

Oxidation of Rubber Vulcanized with a Sulfenamide Accelerator*

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By far the largest proportion of manufactured rubber products are made by procedures which are "inefficient" in that the crosslink yield per mole of sulfur taken is low relative to the maximum obtainable. This is accompanied by alteration of the polymer structure external to the crosslink.¹ Vulcanizing systems giving this result include MBT (benzothiazolinethione) as the primary accelerator. High efficiency can be obtained with MBT and its derivatives, but this is usually avoided. The choice of vulcanizing method is determined by the fact that the physical properties of vulcanized rubber depend on the method used for vulcanization, as does the rate at which these change with time. Vulcanizing systems based on MBT achieve a balance between the kinds of modification of the polymer, which leads to high tensile strength and tear resistance.

In addition, it is possible to obtain vulcanizates which show good resistance to failure under conditions of cyclic deformation (fatigue resistance) relative to most products of efficient vulcanization. Since the classic paper of Neal and Northam,² it has been known that the fatigue resistance of MBT vulcanizates may be enhanced several fold by protection from oxygen either by its exclusion or by addition of antioxidants. Oxygen, therefore, must play a role in fatigue failure, although the temperature is usually so low that ordinary thermal oxidation would be expected to be of negligible importance during the time required for failure under cyclic stress. The good properties of MBT vulcanizates under these conditions and their response to antioxidants make it of interest to establish if any difference in oxidation mechanism is responsible for the difference between these compositions and the products of efficient cure.

Horikx³ showed that main chain breaks occur during oxidation of MBT sulfenamide accelerated vulcanizates by comparing solubility after oxidation with the extent of swelling of the gel fraction. By means of stress relaxation⁴ some differences have been found between efficiently cured vulcanizates and others which suggest that the crosslinking structure may have an influence on the course of the reaction.⁵

This report describes a study of a group of vulcanizates based on an

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MBT sulfenamide accelerated system in which their thermal oxidation is compared in detail with evidence already reported for other compositions. Volatile products of oxidation have been examined as well as changes in solubility of the vulcanized polymer after oxidation. The technique developed by Horikx is used to obtain a quantitative estimate of chain scissions from the solubility changes.

A close correspondence exists between breaks in the main polymer chain and the formation of low molecular weight oxidation products during the reaction of unvulcanized rubber with oxygen. Among these products are acetaldehyde, acetic acid, and levulinolaldehyde.⁶ Since the side chains in rubber are only one carbon atom long, the appearance among the low molecular weight products of fragments with two or more carbon atoms per molecule is evidence for main chain fracture. When a quantitative correspondence in yield of volatile fragments is obtained from two samples oxidized under the same conditions, one may infer in addition that the mechanism of formation of low molecular weight products is the same for the two samples.

Use has been made of these considerations in a series of experiments on the oxidation of vulcanized rubber, which because of its insolubility is not readily analyzed by direct methods. By adding one new factor at a time, it becomes possible to determine the effect of each of the constituents of the rather complex composition which is ordinary vulcanized rubber. Results reported in some detail have shown that for the compositions examined the degradation mechanism is not affected by the introduction of crosslinks involving either carbon-to-carbon bonds or carbon-to-sulfur bonds⁷ nor by the presence of carbon black.⁸ This work has been extended, and brief reports^{9,10} have been made of experimental results which show that none of

TABLE I
Formulas of Compositions Used
(All per 100 rubber (#1 Pale Crepe))

	1	2	3	3a	4	5	6	7
Carbon black ^a	50	50	50	6	50	5	50	—
Stearic acid	3	—	—	—	3	1.5	3	.5
Zinc oxide ^b	3	—	3	6	5	5	5	5
Sulfur	3	—	—	—	2.5	2.5	2.5	2.5
Délac S ^c	1.5	—	—	2	0.7	0.7	0.7	0.7
TMTD ^d	—	—	7	7	—	—	—	—
Cumyl peroxide ^e	—	2.5	—	—	—	—	—	—
Vulcanization								
Time, min.	45	120	360	360	40	40	30	30
Temperature, °C.	150	150	120	120	140	140	145	145

^a MPC, Spheron 6, Godfrey L. Cabot, Inc.

^b Kadox, New Jersey Zinc Co.

^c *N*-Cyclohexylbenzothiazyl sulfenamide, Naugatuck Chemical Division, United States Rubber Company.

^d Bis-(*N,N*-dimethylthiocarbonyl) disulfide, Tuex, Naugatuck Chemical Division.

