

Structural Characterization of Natural and Vulcanized Rubber by Ozonolysis

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Synopsis

A quantitative characterization of natural rubber, both as the raw polymer, and unaccelerated vulcanized samples containing different proportions of sulfur and ranging from soft to hard rubber, is reported. A value of 86% of the chains of natural rubber could be accounted for against 37% as reported by Harries assuming that levulinic acid is the sole degradation product. About 5% of the chain is present as a 3,4 structure which gives rise to formic acid in the degraded product. A small amount of sulfuric acid is present in the degradation product from the vulcanized samples, which decreases with the increase in the percentage of sulfur in the stock as well as the cure time. A chromatographic technique for the separation of levulinic, acetic, and formic acid in the presence of sulfuric acid is reported. It is observed that the total amount of carbon main chain escaping sulfuration decreases and the amount of insoluble fraction increases with increasing proportion of sulfur in the stock.

In a previous communication¹ a chromatographic method for the separation and identification of ozonolytic degradation products of natural rubber has been reported. The present work reports a quantitative estimation of the basic polymer, natural rubber, and vulcanized rubber of different vulcanization coefficient, by the chromatographic separation, detection and the estimation of the ozonolytic degradation products. It was thought that the ozonolytic degradation of vulcanized rubber followed by detection and estimation of the product might give an idea about the distribution of the polymer backbone into parts which is crosslinked with sulfur (expected to resist the formation of ozonide), and that which is remaining uncrosslinked (expected to form ozonide).

EXPERIMENTAL

Ozonolysis of Rubber

About 2 g. of natural rubber (RSS-1) or a powdered, extracted sample of vulcanized rubber was allowed to swell completely in 200 ml. chloroform for 72 hr. in the case of natural rubber and 120 hr. for vulcanized samples,

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the samples being kept in the dark, cold, and in a nitrogen atmosphere during swelling. Ozonolysis of the samples was carried out as reported earlier.¹

Oxidative Hydrolysis

The ozonide was hydrolyzed in the same manner as described earlier¹ by refluxing with 15 ml. of 20 vol. hydrogen peroxide, diluted to 50 ml. by distilled water, for 3 hr. at 60°C. and finally for 30 min. at 100°C. In the case of vulcanized samples the solution was then filtered; the residue left as semisolid mass was washed with hot distilled water and the washings added to the filtrate. The semisolid mass (insoluble fraction) was taken out by repeated washing with benzene and dried in vacuum to a constant weight. The percentage of insoluble fraction was then calculated.

Estimation of Carbon Dioxide

Oxidative hydrolysis of the ozonide was carried out in the closed system shown in Figure 1. Carbon dioxide produced in the hydrolysis process was estimated by connecting the top of the condenser to a sulfuric acid trap to absorb moisture and then to a U tube containing Ascarite (soda lime) to absorb carbon dioxide. The movement of carbon dioxide produced was effected by slow suction with a water pump. The difference between the final and initial weight of the U tube was taken to be the weight of carbon dioxide produced.

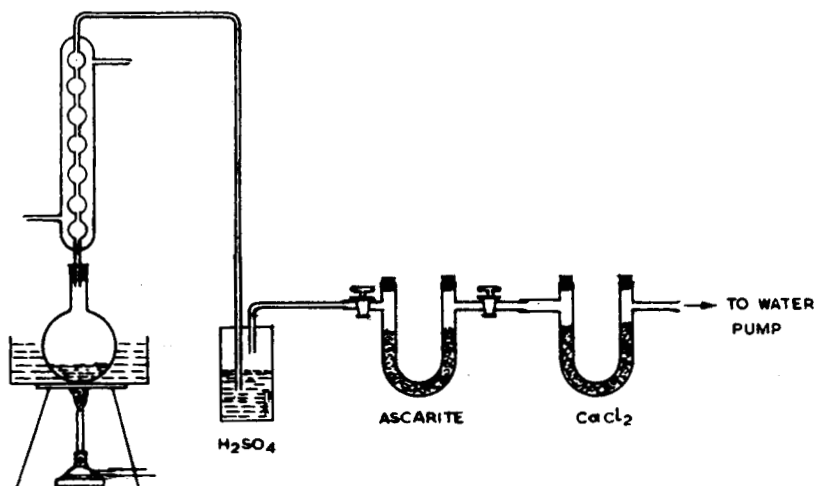


Fig. 1. Sketch for carbon dioxide estimation unit.

