extracting natural rubber. Larger samples, used subsequently, contained traces of toluene which were removed by distillation and being run through a silica gel column. The resultant solvent, in a 1-cm. cell, versus distilled

Krylene	1 and 24	Nonox ZA (1.5 phr)	Santocure	Broadish hump from 330-265 with peaks at 277 and 283	Nonox ZA + Dresinate + BLE
Krylene	1 and 96	425 (1.5 phr)	Santocure	Broadish peak at ca. 280, shifting to ca. 295 on addition of sodium isopropoxide 277 } 268 } Fine structure 259 }	425 + BLE + BLE + BLE Dresinate
Krylene	1 and 24	Santowhite CM (1.5 phr)	Santocure	Broad maximum 310- 275 with peaks at: 282 } 277 } Sharp 257 }	? Dresinate + BLE + Santowhite CM?
Krylene	1 and 24	Flectol H (1.5 phr)	Santocure	Broadish maximum 330-265 with peaks at: 282 } 276 } Sharp 255 }	? Dresinate + BLE + decomposition products
Krylene	1 and 24	Agerite White (1.5 phr)	Santocure	315 282 } 275 }	Agerite White Dresinate + BLE { Dresinate { Agerite White?

<sup>a</sup> Part per hundred rubber.

<sup>b</sup> *N*-Cyclohexyl-2-benzothiazole sulphenamide.

water, had an optical density of 0.25-0.30 at 225  $m\mu$ .

Sectioning of various samples of rubbers was carried out as described previously,<sup>1,2</sup> and 10-20 ultrathin sections (ca. 2  $\mu$  thick and ca. 0.5  $\times$  1.5 cm. in area) were placed in a Petri dish containing 10-20 ml. of methyl cyclohexane. After several sections had been laid out to be run in the infrared region, a 1-cm. quartz cell was filled with solution and its UV spectrum (versus methyl cyclohexane) was run. The Petri dish was covered

after the solution had been replaced, and the UV spectrum of the extract was run again after 24 or 48 hrs. or both.

## RESULTS

The method was found to be applicable only to the rubbers that are not "oil-resistant," e.g., natural rubber and butadiene/styrene copolymers. Oil-resistant rubbers, such as neoprenes and butadiene/acrylonitrile copolymers, need toluene as cutting liquid.

Table I lists the chief maxima in the UV spectra of extracts from various cured polymers containing different antioxidants; identities of polymers, antioxidants, and accelerators for the compounded rubbers are also given. Figures 1-5 exhibit UV spectra of some of the extracts, together with reference spectra of antioxidants, etc.

## DISCUSSION

The results obtained are discussed for each of the figures shown, which relate to standard reference samples containing known antioxidants. Some of the spectra of reference materials are not those of solutions in hydrocarbon solvents, but solvent shifts are not significant.<sup>3</sup>

*Figure 1.* Extracts of cured rubber containing phenyl- $\beta$ -naphthylamine (PBN) or Nonox HFN,<sup>5</sup> which is predominantly PBN,<sup>3</sup> give easily recognized maxima at 309 and 272  $m\mu$  ( $E_{1\%}^{1\text{cm.}}$  = 978 and 1105 respectively). This antioxidant is extracted rapidly and, as shown in Figure 1, there is little difference between methyl cyclohexane extracts of sections of cured