^e Di-Cup (recrystallized), Hercules Powder Company.

these factors affect the mechanism of chain fracture: (1) the presence (or absence) of simple phenolic or amine antioxidants, (2) the temperature of vulcanization, (3) the temperature of oxidation (within rather narrow limits), (4) oxygen partial pressure (from $1/8$ to 1 atm.),^{10b} (5) method of vulcanization. (Each of these factors may, of course, influence the *rate* of oxidation without affecting the mechanism of scission.)

All of the results reported in detail apply to efficiently cured vulcanizates prepared by procedures which give a high yield of crosslinks per molecule of crosslinking agent, and as a consequence a high ratio of crosslinks formed to other modifications of the polymer. These include crosslinking by means of radiation, ditertiary peroxides, methylolphenols, and among curing systems giving sulfur in the crosslink, TMTD (sulfurless) and MBT-dithiocarbamate combinations such as are used in the manufacture of foam sponge. The investigation is now extended to sulfenamide-accelerated inefficient sulfur vulcanizates.

EXPERIMENTAL

Preparation of Samples

The compositions used are tabulated in Table I. All compositions were mixed on conventional two roll laboratory mills. The carbon black, zinc oxide, and fatty acids were added at a mill temperature of about 100°C. which gives the minimum rate of breakdown. All samples containing carbon black were then heated in a press at 155°C. for 3 hr. and cooled to room temperature before the other ingredients were added, to provide for uniform rubber-black interaction. The vulcanizing materials were added below 70°C. Samples were sheeted on a laboratory three-roll calender.

Two different procedures were used for vulcanization. In early experiments with the "high" sulfenamide levels (compositions 1 and 3A of Table I) and with peroxide and TMTD compositions (2 and 3), a procedure described previously⁷ was used. Samples were wrapped on glass forms, sealed in vacuum, and heated in an air oven for the desired length of time. For the efficient combinations the procedure is entirely satisfactory, since these reach a stable extent of cure and the actual vulcanization time is not critical. For the others, the properties of the vulcanized rubber change continuously even after maximum modulus is obtained and so some uncertainty exists as to the proper length of time for cure in vacuum to prepare samples having properties equivalent to press cures. In addition, with samples containing lower sulfenamide levels some difficulty was encountered in getting uniform cure. To avoid these difficulties a new procedure was developed. Samples were calendered onto 0.003 in. aluminum foil, dusted lightly with talc on the exposed surface, then cut to fit and stacked carefully into a square mold to fill it completely when the mold was closed under hydraulic pressure. These stacks were then vulcanized in a press in the usual way.

All samples were leached in at least three changes of solvent, usually acetone. This was either followed by, or entirely replaced by, methanol

for experiments in which methyl ketone determinations were to be made. Each leaching step involved either 3 hr. at the boiling point or 16 hr. at room temperature with the sample fully immersed in solvent. In some instances materials which were desired to be incorporated into the vulcanized samples were dissolved in the final leach and allowed to stand overnight at room temperature. Samples were finally dried briefly in air, then 48 hr. in vacuum at room temperature. (The effects of variation in details of extraction and drying of samples has been studied by E. S. English, who finds no effect on volatile product yield, although the oxidation rates may be affected by the choice of solvent for extraction.) Samples were wrapped in polyethylene film and stored in a refrigerator until used.

Oxidation Procedure

Oxidation experiments were made with an apparatus which has been described previously.¹¹ Gas circulates continuously over the sample and through a trap immersed in a Dry Ice-acetone mixture; oxygen reacting with the rubber is replaced from gas burets.

All experiments in this report were made at atmospheric pressure in oxygen. When the desired amount of oxygen had been absorbed by a sample, it was removed from the oven, cooled rapidly to room temperature, and the rubber and trap contents examined. Solubility and swelling in chloroform, total acid, and methyl ketone were determined by procedures which have been described.^{7,8,11}

Main chain scissions were estimated from the solubility of the oxidized sample using Horikx's³ procedure, with corrections to the physical cross-link density estimate which have been outlined.^{8,9}

RESULTS AND DISCUSSION

The first series of experiments was made with composition 1 of Table I. This had somewhat higher than usual sulfur and accelerator concentrations in order to insure sufficient vulcanization during the heating in vacuum. The time and temperature of cure were chosen to obtain complete combination of sulfur. The solubility after oxidation for several separate series of samples all using the same starting composition is given in Table II, together with data for efficiently cured controls, some of which have been described previously. Scission yields calculated from the solubility measurements are plotted in Figure 1. In the figure the solid line represents the data for experiment 43 (peroxide control) and the triangles experiment 45 (TMTD control). It is apparent that within the experimental error of this method of estimating scissions, there is not a significant difference between the scission yield from samples which have been efficiently cured and those which are inefficiently cured.

