und mögliche Quellen der erhaltenen Unterschiede werden diskutiert. Es wird betrachtet, dass intern selbst-übereinstimmende Abschätzungen des Querbindungsgrades von natürlichen Kautschuk-Vulkanisaten mittels der entwickelten Methoden erhalten werden können.

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Determination of Degree of Crosslinking in Natural Rubber Vulcanizates. Part II

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I. INTRODUCTION

The physical properties of rubber vulcanizates are markedly dependent on the degree of crosslinking. According to the network-statistical theory of rubber elasticity, the general validity of which has been extensively confirmed, the work of deformation per unit volume, W, is given by:

$$W = {}^1/_2\, \rho RTM_c^{-1}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (1)$$

where M_c is the average molecular weight between crosslinks, ρ is the density of the rubber, and λ_1, λ_2, λ_3 are the ratios of stretched to unstretched lengths along the three space coordinates.[1] From this fundamental expression, stress–strain relationships for chosen deformations can be obtained, in particular equation (1) of Part I[2] for simple extension. Both for determining the efficiencies of crosslinking agents and for testing the absolute validity of statistical theory predictions it is clearly necessary to have an independent evaluation of M_c by chemical determination of the degree of crosslinking.

The chemistry of conventional vulcanization processes using sulfur is too complex for reliable determinations of crosslinking to be obtained by chemical means.[3] Recent methods employed to determine degree of crosslinking include: (*1*) chemical evaluations from crosslinking methods using bifunctional agents,[4] and (*2*) independent physical evaluations from sol–gel theory.[5,6] The former method is clearly more absolute and in the only crosslinking process investigated—intermolecular coupling with disazodicarboxylates, good agreement was apparently obtained between statistical theory predictions and the absolute degree of crosslinking.[4]

However, in the application of this method certain deficiencies are apparent. In particular it was assumed that each molecule of disazodicarboxylate combined introduced one crosslink,[4] this assumption being based on the chemistry of interaction of a monofunctional azodicarboxylate with a simple monoolefin.[7] No experimental verification of this assumption was attempted in the case of the crosslinking reaction and thus the uncertainty remains of the extent to which disazodicarboxylates produce crosslinks quantitatively. It was also appreciated that the physical properties of the vulcanizate may be affected at high degrees of crosslinking by the size and polar nature of the crosslinks.[4]

In the present work, chemical determinations of crosslinking have been obtained for the crosslinking of natural rubber by di-*tert*-butyl peroxide. The decomposition of this peroxide in the vapor phase,[8] and in solution,[9] and its reaction with monoolefins,[10] polyisoprenes, and natural rubber[11] have been previously investigated in detail. In the presence of rubber, di-*tert*-butyl peroxide undergoes unimolecular decomposition to two *tert*-butoxy radicals (R.1), which then react either (*a*) by abstracting α-methylenic hydrogen atoms from rubber (RH) forming *tert*-butanol and a polyisoprenyl radical (R·) (R.2), or (*b*) by decomposing to give acetone and methyl radicals (R.3). The latter may also abstract α-methylenic hydrogen atoms from the rubber (R.4) or dimerize to give ethane (R.5). The polyisoprenyl radicals R· undergo combination (R.6), and by a repetition of such processes finally produce a crosslinked rubber hydrocarbon network consisting solely of C—C crosslinks and being devoid of the crosslinking agent:

$$(CH_3)_3C{-}O{-}O{-}C(CH_3)_3 \longrightarrow 2\,(CH_3)_3C{-}O\cdot \qquad \text{(R.1)}$$

$$(CH_3)_3C{-}O\cdot + RH \longrightarrow (CH_3)_3C{-}OH + R\cdot \qquad \text{(R.2)}$$

$$(CH_3)_3C{-}O\cdot \longrightarrow (CH_3)_2C{=}O + CH_3\cdot \qquad \text{(R.3)}$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \qquad \text{(R.4)}$$

$$2\,CH_3\cdot \longrightarrow C_2H_6 \qquad \text{(R.5)}$$

$$2\,R\cdot \longrightarrow R{-}R \qquad \text{(R.6)}$$

If the assumption is made that the only fate of the polyisoprenyl radicals (R·) is the combination reaction (R.6) then the number of crosslinks in the vulcanizate is equal to $^1/_2$ (no. of molecules of *tert*-butanol plus methane) formed. Thus chemical determinations of the degree of crosslinking are readily obtained from the amounts of *tert*-butanol and methane formed during the vulcanization process. The extent to which this basic assumption is valid is considered in the discussion section.

II. EXPERIMENTAL METHODS AND MATERIALS

Materials. *Di-tert-butyl peroxide:* The commercial peroxide (Laporte) was extracted with 10% aqueous sodium hydroxide, washed with water, dried ($CaCl_2$), and fractionated under reduced pressure to give the pure peroxide, b.p. 64.9–65.2°/159 mm., n_D^{20} 1.3890. Infrared spectroscopic analysis confirmed the purity of the peroxide and showed the absence of carbonyl and hydroxyl groups.

tert-Butanol was carefully fractionated, b.p. 81.1°/742 mm. to 81.9°/755 mm. Acetone and carbon tetrachloride were of A.R. grade. *n*-Decane (B.D.H.) was used without further purification.

Natural rubber: The rubber was deproteinized pale crepe (kindly supplied by Dr. G. J. van der Bie of Indonesian Rubber Research Institute (J.P.P. Karet)); *found:* N, 0.09%; $[\eta]$, 5.1 (g./100 ml.)$^{-1}$, gel < 1%. This material was slightly degraded on a warm mill, sheeted out to a thickness of *ca.* 2–3 mm., and dried by heating *in vacuo* at 80° for 5–11 days, the water and other volatile materials being collected in a side-arm tube cooled in liquid air. The viscosity data of the rubber samples, obtained in benzene at 25° using a B.S.S. grade 1 viscometer, are given in Table I. The drying process leads to rubbers having increased $[\eta]$ and Huggins' constant k', but no gel component. Heating the dried rubber under the severest conditions used in the subsequent vulcanization reaction (24 hours at 140°) further increased $[\eta]$ and k', but again no gel was produced. The most probable cause of the increase in $[\eta]$ and k' on drying and heating is a small amount of branching,[12] which may be neglected as compared with the degree of crosslinking subsequently produced by the di-*tert*-butyl peroxide. The number-average molecular weights of the milled rubber samples were determined from $[\eta]$ values using an empirical relationship between $[\eta]$ and osmotic molecular weight found to apply for masticated natural rubber.[13]

TABLE I

VISCOSITY AND MOLECULAR WEIGHT DATA OF NATURAL RUBBER

Rubber type[a]	Milled D.P. Crepe				
	1	2	3	4	5
$[\eta]$ (g./100 ml.)$^{-1}$	2.25	2.46	2.49	2.45	2.29
k'	—	0.44	0.46	0.43	0.44
$\bar{M}_n$ ($\times 10^{-5}$)	2.37	2.62	2.66	2.60	2.43

Rubber type[a]	Dried, Milled D.P. Crepe						
	1[b]	2[c]	3	4	5	A[d]	B[d]
$[\eta]$ (g./100 ml.)$^{-1}$	2.46	2.79	2.87	2.85	2.51	2.64	3.02
k'	0.58	0.52	0.62	0.61	0.54	0.62	0.58

[a] k' values are obtained from the Huggins equation: $\eta_{sp}/c = [\eta] + k'[\eta]^2c$.
[b] *Found:* O, 0.45–0.55%; N, 0.09, 0.10%.
[c] *Found:* O, 0.42, 0.46%; N, 0.10, 0.11%.
[d] A and B were dried, milled D.P. crepe, samples 1 and 2, respectively, which had been heated *in vacuo* for 24 hr. at 140° and 24 hr. at 80°.