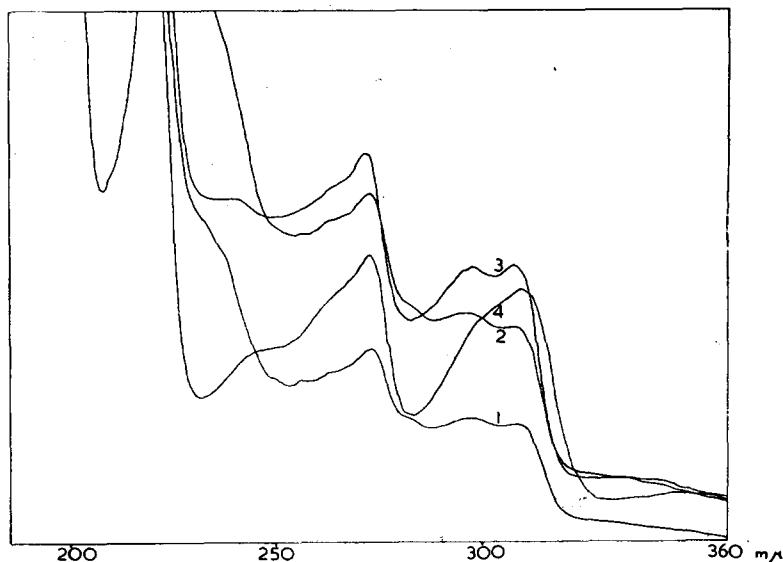


Fig. 1. UV spectra of extracts of natural rubber containing Nonox HFN: (1) methyl cyclohexane extract of microtomed sections after  $\leq 1$  hr.; (2) methyl cyclohexane extract of microtomed sections after ca. 24 hrs.; (3) iso-octane extract of "bulk" polymer after ca. 48 hrs.; (4) Phenyl- $\beta$ -naphthylamine in isopropyl alcohol.

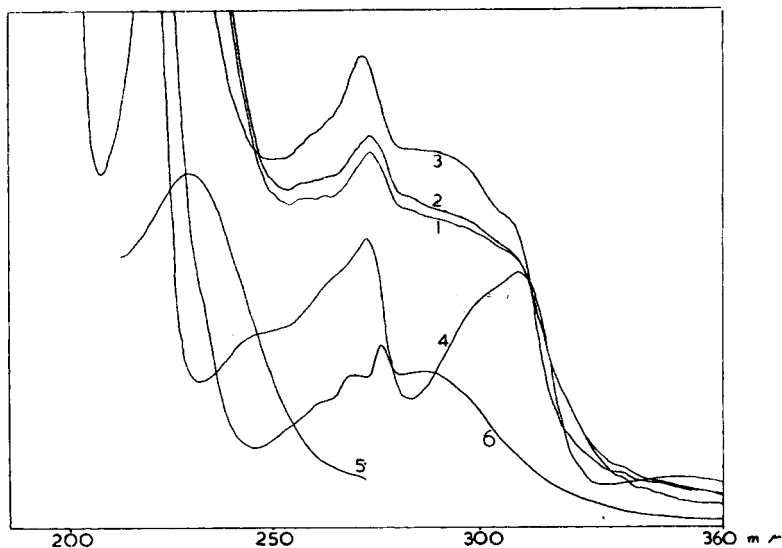


Fig. 2. UV spectra of extracts of Krylene (SBR) containing Nonox HFN and Santoflex AW: (1) methyl cyclohexane extract of microtomed sections after  $\leq 1$  hr.; (2) methyl cyclohexane extract of microtomed sections after ca. 24 hrs.; (3) isooctane extract of bulk polymer after ca. 48 hrs.; (4) phenyl- $\beta$ -naphthylamine in isopropyl alcohol; (5) Santoflex AW in isopropyl alcohol; (6) Dresinate + BLE in isopropyl alcohol (extract of raw Krylene).

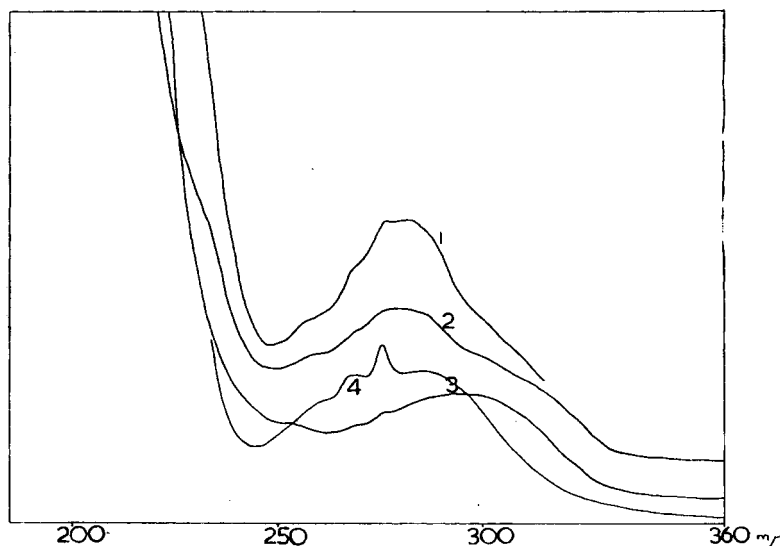


Fig. 3. UV spectra of extracts of Krylene (SBR) containing antioxidant 425: (1) methyl cyclohexane extract of microtomed sections after  $\leq 1$  hr.; (2) methyl cyclohexane extract of microtomed sections after ca. 96 hrs.; (3) = (2) on addition of sodium isopropoxide (50%) and rerunning after ca. 30 min.; (4) isopropyl alcohol extract of raw Krylene (Dresinate + BLE).

natural rubber after 1 and 24 hrs. and an isooctane extract in the cold of the bulk polymer (cut into small pieces) after 48 hrs. A reference spectrum of PBN is also shown on the same figure.