However, the acid yields from some of these samples (Table III) were uniformly low, compared with previously reported results^{7,8,11} and the yields from experiment 45 (Fig. 2), although the methyl ketone yields were ap-

proximately the same as those previously obtained (Table III, Fig. 3). Since a likely explanation for the low acid yields was reaction of the acid produced with some remaining fragment of the vulcanizing agent nor removed by extraction, the series of further experiments listed in Table III was made to trace the source of the discrepancy.

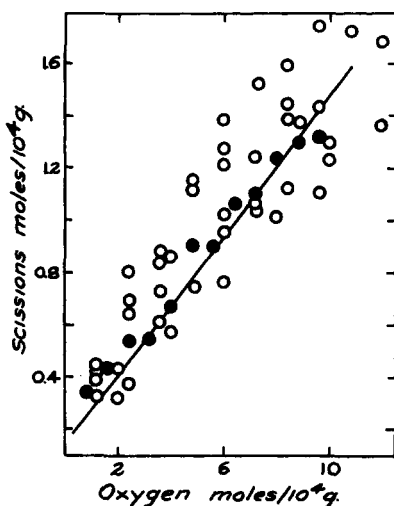


Fig. 1. Scissions calculated from solubility for "high" Delac S samples. The line represents data from a peroxide vulcanizate containing 50 parts of carbon black (experiment 43, Table II). (●) A control from a "sulfurless" TMTD vulcanizate (experiment 45, Table II). (○) Sulfenamide-sulfur vulcanizates.

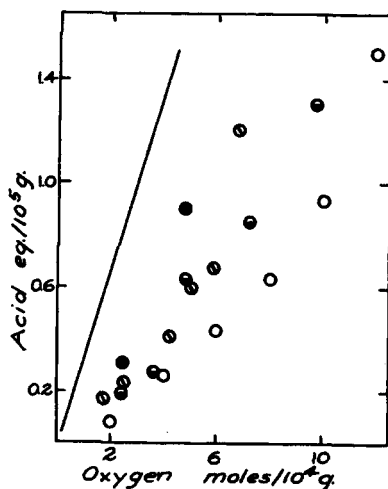


Fig. 2. Influence of added materials on acid yields. Line is drawn through points from the TMTD control experiment. (○) Delac S vulcanizate (experiment 46A). (◐) TMTD vulcanizate with added Delac S. (●, ◐) Peroxide vulcanizates with BLE and Delac S, respectively.

TABLE II
Solubility After Oxidation, "High" Delac S

Experiment	46	46A	46C	46D	46DA	46F	45-2	45	43
Vulcanization, Time, min.	45	45	45	45	45	45	360	360	150
Temperature, °C.	150	150	150	150	150	140	120	120	150
Swelling	6.33	5.98	6.07	7.07	6.13	6.27	9.42	6.60	6.00
Chain density	1.60	1.87	1.81	1.24	1.77	1.66	1.05	1.46	1.88
Added	BLE	BLE	—	—	—	BLE	—	—	—
Oxidation temperature, °C.	140	140	120	120	120	140	140	140	140
Oxygen (moles/10 ⁴ g.)				Solubility (chloroform) after oxidation					
0.80									
0.85							0.033	0.029	0.004
1.20	0.043		0.043		0.037	0.028			0.025
1.60							0.056	0.063	0.029
1.69									
2.0		0.039		0.049					0.021
2.40	0.138		0.089		0.082	0.027		0.086	0.040
2.52							0.077		
3.20								0.086	0.058
3.38									
3.60	0.156		0.097		0.075	0.139	0.111		

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4.00	0.120	0.120	0.120	0.114	0.080
4.21					
4.80	0.224	0.135	0.203	0.181	0.114
5.00					
5.60				0.176	0.119
5.95				0.228	
6.00	0.196	0.213	0.270	0.245	0.128
6.40					
6.75					
7.20	0.357	0.223	0.309	0.260	0.201
8.00				0.232	0.223
8.40	0.336	0.262	0.333	0.297	0.227
8.80				0.325	
9.60	0.330	0.301	0.364	0.338	0.243
10.0					
10.80	0.224	0.301	0.364	0.338	0.243
12.0	0.243	0.343	0.383		