Chemical Determination of Degree of Crosslinking

Determination of tert-Butanol, Acetone, and Di-tert-Butyl Peroxide (by Dr. E. S. Waight and Mr. G. Higgins). Quantitative analysis of mixtures of the three compounds in carbon tetrachloride solution was made by an infrared spectrometric method (*cf.* Raley *et al.*[9]). Using a single-beam spectrometer equipped with rock salt and lithium fluoride prisms, calibration curves relating optical density of a characteristic band to the concentration of the solute (in g./100 g. of carbon tetrachloride) were set up for each compound separately. The bands used were at 3600 cm.$^{-1}$ for *tert*-butanol, 1718 cm.$^{-1}$ for acetone, and 873 cm.$^{-1}$ for di-*tert*-butyl peroxide. The calibration curves were subsequently shown to be applicable to mixtures of the three compounds. In the concentration ranges examined (*tert*-butanol 0.01–0.7 g./100 g. CCl_4; acetone 0.002–0.35 g./100 g. CCl_4 di-*tert*-butyl peroxide 0.1–1.5 g./100 g. CCl_4) no evidence of interference from overlapping bands and association between components was indicated. Determinations of the concentrations of the compounds in standard solutions indicated that the accuracy of the method was better than ±2% for *tert*-butanol and acetone and better than ±5% for the peroxide. Typical analyses of standard solutions are given in Table II.

TABLE II

ANALYSIS OF MIXTURES OF *tert*-BUTANOL, ACETONE, AND DI-*tert*-BUTYL PEROXIDE

Concn. of solute (g./100 g. CCl_4)	$[\overset{t}{\mathrm{Bu}}\text{-OH}]$	$[\mathrm{Me_2C{=}O}]$	$[\overset{t}{\mathrm{Bu}}\text{-OO}\overset{t}{\mathrm{Bu}}\text{-}]$
1: Original	0.2988	0.0494	0.1456
Found by I.R. analysis	0.297 (99.4%)	0.0488 (98.8%)	0.153 (105%)
2: Original	0.1070	0.0669	0.1324
Found by I.R. Analysis	0.106 (99.0%)	0.0675 (100.9%)	0.136 (102.7%)

Determination of Methane and Ethane. Methane and ethane were separated by low temperature distillation in the apparatus shown in Figure 4. The pressures exerted when enclosed in a calibrated volume V at a given temperature then provided their molar quantities. Trials with pure methane and ethane showed this method to be satisfactory. Details of the technique used are given in the next section.

Vulcanization Technique and Analysis of Products. A weighed amount (usually 5.00 g.) of the dried, milled, D.P. crepe rubber was introduced as small strips into the tube A of Figure 1 and pumped out overnight at $<10^{-5}$ mm. Hg pressure. The tap B was closed and a known weight (*ca.* 0.1 g.) of di-*tert*-butyl peroxide contained in the capillary tube C was connected to the vacuum manifold and frozen in liquid oxygen and the apparatus evacuated through tap D. Tap D was closed, tap B opened and the peroxide transferred to A by cooling the latter in liquid oxygen and gently warming the peroxide in C. With A cooled in liquid oxygen, the apparatus was re-evacuated to $<10^{-5}$ mm. Hg and A sealed off at E. The rubber was allowed to imbibe the peroxide for at least 16 hours at room temperature and vulcanization was then effected in the temperature range 110 to 140°.

After vulcanization, tube A was attached to the apparatus of Figure 2 and to the gas-analysis apparatus of Figure 4, and the peroxide decomposition products analyzed for methane and ethane as follows. Tube A was cooled to −78° for 1 hour while the rest of the apparatus was evacuated to $<10^{-4}$ mm. Hg. The seal at F was broken and the gaseous products transferred to the spiral S of Figure 4 during 30 min. by cooling the latter in liquid oxygen. The tap G of Figure 2 was closed and the rubber warmed to room temperature for further degassing of the ethane fraction. The methane fraction in S was, meanwhile, transported by the Töpler pump to the known volume V and its pressure measured. The volume V was then evacuated in readiness for determination of the ethane fraction. The rubber was recooled to −78° for 1 hour and ethane distilled during 30 min. into the spiral S cooled in liquid oxygen. This process was repeated twice more, after which the tap G was closed, the spiral S warmed to −78° and the ethane transferred to the known volume V. Finally the tube A was cooled in liquid oxygen and the total voltatile products (except methane) recondensed into A before sealing off at H.

(In earlier experiments the ethane was determined after only one distillation from the rubber (bracketed values in Table III) and under these conditions only 75–80% of the total ethane formed was accounted for. For the present purposes, the ethane determination is relatively unimportant, it being required only to correlate the yields of methane and ethane with the amount of acetone formed.)

The total volatile products in A were transferred to the tube I of Figure 2 by heating the rubber for 24 hours at 80° while tube I was cooled in liquid oxygen. The peroxide decomposition products were isolated from the rubber by sealing off at J, and then transferred to a known weight of carbon tetrachloride contained in tube M of Figure 3 as follows. The carbon tetrachloride was frozen in liquid oxygen, the apparatus evacuated through taps K and L and then with tap K closed the seal at N was broken and the contents of I rapidly distilled into M, which was finally sealed off under nitrogen at *ca.* 700 mm. Hg. The carbon tetrachloride solution was analyzed for *tert*-butanol, acetone, and di-*tert*-butyl peroxide by the infrared spectrometric method. In control experiments, with known amounts of the three components, the above technique gave high recoveries of all three components. Particular attention was paid to the percentage recovery of *tert*-butanol, and in three repeat experiments the following values were found: 97.0, 98.8, 101.1% recovery. *tert*-Butanol could also be recovered quantitatively after being heated at 140° for 24 hours in the presence of rubber (found: 98.4, 100.7% recovery), indicating the thermal stability of this compound at 140° in the rubber environment. The adequacy of the technique for the quantitative recovery and analysis of the three compounds is confirmed by the good agreement which is found between peroxide input and peroxide accounted for as *tert*-butanol, acetone, and unreacted peroxide (Table III). The slight lack of reactant:product balance when the peroxide is virtually completely decomposed may be indicative of side reactions becoming significant after extensive reaction periods. The details of vulcanization conditions and the analytical data are given in Table III.

Identification of the Peroxide Decomposition Products. (a) Liquid Products. A sample of rubber (5.00 g.) was heated with the peroxide (0.1067 g.) *in vacuo* for 72 hours at 140°. Infrared spectroscopic analysis of the total volatile products revealed the presence of *tert*-butanol and acetone, and the absence of peroxide, other oxygenated compounds, and unsaturated compounds.

(b) Gaseous Products. The gaseous products from the reaction of rubber (50 g.) with peroxide (2.0 g.) *in vacuo* for 26 hours at 140° were separated into methane and ethane fractions as described above. Mass-spectro-