Column Chromatography

A silica gel column 30 cm. long and 1.5 cm. in diameter was prepared with B.D.H. 100-mesh chromatographic silica gel.¹⁻⁴ The same method as reported earlier¹ for the separation of acids, with some modification for

the presence of sulfuric acid in the case of vulcanized samples (described in discussion), was used.

Preparation of Vulcanized Samples

Mixing of sulfur with rubber was done in a Berstoff laboratory mixing mill of size 8×4 in. at about 70°C ., care being taken to ensure uniform dispersion and that breakdown was just sufficient for uniform dispersion. The speed of the slow roll was fixed at 10 rpm, the friction ratio being adjusted at 1.2.

Curing was done with an amount of the mix sufficient to fill a 10×7 in. mold with six circular cavities of size 1.5×0.1 in. in a Wabash hydraulic press 9 (Model No. 12-10, 12 tons, 230 v. a.c. operation, U.S.A.), fitted with temperature control. The pressure used was 50 psi at 160°C . The mold was brought to the curing temperature within $\pm 2^{\circ}\text{F}$. in the closed press and kept for at least 20 min. at this temperature before uncured sheets were inserted into the mold cavity. This was done by opening the press which was closed as quickly as possible after insertion of rubber. The vulcanization time was counted from the instant the press was closed and full pressure applied to the instant the pressure was released. As soon as the press was opened, the sample was put under cold water in order to arrest the reaction. The sheets were wiped dry and were ready for test after being kept for 24 hr. at $27 \pm 2^{\circ}\text{C}$.

The sample was then crushed to powder or made into thin sheets, according to the flexibility of sample, by passing two or three times through the cold, closed nip of the mixing mill. The resultant mass was then subjected to cold extraction for 7 days with alcohol—benzene mixture (1:2), the solvent being changed each day. The sample was then dried at room temperature, subjected to further milling (two or three passes) and finally dried in vacuum for 24 hr. at room temperature.

Combined and Total Sulfur

Combined and total sulfur were determined by the standard Zn-HNO₃ process.⁵

Rubber

The sample of smoked sheet (RSS-1) used in the present investigation was analyzed for acetone extract, ash, rubber hydrocarbon, and protein (by estimating nitrogen) by following the standard method.⁵ The assay of rubber was as follows: acetone extract, 1.75%; rubber hydrocarbon, 96.20%; proteins ($N \times 6.23$), 2.60%; ash, 0.35%.

RESULTS AND DISCUSSION

Characterization of Natural Rubber

It was stated in the earlier report¹ that levulinic acid on secondary decomposition yields acetic acid and malonic acid [eq. (1)]. The latter,