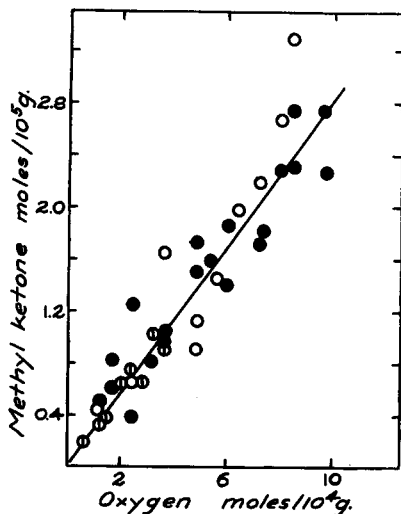


Fig. 3. Methyl ketone yields. (●) Sulfenamide vulcanizates. (○) Raw rubber. (◐) Peroxide vulcanizates containing carbon black.

A preliminary experiment with composition 1 was made at 140°C., the temperature previously used with peroxide vulcanized rubber containing carbon black. The latter absorbed oxygen at about 2 ml./g. hr. The extracted sample of sulfenamide vulcanizate, exposed to oxygen at this temperature, absorbed oxygen at about 34 ml./g. hr., much too fast for convenient experimental control. In order to obtain controllable rates of oxidation, later samples were treated with solutions of an antioxidant in the first two series reported (experiments 46, 46A). To determine the effect of BLE (a reaction product of diphenylamine and acetone) experiments 46B and 46C were made; to determine the effect of Delac S (mercaptobenzothiazole-*N*-cyclohexylsulfenamide), experiments 46E and 45-2. From the results assembled in Table III and Figure 2, it can be seen that both the amine antioxidant and the sulfenamide lead to low acid yields, the accelerator being more effective in this respect. It will be noted that the yield of acid increases rapidly with extent of oxidation, the slope of the plot of acid vs. oxygen eventually approaching that of the curve for TMTD samples.

From these results it was concluded that there is no major difference in scission mechanism between efficiently and inefficiently vulcanized samples. However, independent experiments at the same time showed that the fatigue resistance characteristic of MBT vulcanizates depends on the accelerator to sulfur ratio on the length of time at vulcanizing temperatures, raising the possibility that oxidation mechanism might be similarly dependent. Since the first experiments were made with samples having higher than usual accelerator content and the temperature and time of cure may have been longer than would correspond to the best properties, a second series of samples was tested (4-7 of Table I). These were prepared from

TABLE III
 Acid and Methyl Ketone Yields

Experiment	46DA ^a	46	46A	46B	46C	46E	45	45-2	46F
Composition	1	1	1	2	1	2	3	3a	1
Addend	—	0.5 BLE	1.5 BLE	1.0 BLE	—	2.0 Delac	—	—	0.5 BLE
Temperature, °C.	120	140	140	140	120	140	140	140	140
Oxygen (moles/10 ⁴ g.)	Acid (moles/10 ⁶ g.)								
0.8							0.21		0.12
1.2	0.49				0.10				
1.6							0.51		
1.7								0.17	
2.0			0.08					0.27	
2.4	0.39			0.31	0.11	0.19	0.80		0.13
2.5								0.23	
3.2							1.0		
3.6	1.02				0.36	0.27			0.36
4.0			0.26				1.4	0.47	
4.2								0.41	
4.8	0.91	0.30		0.90	0.26	0.73	1.8		0.28
5.0								0.50	
5.6							2.3		
5.9								0.67	
6.0	1.40	0.51	0.43		0.59			0.92	0.36
6.4							2.2		
6.8								1.2	
7.2	1.92	0.75			0.31	0.85	2.3		0.60
7.3				1.7					
8.0			0.63				2.4	1.02	
8.4	2.35	1.1			0.55				0.49
8.8							3.7		
9.6	2.33	1.4			0.46	1.3	4.0		1.62
10.0			0.93					1.56	
10.8					0.38				
12.0			1.5		0.80	2.8			

^a 46DA data only: methyl ketone (moles/10⁶ g.).

compositions similar to some which have already been studied by means of stress relaxation⁵ and which are reported to show important differences in relaxation behavior from peroxide vulcanizates. Results for these samples are given in Tables IV and V. Scissions calculated from the data of Table IV are plotted in Figure 4. Methyl ketone yields are included in Figure 3. Acid yields are not plotted but show the same pattern as those observed with the first series of samples. It may be noted that the crosslink density as estimated from swelling of the unoxidized samples is about the same in the two sets of Delac S accelerated samples so that by coincidence the first choice of composition yielded vulcanizates having about the same properties as those obtained from press cures with the lower accelerator level.