TABLE III. VULCANIZATION CONDITIONS, PRODUCT ANALYSIS AND CHEMICAL AND PHYSICAL DETERMINATION OF CROSSLINKING

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Initial $\overline{M}_n$ ($\times 10^{-5}$) of rubber	2.60	2.37	2.37	2.60	2.60	2.60	2.60	2.60	2.43	2.37	2.37	2.37	2.37	2.62	2.37	2.37	2.62	2.66
Temp. °C. (±0.1°C.)	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140
Time (hr.)	1.0	1.0	1.0	1.0	1.25	1.5	1.5	1.75	1.75	2.0	2.0	3.75	3.75	6.0	24.0	24.0	72.0	72.0
Moles peroxide/g. rubber ($\times 10^4$)	1.49	1.50	1.46	1.59	1.47$_5$	1.44	1.44$_5$	1.51	1.46	1.46	1.45	1.45	1.43	1.45$_5$	1.57	1.81	1.50$_5$	2.18
Product analysis, moles/g. rubber ($\times 10^5$)																		
tert-Butanol	3.10	3.28	3.31	3.44	3.78	4.62	4.70	5.50	5.53	6.11	6.25	9.75	9.75	14.0	20.7	22.8	20.9	25.3
Acetone	1.21	1.36	1.21	1.54	1.65	1.73	1.80	2.19	2.13	2.26	2.11	3.36	3.55	4.95	7.95	9.65	7.03	14.2
Peroxide (unreacted)	12.7	12.8	12.4	13.4	11.6	10.8	10.8	10.6	10.2	10.0	10.2	7.60	6.60	5.05	—	—	—	—
Methane	0.128	0.139	0.137	0.132	0.143	0.232	0.214	0.205	0.212	0.227	0.211	0.430	0.446	0.778	1.94	2.72	1.72	3.60
Ethane	0.510	(0.47)	(0.40)	(0.494)	0.732	0.744	0.632	1.01	0.967	(0.87)	(0.76)	(1.05)	(1.22)	(1.52)	(2.30)	(3.06)	(2.19)	5.05
% initial peroxide accounted for[a]	99.4	100.6	100.4	99.6	96.8	96.6	97.4	95.7	96.0	97.6	99.3	97.5	92.7	99.7	91.0	89.6	92.6	90.3
Swelling data																		
v_r	0.214	0.199	0.194	0.219	0.227	0.240	0.241	0.252	0.246	0.248	0.249	0.293	0.294	0.333	0.378	0.396	0.384	0.424
v_r, corrected	0.246	0.237	0.233	0.250	0.258	0.268	0.269	0.278	0.274	0.276	0.278	0.315	0.316	0.350	0.393	0.409	0.397	0.436
Degree of crosslinking																		
Chem. detn. of $1/2\ M_c$ ($\times 10^4$)	0.157	0.171	0.172	0.179	0.197	0.242	0.246	0.287	0.288	0.317	0.323	0.508	0.510	0.738	1.13	1.28	1.13	1.45
Phys. detn. of $1/2\ M_c$ ($\times 10^4$)	0.505	0.466	0.449	0.527	0.566	0.619	0.623	0.657	0.654	0.667	0.675	0.924	0.932	1.20	1.62	1.81	1.66	2.13

Sample No.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Initial $\overline{M}_n$ ($\times 10^{-5}$) of rubber	2.66	2.66	2.43	2.60	2.60	2.62	2.43	2.62	2.62	2.60	2.60	2.62	2.62	2.62	2.60	2.66	2.62	2.62
Temp. °C. (± 0.1°C.)	140	140	130	130	130	130	130	130	130	120	120	120	120	120	110	110	110	110
Time (hr.)	72.0	72.0	2.0	3.0	4.5	6.0	6.0	16.25	30.0	12.0	17.0	22.0	48.0	77.0	48.0	72.0	93.25	161.0
Moles peroxide/g. rubber ($\times 10^4$)	2.89	3.02	1.50	1.52	1.46$_5$	1.49	1.54	1.45	1.46	1.60	1.47	1.47$_5$	1.44	1.45$_5$	1.48	1.49	1.50	(1.43$_5$)[b]
Product analysis, moles/g. rubber ($\times 10^5$)																		
tert-Butanol	29.9	30.6	2.11	3.36	4.93	5.85	6.45	12.3	16.4	4.21	5.22	7.29	11.5	15.2	3.89	6.42	7.16	10.7
Acetone	22.6	24.6	0.892	1.17	1.64	1.85	1.90	3.48	4.66	1.25	1.66	1.66	2.94	3.82	1.13	1.41	1.71	2.29
Peroxide (unreacted)	--	--	13.5	12.8	11.4	10.0	10.8	5.05	2.40	12.6	10.2	9.94	5.61	3.62	10.8	10.3	9.48	5.84
Methane	6.71	6.46	0.077	0.265	0.225	0.241	0.210	0.652	0.976	0.177	0.301	0.231	0.491	0.764	0.139	0.244	0.296	0.450
Ethane	9.20	11.0	0.470	0.572	0.640	(0.63)	0.800	(1.14)	(1.39)	0.562	0.651	(0.60)	(0.94)	(1.16)	0.515	0.652	(0.52)	1.07
% initial peroxide accounted for[a]	90.9	91.4	99.7	98.9	99.9	92.9	97.4	88.9	88.4	94.1	92.5	97.7	89.0	90.1	90.1	94.8	92.7	86.0[b]
Swelling data																		
v_r	0.451	0.459	0.172	0.211	0.237	0.261	0.257	0.326	0.362	0.232	0.248	0.262	0.306	0.341	0.229	0.257	0.275	0.306
v_r, corrected	0.462	0.467	0.216	0.244	0.266	0.285	0.283	0.344	0.377	0.260	0.275	0.286	0.324	0.357	0.259	0.280	0.291	0.321
Degree of crosslinking																		
Chem. detn. of $1/2\ M_c$ ($\times 10^4$)	1.83	1.85	0.110	0.181	0.258	0.305	0.333	0.647	0.869	0.220	0.276	0.376	0.599	0.798	0.201	0.333	0.373	0.559
Phys. detn. of $1/2\ M_c$ ($\times 10^4$)	2.53	2.62	0.375	0.497	0.606	0.723	0.710	1.15	1.46	0.580	0.658	0.728	0.993	1.26	0.571	0.701	0.802	0.993

[a] Per cent of initial peroxide present as *tert*-butanol, acetone, and unreacted peroxide.

[b] Low value is probably due to loss of peroxide in the transference of peroxide to rubber in initial stage of vulcanization procedure.

metric analysis of these fractions (kindly undertaken by Dr. J. C. Robb, University of Birmingham) gave the following results:

"Methane" fraction

Compound	Mole %
Methane	87.7
CO(N_2?)	8.0
Ethane	3.9
Butene	0.2
CO_2	0.2

"Ethane" fraction

Compound	Mole %
Ethane	94.5
CO_2	3.9
Butane	1.6

The major gaseous products are, as anticipated, methane and ethane. Further confirmation of methane and ethane being the major components of the two fractions was obtained by comparison of the vapor pressures of the latter with those of standard samples at the same temperature. The methane fraction was measured over the range −196 to −183° and the ethane fraction over the range −130 to −100°:

	Vapor Pressure (mm. Hg)						
"Methane" fraction	10	24	29	40	56	63	84
Methane standard	10	24	29	40	56	63	84
"Ethane" fraction	22	34	40	50	61	120	175
Ethane standard	22	34	40	48	60	118	170

In view of the minor contribution of methane to the total peroxide decomposition products (Table III) and the frequently smaller extents of peroxide decomposition than above, no correction has been made to the chemically determined degree of crosslinking for the higher molecular weight gases present in the methane fraction.

Physical Determination of Degree of Crosslinking

This was based on the equilibrium volume fraction of rubber in the swollen vulcanizate, v_r. Selected pieces of the vulcanizate (*ca.* 1 g.) were accurately weighed and swollen in *n*-decane for 48 hours at 25°. After rapidly removing *n*-decane from its surface with filter paper, the swollen rubber was weighed in stoppered weighing bottles. Preliminary tests indicated that equilibrium swelling is obtained under these conditions and that there is no additional swelling after immersion in *n*-decane for periods up to 6 days. The swollen samples were dried to constant weight *in vacuo* at 80–90° and the rubber reweighed, so giving an estimate of the amount of soluble material in the vulcanizate. The v_r values recorded in Table III have been corrected for the sol content of the vulcanizates.

III. EXPERIMENTAL RESULTS

The experimental results are recorded in Table III. Reference to the amounts of peroxide taken and the relative yields of the various products formed under the different vulcanizing conditions can be made by noting that 5.00 g. of rubber was taken for all experiments except numbers 15, 16, 18, 19, and 20, for which 4.80, 4.22, 3.50, 2.50, and 2.50 g., respectively, were taken. The free volume in the reaction tube for gaseous decomposition of the peroxide was 25–30 ml.

The concentrations of peroxide and decomposition products are given relative to the weight of crosslinked rubber insoluble in *n*-decane. The sol fractions for all rubbers except at low degrees of crosslinking ($1/2\ M_c$, chemical $< ca.\ 0.2 \times 10^{-4}$) were in the range 1–2%. These were shown to be largely nonrubber constituents from their solubility in acetone and alcohol. For the most lightly crosslinked rubber (No. 21), the sol fraction was 3.4%. Although the sol fractions undoubtedly contain some rubber hydrocarbon, it is preferable to relate product concentrations and the chemical determinations of crosslinking to the insoluble fractions since the sol portion will contain a negligible number of the crosslinks (according to network analysis[6] the fraction of crosslinks which are present in a sol of weight fraction S is given by S^2) and the comparative physical estimates of crosslinking based on volume swelling measurements are, by definition, those for the insoluble network.