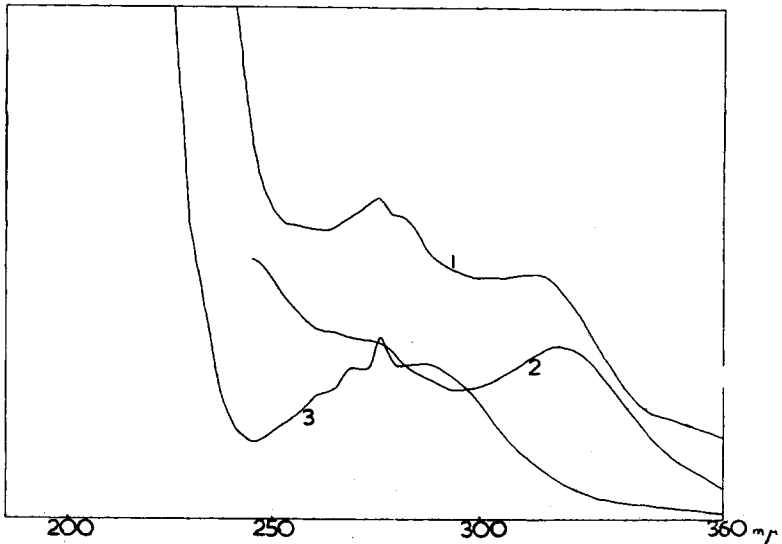


Fig. 4. UV spectra of extracts of Krylene (SBR) containing Agerite White: (1) methyl cyclohexane extract of microtomed sections after  $\leq 1$  hr.; (2) Agerite White in chloroform; (3) isopropyl alcohol extract of raw Krylene (Dresinate + BLE).

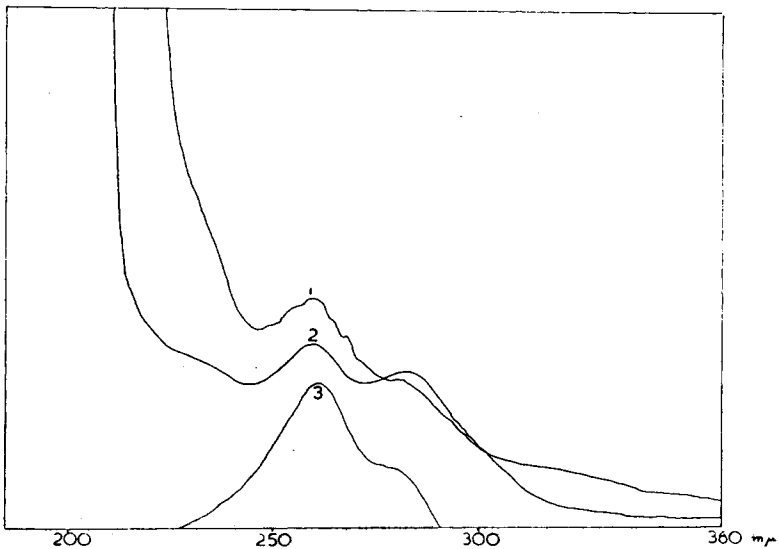


Fig. 5. UV spectra of extracts of butyl rubber: (1) methyl cyclohexane extract of microtomed sections after  $\leq 1$  hr.; (2) methyl cyclohexane extract of microtomed sections after ca. 48 hrs.; (3) zinc dimethyl dithiocarbamate (ZDC) in isopropyl alcohol.

Traces of decomposition products, e.g., oxidized PBN, also appear in the spectrum.

*Figure 2.* Raw Krylene (SBR rubber) contains an antioxidant (BLE)<sup>6</sup> of its own as well as Dresinate, a disproportionated rosin acid soap.<sup>5,6</sup> Methyl cyclohexane extracts of cured samples of Krylene exhibit maxima due to BLE and Dresinate besides antioxidants added during compounding. This is shown in Figures 2-4, which all relate to Krylene samples.

PBN may clearly be identified in Figure 2 but the identification of Santoflex AW (6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline) is by no means as certain.

