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THERMAL DECOMPOSITION OF HOMO- AND COPOLYMERS OF ISOBUTYLENE

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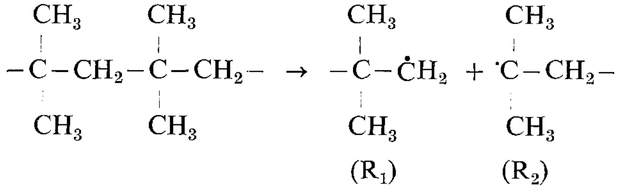
The thermal properties of polyisobutylene and isobutylene-isoprene copolymers were studied. Thermal curves were interpreted with regard to supplementary data. It was found that the degradation of both homo- and copolymers proceeds to a much higher extent in air than in argon. It follows from the results that peroxide formation plays a significant role in the degradation of this group of polymers.

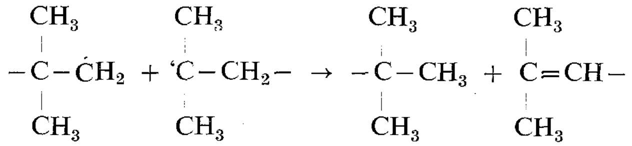
This finding correlates well with the influence of dicumyl peroxide and phenyl-β-naphthylamine on the thermal properties of the isobutylene polymers investigated in this work.

Isobutylene copolymers containing low amounts of dienes, isoprene or butadiene are used to manufacture rubber goods stable to the action of heat. The thermal properties of homo- and copolymers of isobutylene have been the subject of several publications reporting the results of studies carried out by DSC, DTA, GC and MS methods [1–5]. The predominant view is that thermal changes start from polymer backbone cleavage and that monomer or oligomers are then detached from the freshly produced macroradicals.

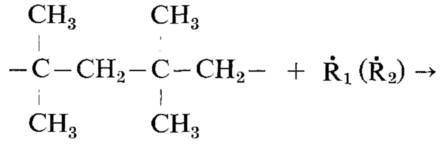
Thermal degradation of polyisobutylene:



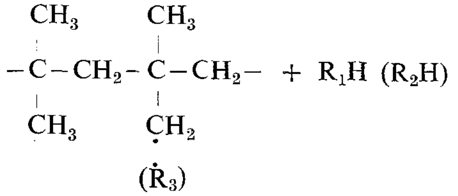
$$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}- \rightarrow -\overset{\mathrm{CH_3}}{\underset{\underset{(\mathrm{R_1})}{\mathrm{CH_3}}}{\mathrm{C}}}-\dot{\mathrm{C}}\mathrm{H_2} + {}^{\cdot}\overset{\mathrm{CH_3}}{\underset{\underset{(\mathrm{R_2})}{\mathrm{CH_3}}}{\mathrm{C}}}-\mathrm{CH_2}- \qquad (1)$$



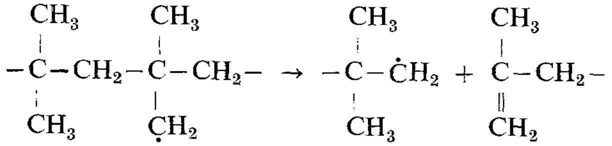
$$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\dot{\mathrm{C}}\mathrm{H_2} + {}^{\cdot}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}- \rightarrow -\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3} + \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}=\mathrm{CH}- \qquad (2)$$



$$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}- + \dot{\mathrm{R}}_1\,(\dot{\mathrm{R}}_2) \rightarrow$$

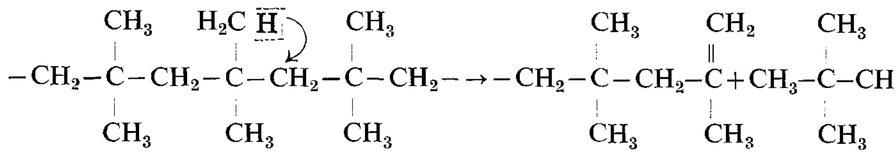


$$-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{\underset{(\dot{R}_3)}{\dot{C}H_2}}{\overset{CH_3}{C}}-CH_2- + R_1H\ (R_2H) \qquad (3)$$



$$-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{\dot{C}H_2}{\overset{CH_3}{C}}-CH_2- \rightarrow -\underset{CH_3}{\overset{CH_3}{C}}-\dot{C}H_2 + \underset{\overset{\|}{CH_2}}{\overset{CH_3}{C}}-CH_2- \qquad (4)$$