The ratios of acetone:*tert*-butanol conform to the anticipated influence of experimental conditions on the relative rates of the competitive processes (R.2) and (R.3), *viz.* that the proportion of acetone is greater under conditions favoring gas-phase decomposition. Thus the ratio is increased by reducing the volume of rubber relative to the volume of the reaction tube (*cf.* No. 17 with Nos. 19 and 20), and is also increased at higher reaction temperatures (*cf.* Nos. 1–14 with Nos. 33–36). Under conditions of constant temperature and constant rubber volume:reaction tube volume, the acetone:*tert*-butanol ratio remains approximately constant with extent of reaction (see Nos. 1–14), as expected from the equilibrium partition of peroxide between condensed and gas phase.

The efficiency of hydrogen abstraction from the rubber hydrocarbon, measured by:

$$100([\overset{t}{\mathrm{Bu}}\text{-OH}] + [\mathrm{CH_4}])/([\overset{t}{\mathrm{Bu}}\text{-OH}] + [\mathrm{Me_2C{=}O}])$$

varies between 70 and 85%, there being a tendency for a higher efficiency of this process at lower reaction temperature. The above evidence for gas-phase decomposition of the peroxide being an important factor in promoting (R.3) and (R.5), considered wasteful in the present context, suggests an efficiency of hydrogen abstraction, and thus of crosslinking, approaching 100% when no gas-phase decomposition is possible, as occurs in technological moulding methods of peroxide vulcanization.

The chemical determination of crosslinking is expressed in Table III as $1/2\ M_c$, where M_c is the average molecular weight between crosslinks. This quantity is equal to $(1/N)$ (the number of crosslinks)/g. rubber, where N is the Avogadro number. Hence it is equal to the measured quantity $^1/_2$ (moles *tert*-BuOH *plus* moles $\mathrm{CH_4}$) produced in crosslinking one gram of rubber.

Physical determinations of crosslinking in units of $1/2\ M_c$ were obtained from the volume swelling ratios, v_r, of Table III by the methods of Part I.

The v_r values were converted first to C_1 values using the empirical Flory-Huggins equation (6) given as the full line of Figure 1 in Part I. These C_1 values then required correction for the finite initial molecular weight of the unvulcanized rubber by use of Figure 2 in Part I. The values of initial molecular weight chosen were those corresponding to the viscosities of the milled, undried rubber (Table I).

The unmodified Flory-Huggins equation (6) of Part I was chosen rather than the modified equation (6a) merely because of its simpler form. Within the practical range of C_1 determination ($20{,}000 > M_c > 5{,}000$), the alternative use of (6a) leads to only small changes in C_1 obtained from the experimental v_r values. However, evaluation of C_1 from v_r outside the practical range requires extrapolation of equations (6) and (6a), when increasingly diverging C_1 values are obtained with extent of extrapolation.

The C_1 values corrected for finite initial molecular weight finally provide physical estimates of $1/2\,M_c$ from the relationship: $C_1 = \rho RT/2\,M_c$, where $\rho = 0.910$ g./ml. is the measured density of the peroxide vulcanizates. To illustrate the considerable influence of finite initial molecular weight on the extent of swelling, the measured v_r values are compared in Table III with v_r (corr.) values, the latter being the anticipated volume swelling ratios for rubber of infinite initial molecular weight.

IV. DISCUSSION

Chemistry of Peroxide Decomposition and Crosslinking Reactions

The detailed investigations of di-*tert*-butyl peroxide decomposition in the gas phase[8] and in solution in alkylbenzenes[9] and olefins[10,11] suggest that the reactions (R.1–R.5) are operative when the peroxide decomposes partly in solution in rubber hydrocarbon and partly in the gas phase. The high over-all percentage of initial peroxide accounted for as *tert*-butanol, acetone, and unreacted peroxide (Table III) confirms that (R.1–R.4) represent the predominant mode of peroxide decomposition. The yields of methane and ethane relative to acetone are also consistent with (R.3–R.5), it being found that:

$$([\mathrm{CH_4}] + 2[\mathrm{C_2H_6}])/([\mathrm{Me_2C{:}O}]) \simeq 1$$

The data of Table III also reveal kinetics of peroxide decomposition consistent with those found previously.[8,9] Taking the observed values of $^1/_2$ (moles Bu^{t}OH + moles Me$_2$C=O) as a measure of the amount of peroxide decomposed, first order rate constants have been obtained in the temperature range 110–140° for the first 50% decomposition:

Temp. (°C.)	k_1 (× 10^5) sec.$^{-1}$	
140	4.62	S.D.[a] (0.15)
130	1.45	(0.08)
120	0.432	(0.021)
110	0.109	(0.007)

[a] S.D. is the standard deviation.

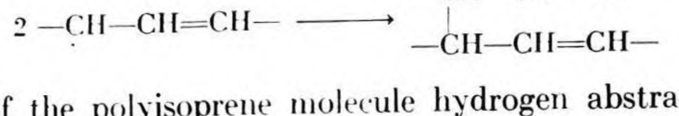
The constancy of the k_1 values determined from the experiments at 140° shows the accuracy of the experimental method used to determine the yields of *tert*-butanol and acetone:

Expt. No.	1	2	3	4	5	6	7
$k_1 \times 10^5$ (sec.$^{-1}$) at 140°	4.25	4.67	4.67	4.72	4.53	4.61	4.69
Expt. No.	8	9	10	11	12	13	
$k_1 \times 10^5$ (sec.$^{-1}$) at 140°	4.66	4.83	4.69	4.72	4.44	4.64	

The rate constants at the other temperatures are less accurate owing to the limited number of rate measurements made. The above rate constants give values for the pre-exponential factor and Arrhenius activation energy of *ca.* 1 × 10^{16} sec.$^{-1}$ and *ca.* 38.5 kcal./mole, respectively, which are in satisfactory agreement with previously published values.[8,9]

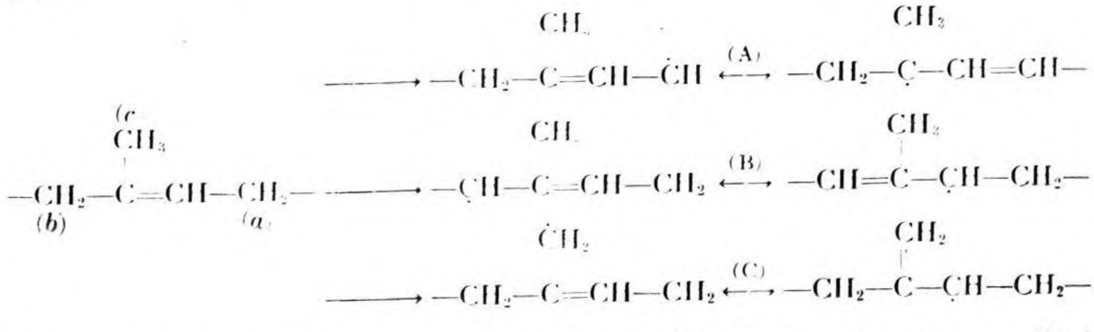
The present data confirm that (R.1)–(R.5) represent the major decomposition paths of the peroxide. It remains now to consider the evidence for combination (R.6) being the sole fate of the polyisoprenyl radicals R· produced in (R.2) and (R.4). It must be admitted that no unequivocal evidence is yet available indicating exclusive combination of these radicals in the case of rubber hydrocarbon. However, there is indirect evidence supporting this contention. The experimentally observed exclusive combination of allylic radicals produced from symmetrical dialkylethylenic monoolefins by the peroxide[10] (R.7)–(R.8) is certainly suggestive of (R.6) occurring with the polyisoprenyl radicals derived from natural rubber:

$$-CH_2-CH=CH- + (CH_3)_3C-O\cdot \longrightarrow -\underset{\cdot}{C}H-CH=CH- + (CH_3)_3C-OH \qquad (R.7)$$



$$2\ -\underset{\cdot}{C}H-CH=CH- \longrightarrow \begin{array}{l} -CH-CH=CH- \\ \quad | \\ -CH-CH=CH- \end{array} \qquad (R.8)$$