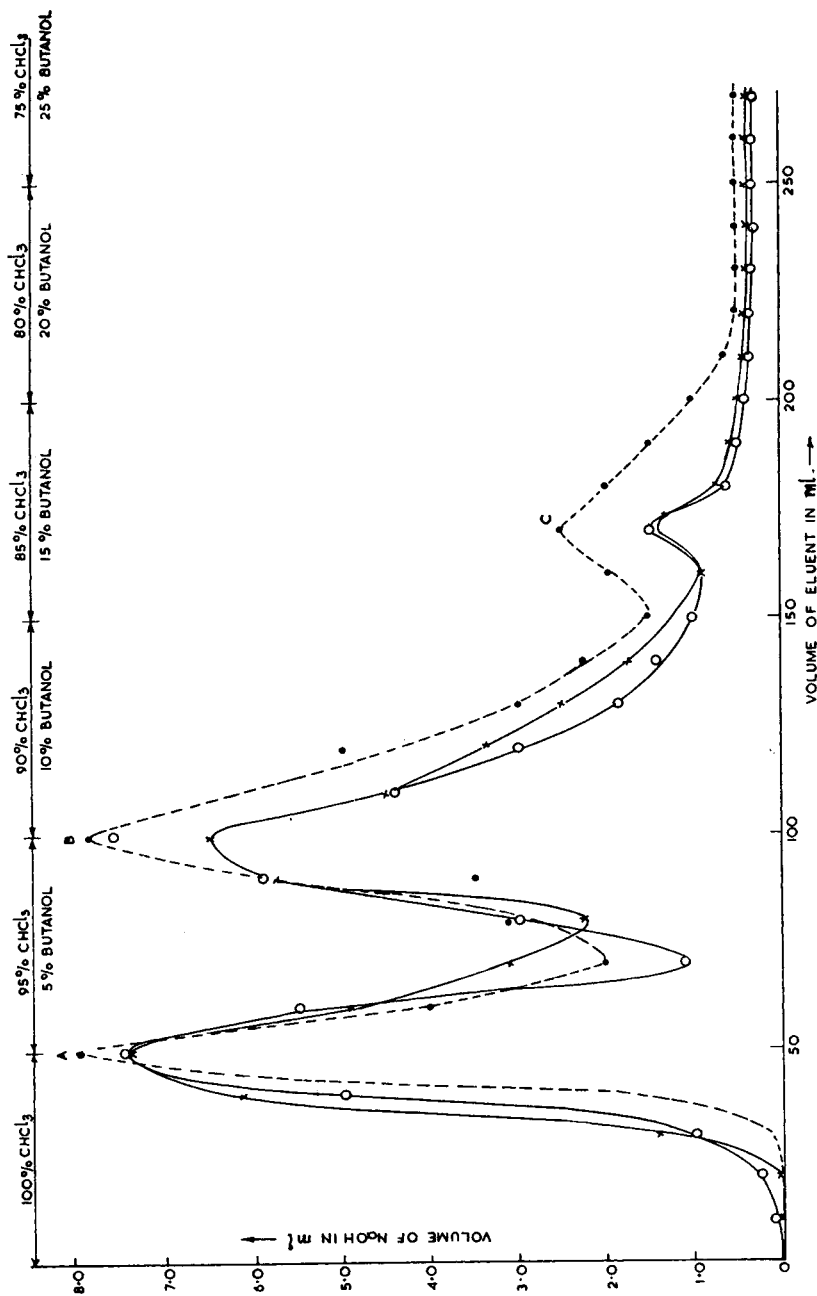


Fig. 2. Chromatographic analysis of the products of ozonolysis on a silica gel column: (O) natural rubber; (X) synthetic polyisoprene; (●) reference acids: (A) levulinic acid, (B) acetic acid, and (C) formic acid.