According to some authors, polyisobutylene degradation proceeds via hydrogen atom transfer [2]:



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{H_2C\,H}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2- \rightarrow -CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{\overset{CH_2}{\|}}{C}}+CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2- \qquad (5)$$

The thermal stability of this group of polymers in air which is of practical importance, has not been considered as yet. They have been assumed to be not susceptible to reaction with oxygen, though it is known that they are readily degraded on the action of peroxides [6]. We have come to the conclusion that the low concentration of α-methylene hydrogen atoms which are at the homopolymer chain ends, and which in the case of copolymers are also built in the backbone, may turn out to be sufficient for hydroperoxide formation and initiation of thermooxidative degradation. We have resolved to verify the hypothesis experimentally.

Experimental

Polyisobutylenes and copolymers of isobutylene and isoprene with various molecular weights and comonomer contents formed the subjects of our studies. Polyisoprene in the form of natural rubber was also used, for the purpose of comparison (Table 1).

The thermal properties of the polyisobutylenes were determined with a Paulik, Paulik – Erdey system Derivatograph and a Du Pont analyser, model 990. The analysis was performed under standard conditions within the range of temperature up to 1073 K, using Al_2O_3 as a standard substance. The temperatures of the onset, maximum and end of the first transition were determined in the manner illustrated in Fig. 1. To obtain data indispensable for the interpretation of thermal curves, we used complementary methods, namely elemental analysis, I.R. spectroscopy,

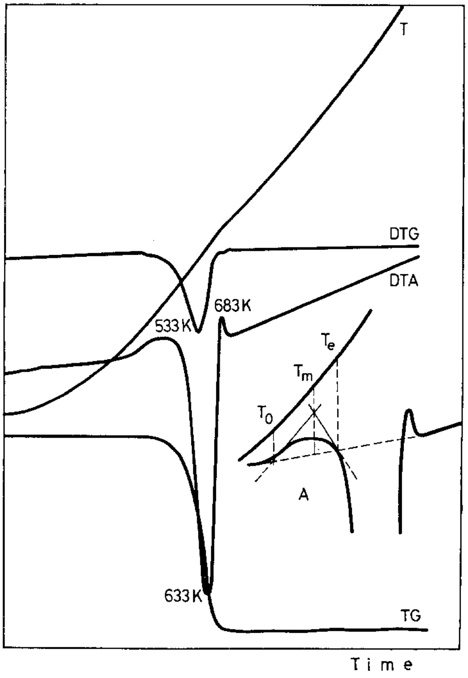


Fig. 1. Thermal curves of polyisobutylene Oppanol 100 in air atmosphere A — the method of the transition temperature evaluation, T_0, T_m, T_e — temperature values of the onset, maximum and end of the transition

Table 1

Properties of polyisobutylenes [1—3], copolymers of isobutylene and isoprene [4—6], and natural rubber [7]

	Name	Producer	M_v^1	Unsaturation[2] %
1	Oppanol B-200	BASF	2 726 000	—
2	Oppanol B-100	BASF	984 000	—
3	Polyisobutylene	Poland	28 300	—
4	Esso Butyl 035	ESSO	215 000	0.6—1.0
5	Esso Butyl 218	ESSO	462 000	1.5—2.0
6	Esso Butyl 325	ESSO	297 200	2.0 - 2.5
7	Natural rubber RSS I	Malaysia	416 000	100

[1] our own investigations
[2] data of producer

molecular weight measurements, and peroxide group concentration measurements. Molecular weight was determined using a Ubbelohde viscometer, with toluene as solvent. The temperature of measurements was 303 ± 0.5 K. The intrinsic viscosity values were reproducible within $\pm 3\%$ of the mean value. Because the viscosity – molecular weight relationship for polyisobutylene is virtually identical with that for Butyl rubber [7], the same values of constants K and α were used for all examined polymers [8–10].