In the case of the polyisoprene molecule hydrogen abstraction by *tert*-butoxy or methyl radicals can occur at the three α-methylenic positions (*a*), (*b*) and (*c*), the relative ease of hydrogen abstraction being (*a*) > (*b*) > (*c*).[14,15] Such processes will lead to six mesomeric structures (A), (B), and (C):

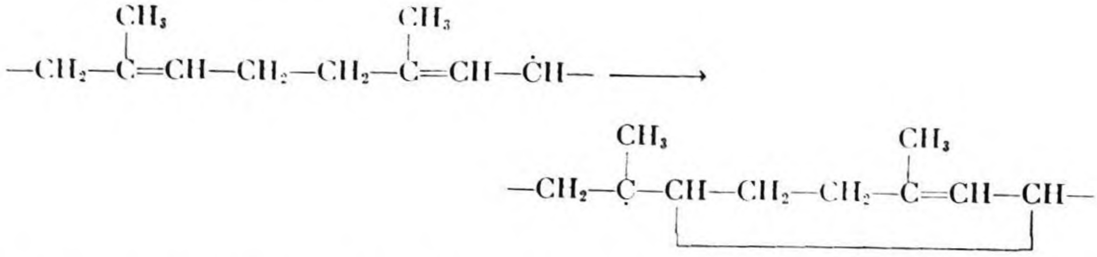


$$\longrightarrow -CH_2-\overset{CH_3}{C}=CH-\dot{C}H \xleftrightarrow{(A)} -CH_2-\overset{CH_3}{\underset{\cdot}{C}}-CH=CH-$$

$$\underset{(b)}{-CH_2}-\overset{\overset{(c)}{CH_3}}{C}=CH-\underset{(a)}{CH_2}- \longrightarrow -\underset{\cdot}{C}H-\overset{CH_3}{C}=CH-CH_2 \xleftrightarrow{(B)} -CH=\overset{CH_3}{C}-\underset{\cdot}{C}H-CH_2-$$

$$\longrightarrow -CH_2-\overset{\dot{C}H_2}{C}=CH-CH_2 \xleftrightarrow{(C)} -CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{\cdot}{C}H-CH_2-$$

In the case of monoolefins containing the trialkylethylene structure, radical combination is again the sole fate of the resonance stabilized radicals, and infra-red spectroscopic evidence confirms the presence of $R-CH=CH-R^1$ and $CH_2=CRR^1$ groups in the dehydropolymeric products as required by the resonance structures (A) and (C).[11] When the radicals (A)–(C) are formed from di- and polyisoprenes it becomes possible for the radicals to undergo cyclization to produce substituted *cyclo*hexenyl or *cyclo*pentenyl radicals prior to combination, *e.g.*:

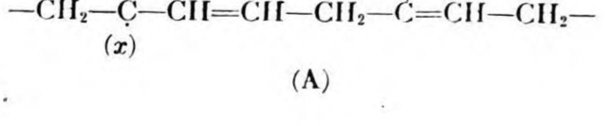


$$-CH_2-\overset{CH_3}{C}=CH-CH_2-CH_2-\overset{CH_3}{C}=CH-\dot{C}H- \longrightarrow -CH_2-\overset{CH_3}{\underset{\cdot}{C}}-CH-CH_2-CH_2-\overset{CH_3}{C}=CH-CH-$$

Experimental demonstration for such cyclization is found in the fact that the dehydropolymeric products from 2,6-dimethylocta-2,6-diene and digeranyl retain only 82 and 72%, respectively, of the unsaturation of the original olefin compared with 100% retention of unsaturation in dehydropolymers derived from monoolefins.[10,11]

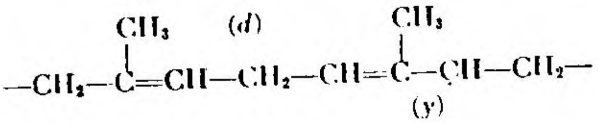
Application of the following simple probability argument to the earlier semiquantitative data of Farmer and Moore[11] shows that, despite the complexity of the radical forms obtainable from polyisoprenes and the tendency for such radicals to cyclize, the predominant fate of all radical species is combination. It is assumed that all isoprene units have equal reactivity and may undergo only one hydrogen abstraction during the extent of the reaction measured, and that radicals are exclusively terminated by combination. Let p be the probability that any isoprene unit undergoes hydrogen abstraction. Then, for example, for the reaction of 3 moles of 2,6-dimethylocta-2,6-diene with 1 mole of peroxide under conditions leading to complete decomposition of the latter, $p = {}^1/_3$, and the anticipated recovery of monomer is $100\ (1\text{-}p)^2 = 44\%$. The experimental value of monomer recovered was about 50%. Similarly, for the reaction of 1.5 moles of digeranyl (containing four isoprene units) with 1 mole of peroxide, $p = {}^1/_3$, and thus the anticipated recovery of digeranyl is $100(1\text{-}p)^4 = 20\%$, compared with the experimental value of 20%. It is therefore concluded that no experimental evidence is available suggesting that polyisoprenyl or the derived cyclic radicals undergo stabilization by disproportionation, since the latter process would lead to products mainly of the same molecular complexity as the parent olefin and so would result in less dehydropolymer than would be predicted by the above argument.

A further possible complication is that a measure of nonrandom crosslinking may occur. For example, coupling of the mesomeric radicals (A) and (B) will lead to crosslinked units having a 1,4-diene structure possessing a central α-methylenic group, (d), of enhanced reactivity towards hydrogen-abstracting radicals:[14,15]



$$-CH_2-\underset{(x)}{\overset{CH_3}{C}}-CH=CH-\overset{(d)}{CH_2}-\overset{CH_3}{C}=CH-CH_2-$$

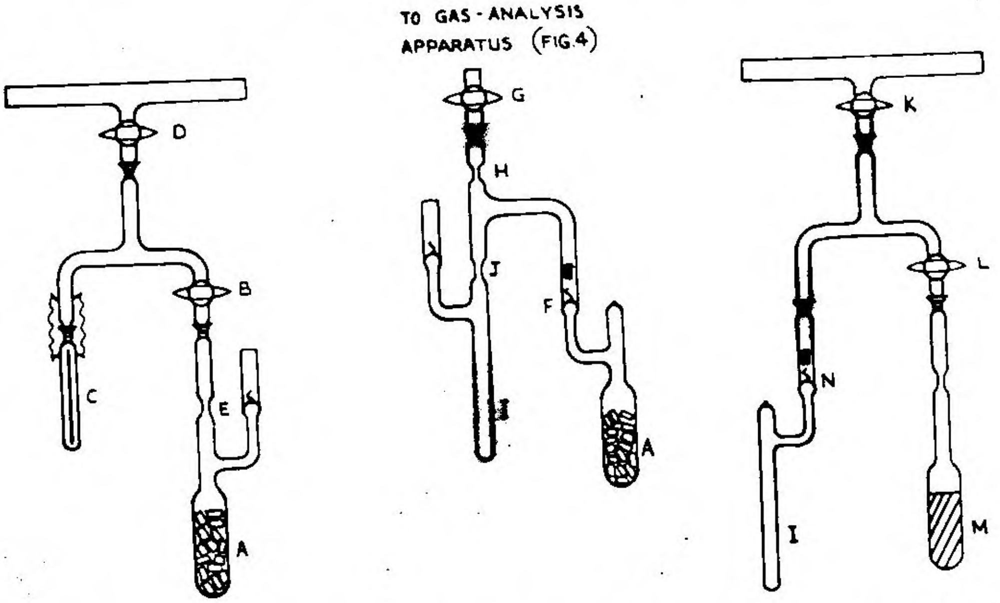
(A)



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{(d)}{CH}-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-\underset{(y)}{CH}-CH_2-$$

(B)

A chain segment between (*x*) or (*y*) and (*d*), produced by a subsequent coupling reaction at (*d*), would lead to a colonization of crosslinks, and so result in a loss of elastically effective crosslinks. However, calculations based on extrapolation of relative hydrogen-abstraction reactivities[14,15] to the temperatures employed in the present work, and consideration of the



Figs. 1, 2, and 3. Apparatus for the preparation of vulcanizates, and for the isolation and analysis of peroxide decomposition products.