The possibility has been considered that unsuspected volatile compounds might be formed during the oxidation of sulfenamide-sulfur compositions

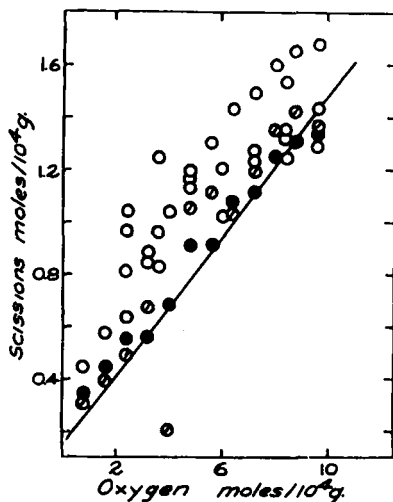


Fig. 4. Scissions from "low" Delac S samples. Symbols are the same as in Fig. 1 except that barred circles represent sulfenamide samples containing no carbon black.

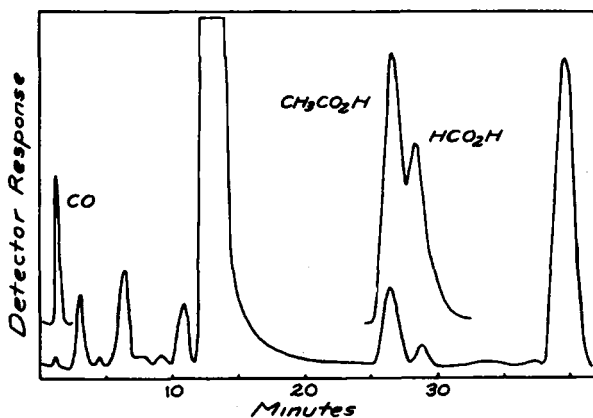


Fig. 5. Chromatograms of volatile oxidation products from sulfenamide-sulfur vulcanizate (below) and peroxide vulcanizate. Only portions of the chromatogram for the latter are shown, in the regions where there are differences. Oxidation at 120°C., 1 atm. oxygen. Separations using F & M model 202C chromatograph. Column 20% CEG on Chromosorb W. He flow 30 ml./min. Temperature 50°C. for 6 min. then programmed to 156°C. at 3.3°/min.

which cause fortuitous agreement in the analyses; analytical methods for functional groups do not establish the identity of the entire compound. Testing this hypothesis has been made easier by the development of a substrate for gas chromatography which permits separation of the low molecular weight oxidation products.^{10a} Portions of chromatograms of the volatile products from a sulfenamide vulcanizate and a peroxide vulcanizate are drawn in Figure 5. The curve reproduced in full is for the sulfenamide

TABLE IV
Solubility After Oxidation
"Low" Delac S

Experiment	46-4	46-5	46-6	46-7	46-6a	46-6b	46-6c
Carbon black	50	5	50	0			
Swelling			6.70	7.74			
ν	0.85	0.99	1.41	1.69			
Oxygen (moles/10 ⁴ g.)							
0.8	0.072		0.063	0.027			
1.2		0.151					
1.6	0.108	0.074	0.096	0.037			
2.0							
2.4	0.156	0.130	0.167	0.056	0.244	0.215	0.113
2.8			0.187				
3.2		0.150	0.199	0.094			
3.6	0.177	0.163			0.171	0.316	0.217
4.0	0.314		0.247	0.111			
4.4		0.167					
4.8	0.185	0.185	0.299	0.187	0.277	0.290	0.279
5.2		0.340					
5.6	0.278	0.242	0.340	0.206			
6.0		0.294			0.304		0.240
6.4	0.262		0.385	0.182			
6.8		0.362					
7.2	0.366	0.327	0.416	0.232	0.333	0.276	0.322
7.6		0.420					
8.0	0.299	0.382	0.458	0.277			
8.4	0.356	0.426			0.351	0.430	0.326
8.8	0.388	0.371	0.480	0.295			
9.2		0.464					
9.6	0.480		0.490	0.280	0.389	0.483	0.345

vulcanizate. Except as indicated by the peaks for acetic and formic acids (carbon monoxide results from decarboxylation of formic acid in the injection port) sketched into the same scale, the two chromatograms appear identical.