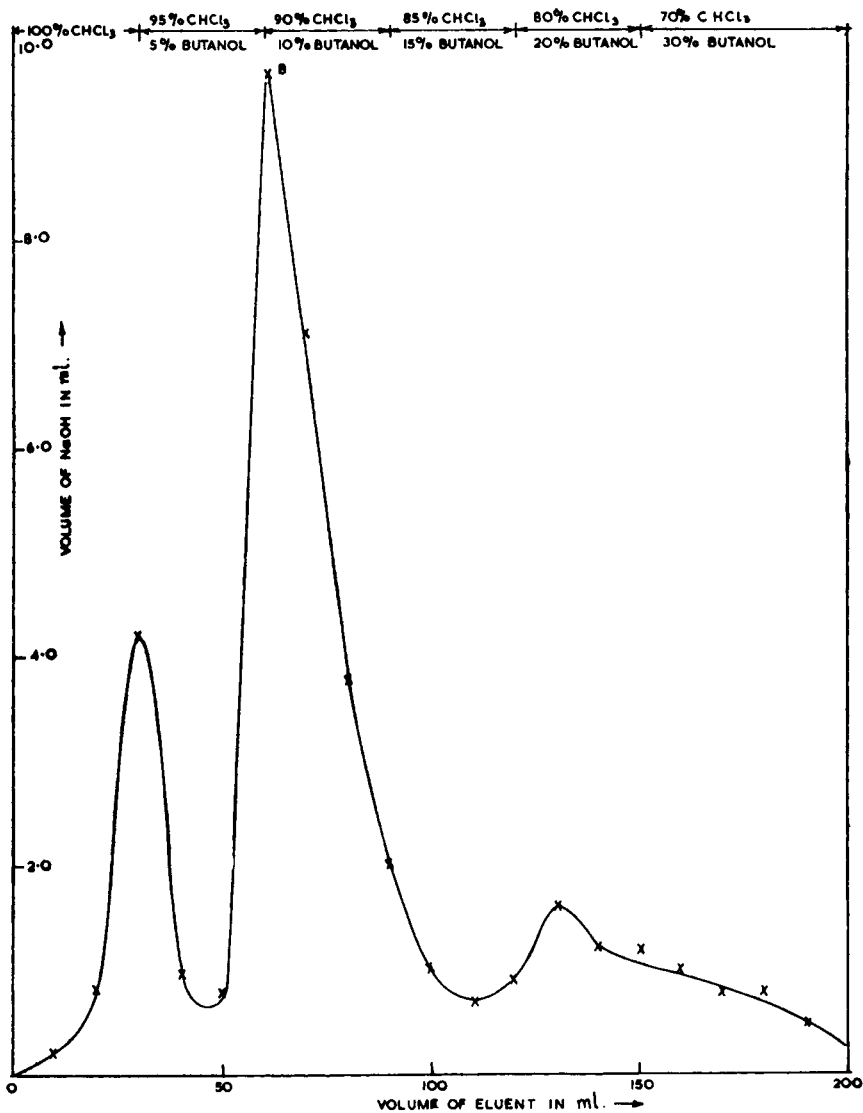


Fig. 3. Quantitative estimation of acids from natural rubber on a silica gel column: (A) levulinic acid; (B) acetic acid; (C) formic acid.

on further decomposition, yields another molecule of acetic acid and a molecule of carbon dioxide [eq. (2)].

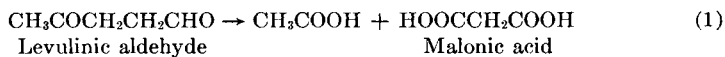


TABLE I
Quantitative Characterization of Natural Rubber

Levulinic acid, % C skeleton	Acetic acid, % C skeleton	Formic acid, % C skeleton	CO ₂ , % C skeleton	Total % C skeleton	Levulinic acid (estimated as 2,4-dinitro phenylhydrazine), % C skeleton
23.26	32.17	5.19	1.01	61.63	23.09

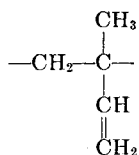
The extra precaution taken during the present experiments was absorption of any carbon dioxide formed during oxidative hydrolysis and prevention of volatile acids from escaping by using ice-cold water in the condenser in order that a quantitative picture may be obtained. Complete oxidation of levulinic aldehyde was ensured by the negative test for the aldehyde in the eluent. On comparison of Figure 3 with Figure 2 it is observed that prolonged oxidative hydrolysis decomposes a higher proportion of levulinic aldehyde, thereby increasing the yield of acetic acid at the expense of levulinic acid which is the expected product in the absence of any secondary decomposition. Results presented in Table I and Figure 3 were obtained after chromatographic separation of the acids on the silica gel column by the method reported earlier.¹

It is evident from the reactions mentioned in eqs. (1) and (2) that two molecules of acetic acid and one of carbon dioxide are expected from the oxidative decomposition of a molecule of levulinic aldehyde, which means that for every four atoms of the carbon skeleton as acetic acid one carbon atom would be lost as carbon dioxide. The results in Table I however, show only 1.01% of carbon skeleton as carbon dioxide against 32.17% as acetic acid. This shows that estimation of carbon dioxide is definitely in error, provided acetic acid is not produced by the reactions other than those mentioned above.