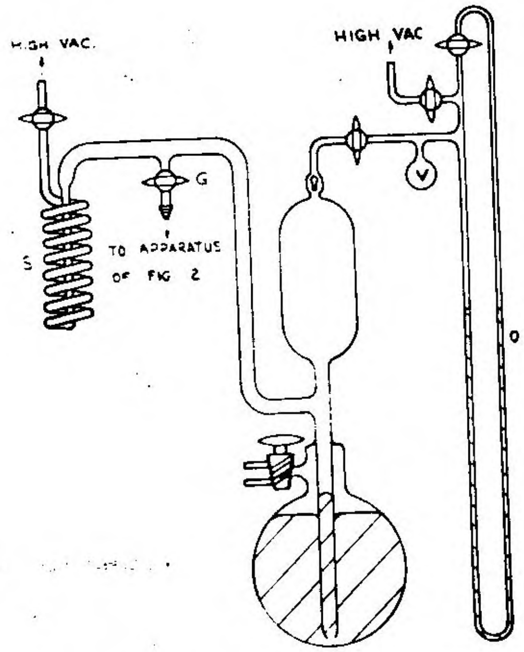


Fig. 4. Apparatus for the analysis of methane and ethane.

small fraction of the isoprene units that become located at crosslinks show that this complication can be neglected for rubbers in the elasticity range.

Another possibility is the coupling of radical species such as (C) (see above) to yield vinylic groups, $CH_2{=}CRR^1$, capable of addition polymerization. Additional crosslinking by this mechanism is regarded as unimportant in the present system because of: (*1*) the minor contribution of the radicals (C) to the total polyisoprenyl radicals, and (*2*) the low degree of polymerization effected with olefins of the type $CH_2{=}CRR^1$, where R and R^1 contain α-methylenic hydrogen atoms.

Disproportionation of polyisoprenyl radicals, crosslink colonization, and addition polymerization also seem improbable from a consideration of crosslinking at different temperatures. Even a small difference in the activation energies of the radical combination and the above processes would lead to a detectable change in efficiency of rubber crosslinking with variation in temperature. In fact no systematic variation of the chemical to physical

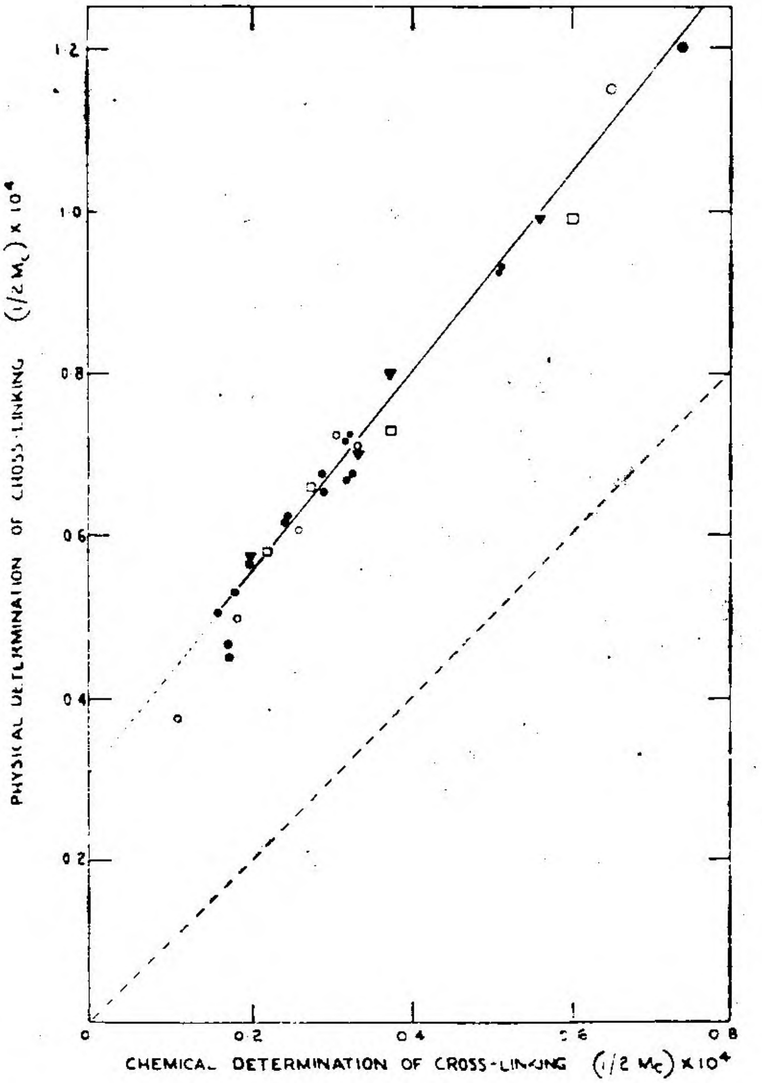


Fig. 5. Comparison of physical and chemical values of degree of crosslinking (1/2 M_c). Full line, experimental. Broken line, theory. (●) Vulcanization at 140°C., (O) at 130°C., (□) at 120°C., (▼) at 110°C.

values of crosslinking at different reaction temperatures was observed in the range of 110–140°C. (See Figs. 5 and 6.) There appears, therefore, some experimental justification for the assumption made here that all polymer radicals derived from the rubber by α-methylenic hydrogen abstraction undergo exclusive combination to give elastically effective crosslinks, and thus that the yields of *tert*-butanol and methane can be used to determine the degree of crosslinking.

Physical and Chemical Determinations of Degree of Crosslinking

It is pertinent to consider the measure of agreement between the chemical and physical determinations of degree of crosslinking, $1/2\,M_c$, for rubber of infinite initial molecular weight. Values of $1/2\,M_c$ determined from swelling measurements using the Flory-Huggins equation (6) of Part I are plotted against the chemical values of $1/2\,M_c$ in Figure 5 and as curve (A) in Figure 6. Curve (B) of Figure 6 shows the comparison of chemical with physical values using the modified equation (6a) of Part I. There is seen

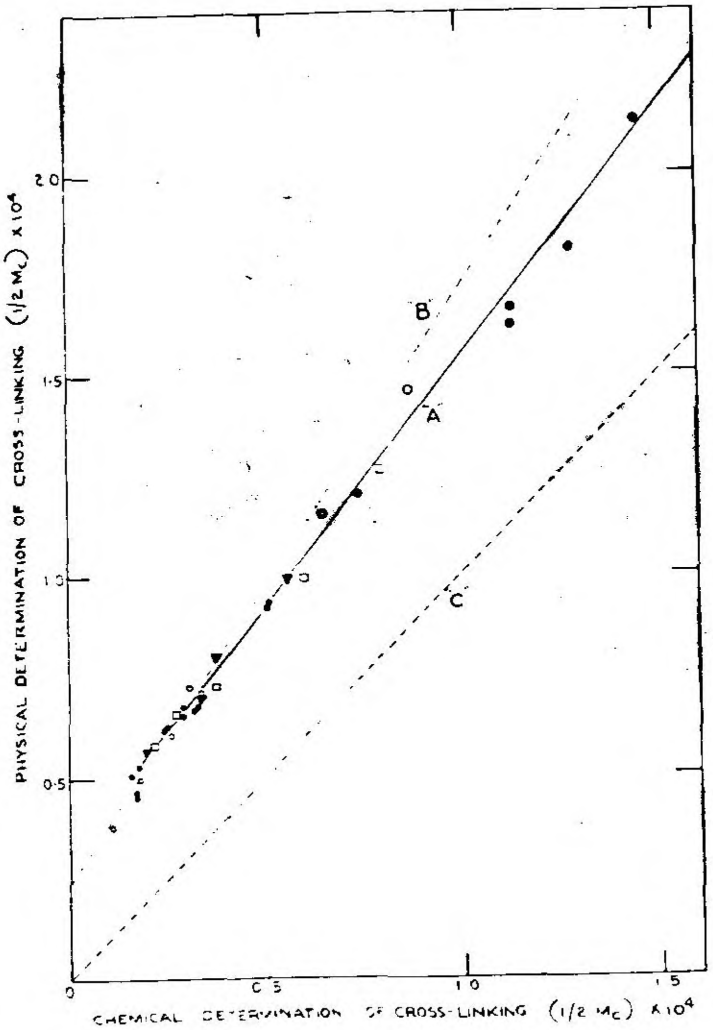


Fig. 6. Comparison of physical and chemical values of degree of crosslinking ($1/2\,M_c$). Curve (A), experimental, using equation (6) of Part I[2], Curve (B), experimental, using equation 6(a) of Part I[2]. Curve (C), theory. (●) Vulcanization at 140°C., (○) at 130°C., (□) at 120°C., (▼) at 110°C.