*Figure 3.* Fine structure at 277, 268, and 261  $m\mu$  due to Dresinate may easily be recognized by comparison with a reference spectrum of an extract of raw (uncured) Krylene. The somewhat broad maximum at ca. 282  $m\mu$  shifts to ca. 295  $m\mu$  on addition of alkali, characteristic of going from phenolic OH to the ionized O<sup>-</sup> state. The positions of the maxima, however, are not correct for antioxidant No. 425 [2,2'-methylene-bis(4-ethyl-6-*tert*-butyl phenol), Anchor Chemical Co. Ltd., Clayton, Manchester, England], because of the interfering absorption of BLE which peaks at 287  $m\mu$ .

*Figure 4.* A characteristic long wavelength maximum at 315  $m\mu$  ( $E_{1\text{cm.}}^{1\%} = 1830$  for Agerite White itself), together with a weaker maximum at 275  $m\mu$ , appears in extracts of a cured rubber containing Agerite White (*N,N'*-di- $\beta$ -naphthyl-*p*-phenylenediamine).<sup>5,6</sup> These are shown in Figure 4, together with additional weaker bands due to Dresinate or BLE.

*Figure 5.* An extract of sections of butyl rubber, which has no specific antioxidant, exhibits maxima at 260 and 283  $m\mu$  in the UV, as shown in Figure 5. These are ascribed to zinc dimethyl dithiocarbamate (ZDC), the main reaction product of a tetramethyl thiuramdisulfide (TMT) sulfurless cure. ZDC has absorptions at 261 and 280  $m\mu$  and is shown, for comparison, in Figure 5.

### SUMMARY

The examples given are only an indication of the capabilities afforded by the use of a UV-transparent liquid (methyl cyclohexane) as cutting liquid. It has been used successfully for identification of antioxidants as well as polymers in unknown cured black-loaded samples of rubbers. It is not proposed to extend this work, however, so it is being reported at this stage.

The extraction suffers from several drawbacks:

1. Some antioxidants, e.g., Nonox ZA (*N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine), Santowhite CM (di-*o*-cresol monosulfide),<sup>5,6</sup> and Flectol H (acetone-aniline reaction product),<sup>5,6</sup> are not extracted from microtomed sections of cured rubbers by the solvent used. These antioxidants can be found in extracts from bulk rubber and extract quite quickly;<sup>3</sup> thus, oxidation must occur during cutting and extraction.

2. In many of the UV spectra, maxima are very broad; the explanation

may well be that oxidation of the rubber and antioxidant occurs very much faster in thin sections than in a piece of rubber.

3. If mineral oil is present in the cured rubber, it is extracted and "masks" some antioxidants.

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### Synopsis

Several types of cured black-loaded rubbers, including natural rubber, butadiene/styrene copolymers, polybutadienes, and butyl rubbers, can be microtomed with an ultraviolet-transparent solvent (methyl cyclohexane) as cutting liquid. The ultrathin sections obtained are used to characterize the rubber and the inorganic fillers, if any, and at the same time the antioxidant present is extracted rapidly from the very thin films by the solvent. An ultraviolet spectrum of the resultant extract enables some antioxidants and reaction products of cures to be rapidly characterized.

### Résumé

Plusieurs types de caoutchouc traités et chargés de carbon-black, comprenant le caoutchouc naturel, des copolymères butadiène/styrène, des polybutadiènes et des caoutchoucs-butyle, peuvent être microtomés en utilisant un solvant (méthylcyclohexane) transparent à l'U.V. comme liquide permettant la coupure. Les sections ultra-minces obtenues sont utilisées pour caractériser le caoutchouc et les charges inorganiques présentes, s'il y en a, et en même temps l'anti-oxydant présent est rapidement extrait des très minces films par le solvant. Un spectre U.V. de l'extrait résultant permet de caractériser très rapidement certains anti-oxydants et produits de réaction des traitements effectués.

### Zusammenfassung

Von einigen vulkanisierten, russgefüllten Kautschuktypen, nämlich Naturkautschuk, Butadien-Styrolcopolymeren, Polybutadienen und Butylkautschuk können unter Benützung eines UV-durchlässigen Lösungsmittels (Methylcyclohexan) als Schneidflüssigkeit Mikrotomschnitte angefertigt werden. Die erhaltenen, ultradünnen Schnitte werden zur Charakterisierung des Kautschuks und des eventuell vorhandenen anorganischen Füllstoffs verwendet und gleichzeitig wird das anwesende Antioxydans aus den sehr dünnen Filmen durch das Lösungsmittel rasch extrahiert. Ein UV-Spektrum des erhaltenen Extrakts ermöglicht die rasche Charakterisierung einiger Antioxydantien und Reaktionsprodukte der Vulkanisationsreaktion.

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