From the results assembled here it is evident that within the limits of the analytical methods used, there is no substantial difference in behavior during oxidation between the samples, conditioned by the method used for their vulcanization. Yields of methyl ketone are slightly lower and of acid substantially lower from the sulfur vulcanizates than those obtained in the absence of the accelerator based on MBT, but both of these effects may be traceable to insoluble fragments remaining from the accelerator after vulcanization and extraction. It should be emphasized perhaps that this evidence does not prove that random scission occurs during oxidation, and there is some reason to believe that it is in fact not random. As a consequence the numerical values calculated for chain scissions are not necessarily of absolute significance, since some assumptions have been made for their calculation which are not independently proven.³ They do provide a

TABLE V
Acid and Methyl Ketone Yields, "Low" Delac S

Composition	4		5		6		7		7R
	Acid	Ketone	Acid	Ketone	Acid	Ketone	Acid	Ketone	Acid
(Oxygen (moles/10 ⁴ g.)	Product (equivalents/10 ⁵ g.)								
0.8	0.11				0.07		0.05		
1.2				0.45					
1.6		0.61	0.05		0.81		1.02		
2.0									0.12
2.4	0.18			0.65	0.15	1.25	0.13		
2.8									
3.2			0.25			0.81		0.81	
3.6				1.65		0.96			
4.0	0.33				0.68		0.32		0.45
4.4			0.38						
4.8		1.50		1.12		3.80 ^a		1.28	
5.2			0.61			1.59			
5.6	0.45			1.45	1.14		0.54		
6.0			0.50						0.52
6.4				1.98		3.32 ^a		1.72	
6.8			0.65						
7.2	1.41			2.19	1.69	1.72	0.75		
7.6			1.06						
8.0		2.29		2.67				2.20	1.30
8.4			1.35			2.74			
8.8	1.66			3.38	2.66		1.17		
9.2			2.00						
9.6		5.30 ^a				2.73		2.80	
10.0									2.80

^a These values believed high from external contamination.

convenient form in which to compare solubility changes and are probably correct within a factor of two (the uncertainty in estimates of scission efficiency for unvulcanized rubber). The conclusions drawn here do not rely on the quantitative correctness of scission yields but on the close similarity of the results from each kind of vulcanized rubber, when treated in the same way. Thus, comparison of compositions 6 and 7 confirms previous conclusions about the effect of carbon black on apparent crosslink density⁸ that covalent linkages to carbon are negligible compared with network crosslinks.

It appears inescapable that the overall degradation mechanism is similar for all natural rubber vulcanizates irrespective of extraneous factors, such as the presence or absence of filler or the method of vulcanization. This is not a surprising conclusion when the composition of vulcanized rubber is considered. It means that the important differences in physical properties and in aging behavior of rubber vulcanized in different ways must be attributed to some process other than the way in which the hydrocarbon is degraded by oxygen. An example of a possible process, not detectable by the procedures

used here, is a process of crosslink exchange or of bond breakage and new bond formation with no net change in crosslink density.

I am indebted to E. Philipp for technical assistance.

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Synopsis

The solubility and the volatile product yields after oxidation from rubber vulcanized, with sulfur accelerated with an MBT-sulfenamide have been compared with the same quantities for peroxide and TMTD vulcanizates. No significant difference was found. It is concluded that the chain scission mechanism is independent of the nature of the crosslinking.

Résumé

La solubilité et le pourcentage de produit volatil après oxydation du caoutchouc, vulcanisé par du soufre, accélérée par le MBT sulfénamide, ont été comparés avec les mêmes quantités pour les vulcanisats au peroxyde et à TMTD. Aucune différence significative n'a été trouvée. On en conclut que le mécanisme de rupture est indépendant de la nature du pontage.

Zusammenfassung

Löslichkeit sowie Ausbeute an flüchtigen Produkten nach der Oxydation wurden bei einem mit Schwefel bei Gegenwart von MBT-Sulfenamid als Beschleuniger vulkanisierten Kautschuk mit Peroxyd- und TMTD-Vulkanisaten verglichen. Es bestanden keine wesentlichen Unterschiede. Man kommt zu dem Schluss, dass der Kettenspalungsmechanismus unabhängig von der Natur der Vernetzung ist.

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