to be a considerable divergence between the experimental values and those required by elasticity theory (broken line), this divergence being in the sense of the physical value of crosslinking always being greater than the chemical value. The divergence apparently increases with increasing degree of crosslinking. Greater divergence from theory will be observed if the present assumption of exclusive combination of polyisoprenyl radicals is invalid.

The main divergence between physical and chemical determinations of crosslinking is expressed by an intercept term of about 0.3×10^{-4} and 0.24×10^{-4} on the axis of the physical determination of $1/2\ M_c$ at zero degree of chemical crosslinking, using equations (6) and (6a) of Part I, respectively. These intercepts imply that infinitely long rubber molecules before crosslinking would behave elastically as if they possessed crosslinks. In keeping with previous suggestions, these nonchemical crosslinks may be considered pictorially as chain entanglements, giving the equivalent of one crosslink for every 245 or 305 isoprene units, respectively, for the above values of the intercept. [Mr. L. Mullins has pointed out that this interpretation would lead to a correction for finite initial molecular weight in addition to the Flory end-correction. If entanglements are the cause of the intercept, it seems reasonable to assume a constant average frequency of entanglements along the rubber molecules except in segments with free ends. With no entanglement contribution for the free-end fraction, containing a proportion $2M_cM^{-1}$ of isoprene units, the contribution of apparent crosslinks ascribable to entanglements is of the form:

$$\Delta(1/2\ M_c) = 0.3(1 - 2\ M_cM^{-1}) \times 10^{-4}$$

Thus, the Flory end-correction and this possible entanglement correction together relate the physical degree of crosslinking $(1/2\ M_{c,\text{ phys.}})$, to the absolute degree of crosslinking $(1/2\ M_{c,\text{chem.}})$, by:

$$(1/2\ M_{c,\text{phys.}}) = (1/2\ M_{c,\text{chem.}})(1 - 2\ M_{c,\text{chem.}}\cdot M^{-1}) + 0.3(1 - 2\ M_{c,\text{chem.}}\cdot M^{-1}) \times 10^{-4}].$$

The physically determined values of $1/2\ M_c$ may be increasingly overestimated at higher degrees of crosslinking, accounting qualitatively for increasing divergence between physical and chemical determinations of $1/2\ M_c$, due to: (*1*) the statistical theory not being obeyed to an increasing extent (the value of C_2 being zero only at high degrees of swelling)[2]; and to (*2*) the finite extensibility of chains at high degrees of crosslinking contributing to the experimental values of C_1.

Finally, a comparison is made in Figure 7 between the present results with peroxide crosslinking, curve (C), and the previous results of Flory *et al.*[4] based on decamethylene dismethyl azodicarboxylate as the crosslinking agent, curve (A). For a better comparison, the physical measurements expected for the disazodicarboxylate crosslinked rubbers in the highly swollen state have been calculated by Mr. L. Mullins, and are represented as curve (B). Applying the somewhat larger empirical end-correc-

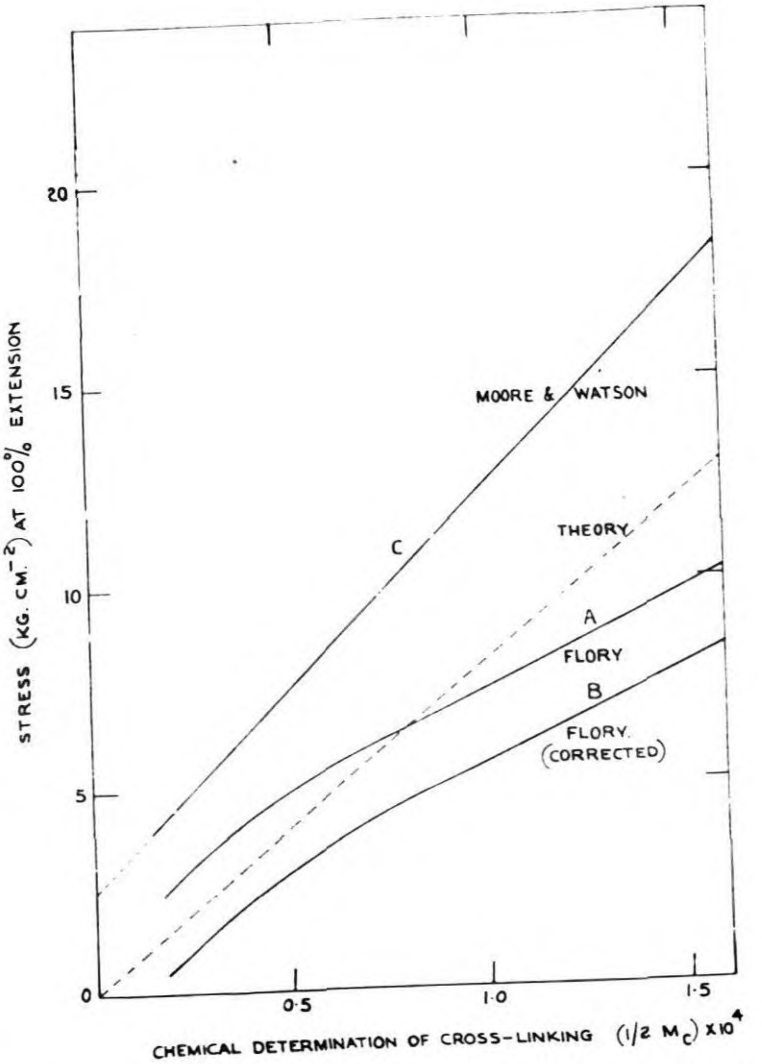


Fig. 7. Comparison of di-*tert*-butyl peoxide and disazodicarboxylates as crosslinking agents. Curve (A), results of Flory *et al.*,[4] using decamethylene dismethyl azodicarboxylate. Curve (B), results of curve (A), corrected to those obtained for the vulcanizate in the swollen state. Curve (C), present results with peroxide crosslinking.

tion[2] than that previously envisaged[4] will only slightly modify curve (B). A comparison of curves (B) and (C) suggests, therefore, that the disazodicarboxylate is a relatively inefficient crosslinking agent, and support for this has been found in recent studies[16] of the reaction of ethylazodicarboxylate with a diisoprene.

Since the method detailed in Part I provides a means of converting experimental v_r values into physical values of $1/2\ M_c$, the data of Figures 5 and 6 can be used to determine the chemical degree of crosslinking for conventional vulcanizates of known initial molecular weight. Thus by measurement of v_r for any vulcanizate, an experimentally simple procedure, the number of effective primary valence crosslinks/g. rubber can be determined and related to the amounts of vulcanizing agents chemically reacted, so giving a measure of the crosslinking efficiency of vulcanizing agents and quantitative expression to the function of accelerators and auxiliary compounds (zinc soaps, etc.) used in conventional vulcanization.