The mixtures of polymers with dicumyl peroxide or phenyl-β-naphthylamine were made in the N50 mixer of a Plasti-Corder apparatus at 330 K, during 180 s. The degradation of the investigated elastomers under these conditions was negligible.

Peroxide group content was determined by the Mair-Graupner method [11].

Results and discussion

On the heating of polyisobutylenes over 450 K, chemical changes are revealed. Figure 1 shows thermal curves of Oppanol B-100 in air atmosphere, and Fig. 2 shows DSC and DTA curves in an inert atmosphere. Three distinct changes are observed in the curves of all the investigated homo- and copolymers of isobutylene (Table 2).

The changes taking place above 590 K are connected with total polymer decomposition. The negative thermal effect and mass loss of the sample during the second change indicate that this is a thermal destruction, with the energy being used primarily for covalent bond cleavage. The products formed do not undergo oxidation or combustion to any appreciable extent, since the rate of oxygen diffusion into the sample is insufficient. The third exothermic peak seen in the DTA curves is a sign of the combustion of the small permanent residue, consisting mainly of carbon, from the completed polymer destruction.

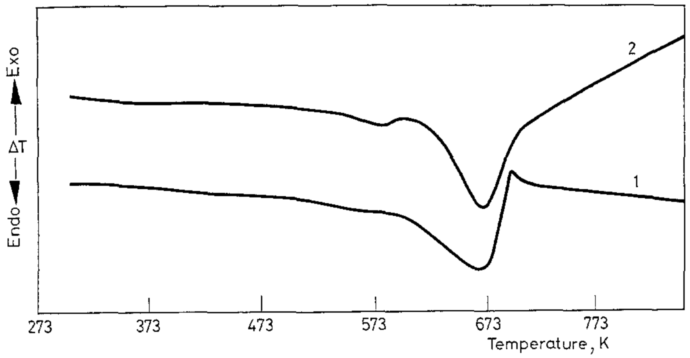


Fig. 2. DSC(1) and DTA(2) curves of polyisobutylene Oppanol B-100, in inert atmosphere

Table 2

Thermal transition of the investigated polymers in air atmosphere

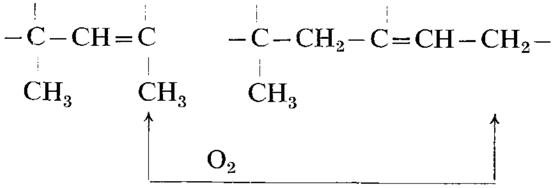
	Temperature of the peak, K		Transition	Loss of mass
	start	maximum		
1	450	520 – 550	exothermic	about 5 %
2	590	620 - 640	endothermic	over 80 %
3	670	680 – 710	exothermic	nearly 100 %

Of particular interest from the practical point of view is the first change, starting at 450 – 470 K, and most attention was therefore paid to this change. We found that the change is connected with a considerable drop in molecular weight and a small mass loss of the sample, amounting to 5%. At the same time the polymer retains its elastic properties; the thermal effect to the change in air is low (about 110 kJ/g) and positive.

This change can thus be qualified as degradation, accompanied by side-reaction. The changes in molecular weight due to the heating of polyisobutylene and isobutylene copolymers to the temperature of the first transition in air and inert gas are shown in Table 3. We found a positive relationship between the degree of degradation and the molecular weight of the polyisobutylene. This was not an unexpected result, taking into account that the probability of chain cleavage grows as the number of mers increases.

The degradation of both homo- and copolymers proceeds to a much higher extent in air than in argon, which demonstrates the participation of oxygen in this reaction.

Our studies showed that homo- and copolymers of isobutylene contain peroxide groups before as well as after heating. The peroxide concentration was inversely proportional to the molecular weight of the polyisobutylene and was distincly dependent on the number of isoprene mers in the macromolecule. This leads to the conclusion that oxygen reacts with the following groups:



$$-\underset{CH_3}{\overset{CH_3}{C}}-CH=\underset{CH_3}{\overset{CH_3}{C}} \qquad -\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH-CH_2- \qquad (6)$$

The results of measurements of the peroxide group content in homopolymers of isobutylene and its copolymers with isoprene are given in Table 4.