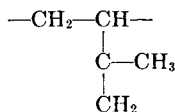
The results in various columns of Table I when added together, account for only 62% of the carbon chains of the polymer, leaving a wide deviation from the theoretical value. If carbon dioxide is estimated from the determination of acetic acid as above, a further 7.03% of carbon skeleton could be accounted for, making a total of 69%. Further loss of carbon in the skeleton might occur due to the escape of some of the volatile products during the ozonation or to loss during the hydrolysis step. It was found that it is very difficult to prevent volatile materials from being swept away, even at Dry Ice temperature. However, if all the acids obtained were expressed as levulinic acid as was done by earlier workers,⁶ carbon amounting to 86% of the polymer backbone could be accounted for against 37% as reported by Harries.⁶ Another explanation for the difference between the observed and calculated values is that some of the polymer molecules might have escaped degradation in spite of the fact that ozonoly-

sis was carried out for 8 hr. until the material was completely in solution and no further absorption of ozone occurred. In fact Pummerer and Richtzenhain⁷ find that when carbon tetrachloride is used as solvent, if the ozonolysis is stopped short of complete reaction, the portion remaining in solution is only highly oxidized rubber, whereas the precipitated material is the fully reacted ozonide. In the present case, chloroform was used as the solvent; where all the products were soluble and no such fractionation was possible. Estimation of levulinic acid as the 2,4-dinitrophenylhydrazone gives a value (23.09%) close to that obtained by chromatography (23.26%).

Since formic acid may represent the carbon skeleton derived from a 1,2, or a 3,4 structure.¹ Table I indicates that natural rubber contains about 5% of the C-skeleton as either 1,2, or 3,4 structure. This is about double the value reported by Binder and Ransaw,⁸ Solomon et al.,⁹ and Dinsmore.¹⁰



1,2 structure

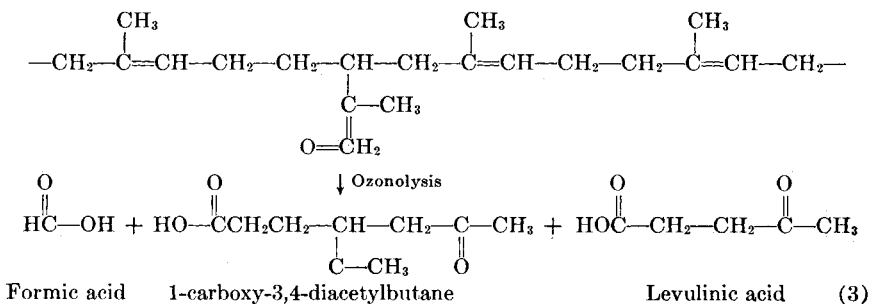


3,4 structure

The absence of absorption at 910 cm^{-1} in the infrared spectrum corresponding to 1,2 structure was, however, reported by the above authors. The 5% of carbon skeleton represented by formic acid may therefore be taken to arise from 3,4 structure present in natural rubber. The present work thus provides the only chemical determination so far of the heterogeneity of the natural rubber molecule.

A possibility that has not been taken into account in postulating the per cent yield of the carbon skeleton of the natural rubber molecule is that whenever there is a 3,4 structure in the chain which gives rise to formic acid from the attack of the side chains, the corresponding part of the main trunk chain is also modified. The exact modification will depend upon many factors, including whether the 3,4 structures are isolated in the chain or occur in clusters. If they appear in clusters, the next question would be the mode of attachment, e.g., head-to-tail, head-to-head, etc.

For the case of a single 3,4 structure interposed between 1,4 structures we may write eq. (3):



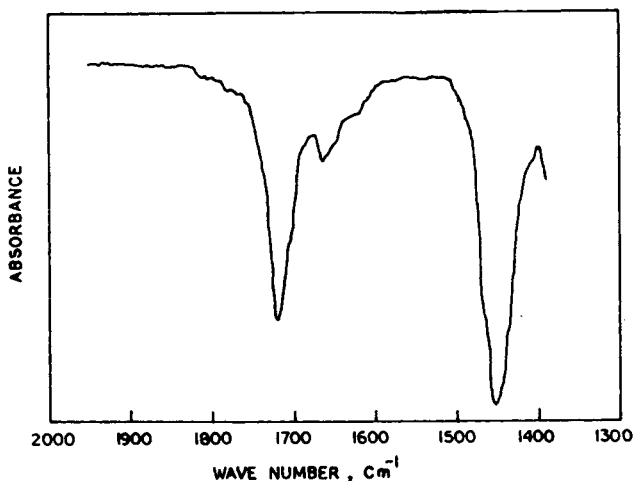


Fig. 4. Infrared spectrum of water-insoluble fraction of ozonolyzed natural rubber.