The authors thank Mr. L. Mullins for his cooperation, and Dr. E. S. Waight and Mr. G. Higgins for the spectroscopic data and for contributing the section on the analysis of *tert*-butanol, acetone and di-*tert*-butyl peroxide.

References

1. Treloar, L. R. G., *Physics of Rubber Elasticity*, Oxford Univ. Press, 1949, p. 61.
2. Mullins, L., *J. Polymer Sci.*, **19,** 225 (1956).
3. Bateman, L., Glazebrook, R. W., Moore, C. G., and Saville, R. W., *Proc. Third Rubber Technol. Conf., London*, Preprint No. 51 (1954).
4. Flory, P. J., Rabjohn, N., and Shaffer, M. C., *J. Polymer Sci.*, **4,** 225 (1949).
5. Bardwell, J., and Winkler, C. A., *India Rubber World*, **118,** 509 (1948); *Can. J. Research*, **B27,** 116, 128, 139 (1949).
6. Charlesby, A., *J. Polymer Sci.*, **11,** 513 (1953).
7. Rabjohn, N., *J. Am. Chem. Soc.*, **70,** 1181 (1948).
8. Raley, J. H., Rust, F. F., and Vaughan, W. E., *J. Am. Chem. Soc.*, **70,** 88 (1948).
9. Raley, J. H., Rust, F. F., and Vaughan, W. E., *J. Am. Chem. Soc.*, **70,** 1336 (1948).
10. Farmer, E. H., and Moore, C. G., *J. Chem. Soc.*, **1951,** 131.
11. Farmer, E. H., and Moore, C. G., *J. Chem. Soc.*, **1951,** 142.
12. Wood, R. I., *J. Rubber Research Inst. Malaya*, **14,** No. 279 (1952).
13. Chambers, W. T., and Watson, W. F., unpublished data.
14. Bolland, J. L., *Trans. Faraday Soc.*, **46,** 358 (1950).
15. Bateman, L., *Quart. Revs. (Chem. Soc.)*, **8,** 147 (1954).
16. Moore, C. G., unpublished data.

Synopsis

Natural rubber vulcanizates have been prepared by a method permitting determinations by chemical analysis of the number of crosslinks introduced. The crosslinking agent was di-*tert*-butyl peroxide, and the peroxide and its decomposition products—*tert*-butanol, acetone, methane, and ethane—were determined by infrared spectroscopic and manometric methods. *tert*-Butanol and methane result from the abstraction of α-methylenic hydrogen atoms from the rubber hydrocarbon by means of *tert*-butoxy and methyl radicals, respectively. On the assumption that the resultant rubber hydrocarbon radicals undergo exclusive mutual combination a chemical evaluation of degree of crosslinking, $1/2\ M_c$, is given by $^1/_2$(moles of *tert*-butanol + moles of methane), where M_c is the average molecular weight between crosslinks. Physical values of $1/2\ M_c$ for rubber of infinite initial molecular weight have been obtained by determining the volume fraction of swollen rubber, v_r, in *n*-decane, and by using the method described in Part I for correcting for the finite initial molecular weight of the rubber. A comparison of the physical and chemical values of $1/2\ M_c$ indicates that the former is greater than the latter for all degrees of crosslinking, the major divergence being accounted for by an additive term which is pictorially visualized as due to entanglements.

Résumé

Des vulcanisats de caoutchouc naturel ont été préparés suivant une méthode permettant la détermination chimique du nombre de pontages intermoléculaires. L'agent de pontage était le peroxyde de di-tertiaire-butyle; celui-ci de même que ses produits de décomposition, savoir le tertiaire-butanol, l'acétone, le méthane et l'éthane ont été évalués par spectrométrie infrarouge et par des méthodes manométriques. Le tertiaire-butanol et le méthane résultent d'une réaction d'un atome d'hydrogene alpha-méthylénique de l'hydrocarbure de caoutchouc avec des radicaux tert. butoxyliques et méthyliques. En admettant que les radicaux hydrocarbonés formés s'additionnent mutuellement, on peut évaluer chimiquement le degré de pontage, $1/2\,M_c$ au moyen de la somme $^1/_2$ (moles tert.butanol + moles de méthane); M_c exprime le poids moléculaire moyen entre deux ponts. Des valeurs physiques de $1/2\,M_c$ ont également été obtenues pour un caoutchouc de poids moléculaire infini en déterminant la fraction de volume du caoutchouc gonflé, v_r, dans le décane normal, en utilisant la méthode décrite dans la première partie en corrigeant les données en tenant compte du poids moléculaire initial du caoutchouc. La comparaison des résultats physiques et chimiques des valeurs de $1/2\,M_c$ indiquent que les premiers sont plus élevés que les derniers à tous les degrés de pontage; l'écart principal peut être représenté par un terme additif, qui peut être considéré comme tenant compte de l'interpénétration intermoléculaire des segments.

Zusammenfassung

Es wurden natürliche Kautschukvulkanisate mittels einer Methode hergestellt, die durch chemische Analyse Bestimmungen der Anzahl von eingeführten Querbindungen gestattet. Das Querbindungsmittel war di-*tert*-Butylperoxyd, und das Peroxyd und seine Zersetzungsprodukte, nämlich *tert*-Butanol, Aceton, Methan und Athan wurden durch infrarote spektroskopische und manometrische Methoden bestimmt. *tert*-Butanol und Methan stammen von der Entfernung von α-methylen Wasserstoff-Atomen aus dem Kautschuk-Kohlenwasserstoff mittels *tert*-Butoxy-, beziehungsweise Methyl-Radikalen her. Unter der Voraussetzung, dass die daraus hervorgehenden Kautschuk-Kohlenwasserstoff-Radikale einer exklusiven gegenseitigen Vereinigung unterliegen, wird eine chemische Abschätzung des Querbindungsgrades $1/2\,M_c$ durch $^1/_2$ (Mol von *tert*-Butanol + Mol von Methan) gegeben, wo M_c das mittlere Molekulargewicht zwischen Querbindungen ist. Physikalische Werte von $1/2\,M_c$ für Kautschuk von unendlichem anfänglichen Molekulargewicht wurden durch Bestimmung der Volumenfraktion von gequollenem Kautschuk, v_r, in n-Dekan erhalten, und durch Benutzung der in Teil I zur Korrektion für das endliche anfängliche Molekulargewicht für Kautschuk beschriebenen Methode. Ein Vergleich der physikalischen und chemischen Werte von $1/2\,M_c$ gibt an, dass der erstere für alle Querbindungsgrade grösser als der letztere ist, wobei der hauptsächlichen Abweichung durch einen zugefügten Ausdruck Rechnung getragen wird, welche bildlich als durch Verwirrung bedingt dargestellt wird.

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Anomalous Relation of Apparent Viscosity to Temperature in High Molecular Weight Polyisobutylene under Shear in a Capillary Viscometer*

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I. INTRODUCTION

This paper presents previously unreported, anomalously high temperature coefficients of viscosity observed for polyisobutenes over small temperature ranges. This seeming anomaly appears to have the same explanation as a different type of observations reported several times over the past several decades. The investigators who reported the earlier observations have not all agreed on their explanation. The bases for two alternative explanations of the present and the previous observations are very important in the behavior of high polymers. It seems worth while therefore to prepare this discussion of our observations and of the two explanations one of which probably applies to them as well as to the different, previously reported observations.

Our observations are on plots of apparent viscosity *versus* temperature at fixed rate of shear. The viscosities were measured for high molecular weight polyisobutylenes of several different molecular weights, using a capillary-type viscometer. At temperatures above 100°C., the variations of viscosity with temperature are comparatively small. Their magnitude is about that indicated by flow activation energies in the neighborhood of 3 kcal. This behavior is characteristic of the viscosities of high polymers at fixed rate of shear. However, over some small temperature interval (<10° C.) in the region between 40 and 100°, the variation of viscosity with temperature is very large. In this interval, a temperature decrease of several degrees produces a viscosity increase of a factor of two or more. For some samples the variation of viscosity with temperature appears to be nearly infinite at the lower end of this interval. The temperature at which these intervals are located (later designated as T_f) increases with increasing molecular weight of the polymer.

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