For the purpose of comparison we determined the concentration of peroxides in natural rubber, and, as was expected, this was found to be higher.

Table 3

Changes in molecular weight due to the heating of polyisobutylene and isobutylene

	Polyiso-		
	Liquid polyisobutylene		
	a	*b*	*c*
Viscosity-average molecular weight, M_v	28 300	24 950	26 140
Degree of degradation, p	—	1.13	1.08

	Isobutylene-isoprene		
	Esso Butyl 035		
Viscosity-average molecular weight, M_v	215 000	100 300	126 000
Degree of degradation, p	—	2.14	1.71

$$p = \frac{a}{b} \text{ or } \frac{a}{c}$$

a — unheated samples
b — samples heated to the temperature of the first transition in air in furnace of deri-
c — samples heated to the temperature of the first transition in inert gas in furnace of

Table 4

Peroxide group contents of homopolymers of isobutylene, its copolymers with isoprene, and natural rubber

Polymer	$\frac{\text{mole —OOH}}{\text{monomeric unit mole of elastomer}}$	
	unheated polymer	polymer heated to temperature of first transition
Oppanol B-100	0.0476	0.0127
Oppanol B-200	0.0174	0.0161
Esso Butyl 035	0.0245	0.0189
Esso Butyl 218	0.0260	0.0160
Esso Butyl 325	0.0562	0.0169
Natural rubber RSS-I	0.1436	0.0257

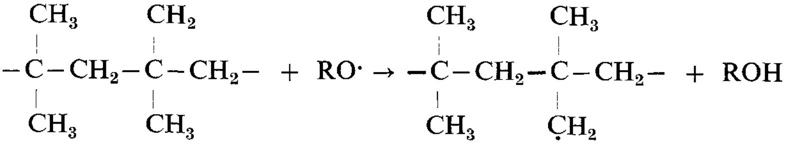
Heating of polymers to the temperature of the first exothermic transition recorded in the thermal curves caused the peroxide concentration to drop. Decomposition of the peroxide should bring about degradation. We anticipated the mechanism of this reaction to be as follows:

copolymers to the temperature of the first transition in air and inert gas

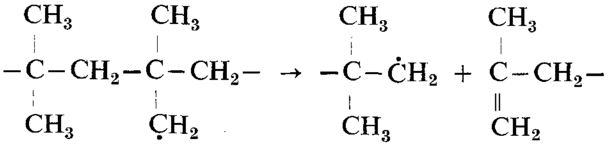
butylenes					
Oppanol B-100			Oppanol B-200		
a	*b*	*c*	*a*	*b*	*c*
984 000	490 000	792 000	2 726 000	1 012 000	1 127 000
—	2.01	1.34	—	2.69	2.42
copolymers					
Esso Butyl 218			Esso Butyl 325		
462 400	182 400	215 000	297 200	135 900	226 900
—	2.54	2.15	—	2.19	1.31

vatograph
derivatograph

$$\mathrm{ROOR} \longrightarrow 2\,\mathrm{RO}^{\bullet} \qquad (7)$$



$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_2}{\underset{CH_3}{C}}-CH_2- + RO^{\bullet} \rightarrow -\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{\dot{C}H_2}{C}}-CH_2- + ROH \qquad (8)$$



$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{\dot{C}H_2}{C}}-CH_2- \rightarrow -\overset{CH_3}{\underset{CH_3}{C}}-\dot{C}H_2 + \overset{CH_3}{\underset{\|\atop CH_2}{C}}-CH_2- \qquad (9)$$

However, because of the low concentration of peroxide groups in polyisobutylenes, it was difficult to obtain more details on the mechanism of their action. In view of this situation, we decided to examine the effect of cumyl peroxide on the degradation of the polymers under investigation.

Table 5 shows the changes in molecular weight of homo- and copolymers of isobutylene heated to the temperature of the first transition in the presence of dicumyl peroxide. The results in Table 5 confirm that dicumyl peroxide causes a stronger degradation, the higher the molecular weight of the polymer. This phenomenon

Table 5

Changes in molecular weight of homo- and copolymers of isobutylene heated to the
of dicumyl

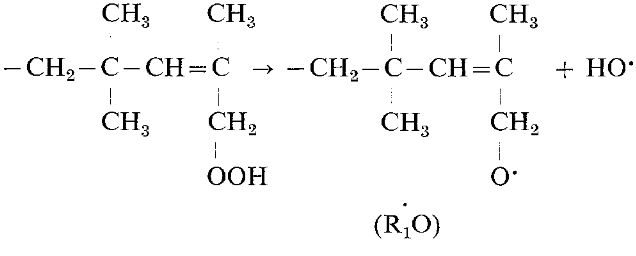
	Polyiso-		
	Liquid polyisobutylene		
	a	*b*	*d*
Viscosity-average molecular weight, M_v	28 300	24 950	20 100
Degree of degradation, *p*	—	1.13	1.41
	Isobutylene — isoprene		
	Esso Butyl 035		
Viscosity-average molecular weight, M_v	215 000	100 300	90 900
Degree of degradation, *p*	—	2.14	2.36

$p = \frac{a}{b}$ or $\frac{a}{d}$

a — unheated samples
b — samples heated to the temperature of the first transition in air in furnace of deri-
d — samples heated to the temperature of the first transition in air in furnace of derivato-

is a sign of the higher probability of longer chain cleavage. The considerably lower extent of degradation in the case of the copolymers is caused by chain branching. Our results testify that, in spite of the low degree of unsaturation of polyisobutylene and copolymers of isobutylene and dienes, the role of oxygen in the mechanism of their degradation is significant and should not be neglected. Initiation of thermooxidative degradation of the peroxide group may take place due to decomposition of the peroxide groups in the polymer or cleavage of the polymer backbone. The participation of oxidative processes is controlled by oxygen diffusion.

Thermooxidative degradation of polyisobutylene:



$$\begin{array}{ccccccc} & CH_3 & CH_3 & & CH_3 & CH_3 & \\ -CH_2- & C-CH= & C & \rightarrow -CH_2- & C-CH= & C & + HO^{\bullet} \\ & CH_3 & CH_2 & & CH_3 & CH_2 & \\ & & OOH & & & O^{\bullet} & \\ & & & & (R_1\dot{O}) & & \end{array} \qquad (10)$$

temperature of the first transition in the presence of cumyl peroxide. Concentration of peroxide 1 mmole/100 g polymer

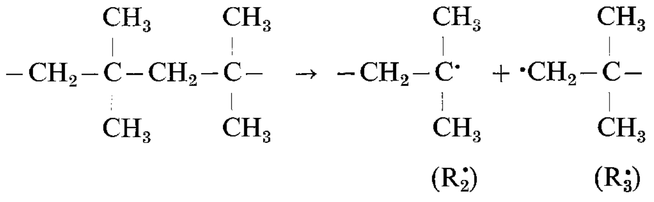
butylenes

Oppanol B-100			Oppanol B-200		
a	*b*	*d*	*a*	*b*	*d*
984 000	490 000	69 230	2 726 000	1 012 000	136 000
—	2.01	14.21	—	2.69	20.04

copolymers

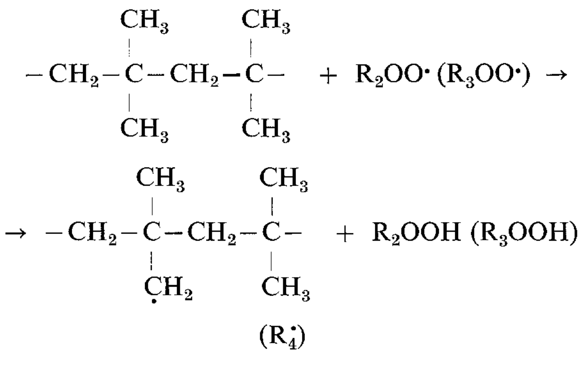
Esso Butyl 218			Esso Butyl 325		
462 400	182 400	118 000	297 200	135 900	100 800
—	2.54	3.92	—	2.19	2.95

vatograph
graph in the presence of cumyl peroxide.



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}- \rightarrow \underset{(R_2^\bullet)}{-CH_2-\underset{CH_3}{\overset{CH_3}{C^\bullet}}} + \underset{(R_3^\bullet)}{{}^\bullet CH_2-\underset{CH_3}{\overset{CH_3}{C}}-} \quad (11)$$

$$R_2^\bullet(R_3^\bullet) + O_2 \rightarrow R_2OO^\bullet\ (R_3OO^\bullet) \quad (12)$$



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}- + R_2OO^\bullet(R_3OO^\bullet) \rightarrow$$

$$\rightarrow -CH_2-\underset{\underset{\bullet}{C}H_2}{\overset{CH_3}{C}}-CH_2-\underset{\underset{(R_4^\bullet)}{CH_3}}{\overset{CH_3}{C}}- + R_2OOH\ (R_3OOH) \quad (13)$$

Table 6

Percentage distribution of volatile products of polyisobutylene and isobutylene-isoprene copolymers, calculated on basis of $m/e = 57$

	m/e ratio and nature of hydrocarbon					
	39 allene	41 propylene	55 isobutane	67 isoprene	83 hexane	together
Oppanol B-200	40.72	28.42	25.66	1.51	2.92	99.23
Esso Butyl 035	4.74	19.27	18.50	2.49	6.47	51.47
Esso Butyl 325	9.53	31.49	28.74	6.57	9.66	85.99

Table 7

Activation energies of destruction of polyisobutylene and isobutylene—isoprene copolymers

Polymer	E, kJ/mole	
	in air	in inert gas
Liquid polyisobutylene	73.3[1]	—
Oppanol B-100	84.6[1] 95.5[2]	154.1[2]
Oppanol B-200	96.2[1]	—
Esso Butyl 035	123.5[1]	—
Esso Butyl 218	125.2[1]	—
Esso Butyl 325	105.1[1] 108.0[2]	221.1[2]

[1] Calculation made with data obtained with derivatograph

[2] Calculation made with data obtained with Du Pont 990 analyser

Table 8

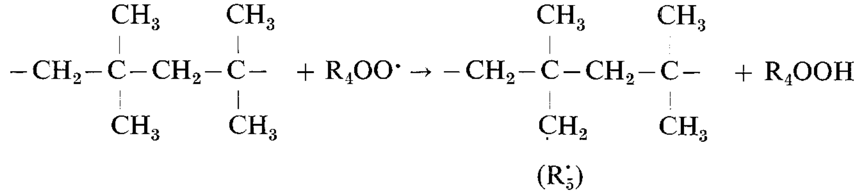
Changes in the molecular weights of isobutylene-isoprene copolymers heated to

	Esso Butyl 035		
	a	b	e
Viscosity-average molecular weight, M_v	215 000	100 300	203 200
Degree of degradation, p	—	2.14	1.06

$$p = \frac{a}{b} \text{ or } \frac{a}{e}$$

a — unheated samples
b — samples heated to the temperature of the first transition in air in furnace of deri-
e — samples heated to the temperature of the first transition in air in furnace of derivato-

$$R_4^{\bullet} + O_2 \rightarrow R_4OO^{\bullet} \qquad (14)$$



$$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}- + R_4OO^{\bullet} \rightarrow -CH_2-\overset{CH_3}{\underset{\underset{(R_5^{\bullet})}{\dot{C}H_2}}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}- + R_4OOH \qquad (15)$$

$$R_5^{\bullet} \rightarrow R_6^{=} + R_1^{\bullet} \qquad (16)$$

$$R_xOOH \rightarrow R_xO^{\bullet} + {}^{\bullet}OH \qquad (17)$$

$$R_xOOH + R_yOOH \rightarrow R_xO^{\bullet} + R_y^{\bullet} + O_2 + H_2O\,. \qquad (18)$$

The heating of homopolymers of isobutylene and its copolymers with isoprene to the temperature of the first transition causes not only chain cleavage, but also a small mass loss. The degradation is consequently accompanied by side-reactions. It is evident from the literature that on the heating of polyisobutylene, the monomer and its oligomers are liberated. However, in previous studies polyisobutylene was subjected to deep destruction at a high temperature. Under such conditions the concentration of the monomer and its oligomers is high. But it is not clear what products are liberated at the temperature of the first transition. Therefore, using mass spectroscopy, we examined the products formed on the heating of homo- and copolymers of isobutylene to the temperature of the first transition. Microsamples were placed in the pyrolytic head of a chromatograph coupled with a mass spectrometer. The results are given in Table 6. It turned out that most of the volatile products are low-molecular weight hydrocarbons, mainly butene and unsaturated hydrocarbons. In the case of the copolymers, the products contain somewhat more isoprene (Table 6).

the temperature of the first transition in the presence of phenyl-β-naphtylamine

Esso Butyl 218			Esso Butyl 325		
a	*b*	*e*	*a*	*b*	*e*
462 400	182 400	260 500	297 200	135 900	230 900
—	2.54	1.64	—	2.19	1.29

vatograph
graph in the presence of phenyl-β-naphthylamine.

From the thermogravimetric data, we calculated the activation energies of destruction of polyisobutylene and copolymers of isobutylene and isoprene, with the Freeman-Carrol method [12]. The calculation results are given in Table 7. Comparison of the data obtained with the same apparatus, the derivatograph, suggests the existence of some regularity, for the activation energy of destruction increases with the increase in molecular weight of the homopolymers.

The activation energies of isobutylene-isoprene copolymers are higher than those of polyisobutylenes. However, the effect of oxygen is more distinct, in inert gas the activation energy of destruction is higher by 59 kJ/mole for the homopolymer and by 113 kJ/mole for the copolymer.

We also examined the effects of antioxidants on the thermooxidative degradation of polyisobutylene.

Table 8 gives, as an instance, changes in the molecular weights of isobutylene-isoprene copolymers heated to the temperature of the first transition in the presence of phenyl-β-naphthylamine.

It is evident from the data that phenyl-β-naphthylamine exhibits a clear protective action, which confirms our hypothesis on the significant part oxygen plays in the thermal degradation of the polymers under investigation.

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Résumé — On a étudié les propriétés thermiques des copolymères polyisobutylène et isobutylène-isoprène. On a interprété les courbes thermiques en considérant des données supplémentaires. On a établi que la dégradation tant des homo- que des copolymères s'effectue d'une manière beaucoup plus importante dans l'air que dans l'argon. Nos résultats montrent que la formation du peroxyde joue un rôle important sur la dégradation de ce groupe de polymères.

Cette conclusion est en bon accord avec l'influence du peroxyde de dicumyle et de la phényl-β-naphtylamine sur les propriétés thermiques des polymères d'isobutylène étudiés dans notre travail.

Zusammenfassung — Die thermischen Eigenschaften von Polyisobutylen- und Isobutylen-Isopren-Kopolymeren wurden untersucht. Die thermischen Kurven wurden unter Berücksichtigung ergänzender Angaben gedeutet. Es wurde festgestellt, dass die Zersetzung sowohl von Homo- als auch von Kopolymeren in Luft in einem viel grösseren Ausmass verläuft, als in Argon. Aus den Ergebnissen folgt, dass die Peroxidbildung bei der Zersetzung dieser Gruppe von Polymeren eine bedeutende Rolle spielt.

Diese Aussage ist in guter Übereinstimmung mit dem Einfluss von Dicumylperoxid und Phenyl-β naphthylamin auf die thermischen Eigenschaften der untersuchten Isobutylenpolymere.

Резюме — Изучены термические свойства полиизобутилена и изобутилен-изопрен сополимеров. Термические кривые интерпретированы на основе дополнительных данных. Установлено, что распад полимеров и сополимеров протекает гораздо в большей степени на воздухе, чем в атмосфере аргона. Из результатов исследования вытекает, что образование перекисей играет значительную роль в деструкции этой группы полимеров. Этот вывод хорошо согласуется с влиянием перекиси дикумила и фенил-β-нафтиламина на термические свойства исследованных полимеров изобутилена.