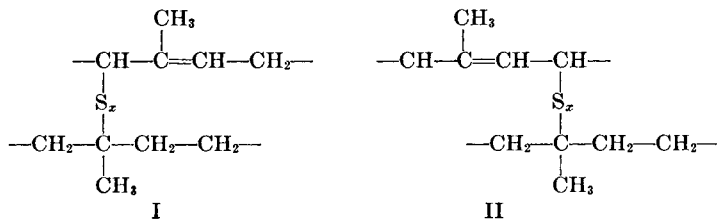
was formed which dissolved on standing, showing that no well-defined hydrazone was obtained. The experiment, repeated at a lower temperature, showed the same behavior. Infrared analysis of the gummy sample (Fig. 4), however, showed two absorption bands at 1725 and 1475 cm^{-1} . These correspond to ester keto groups (CO^- and COCH_3^- , respectively). The reason for the absence of well-defined hydrazone may presumably be due to the absence of an adequate number of keto groups in the keto acids or to the steric hindrance of the long chain acid.

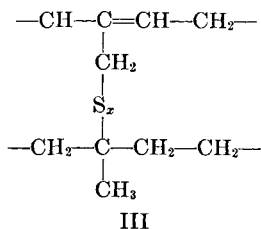
Infrared analysis thus lends at least qualitative support to the contentions laid down in the earlier part of the communication.

The same sample was also subjected to NMR analysis. However no additional information was obtained, except for some indication of the presence of olefinic structure and the $-\text{COCH}_3$ group.

Characterization of Unaccelerated Natural Rubber Vulcanizates

The concept of the structure of the vulcanizate has undergone a complete change in recent years, and today it is deemed that the double bonds are not the only sites at which sulfur can be attached to form crosslinks. Sulfur attachment can also take place with relative ease by the detachment of α -methylene hydrogen atoms. Some possible structures of a soft rubber vulcanizate are shown as structures I-III.





It may be evident that if structures I-III are present simultaneously, the formation of crosslinked units will not parallel saturation of double bonds. Another complicating factor in the ozonolysis study in the case of vulcanized rubber is the availability of potential sites of attack other than the polyisoprene chain, as shown by Barnard¹¹ and also by Banerjee.¹² These are the crosslinks themselves as well as the cyclic sulfides which are formed in abundant numbers in this type of compound. However, the contribution of this factor may be much less important, since the olefinic double bond in rubber reacts with ozone much more rapidly, making the degradation by ozone of the polysulfide crosslinks in vulcanized rubber relatively unimportant compared with the degradation of rubber trunk chains.

Fractionation of the Ozonolysis Product. In the present study vulcanized samples containing different percentages of sulfur in the stock were extracted for removal of free sulfur and then subjected to ozonization and oxidative hydrolysis as described above. The product was filtered from aqueous solution after repeated washing with hot water. The filtrate, which would contain all the degraded acids along with any water-soluble sulfonic and/or sulfuric acids was then subjected to chromatographic separation on a silica gel column. The precipitate, which was semisolid in nature, was expected to contain mainly the thio compounds formed by sulfuration, possibly oxidized to some extent by ozone. This semisolid gummy material eluted by repeated washing with benzene, the solution slowly evaporated in a tarred crystallizing dish and the residue dried *in vacuo* to constant weight. This is expressed as the per cent of total stock in Table II.

Sodium fusion indicated that the brown semisolid mass contained sulfur. It dissolved in sodium hydroxide solution and could be subsequently reprecipitated by acidifying with dilute hydrochloric acid as greyish flocks, which after washing and drying had the following properties: (a) dissolved slowly in a cold saturated solution of sodium bicarbonate; (b) melting point indefinite, depending on the state of vulcanization of the original sample; (c) soluble in acetic acid, alcohol, and acetone, insoluble in ether, and slightly soluble in rubber solvents.

Chromatography of the Ozonolysis Product. In the chromatographic separation of the filtrate containing the acids from the hydrocarbon residue, difficulty was encountered due to the simultaneous presence of sulfuric acid, which was found in all fractions, making the estimations nonquantitative and producing trailing in the curve. The effect of sulfuric acid on the

TABLE II
Data for Ozonolysis of Vulcanized Rubber (Cure Temperature 160°C.)

Total sulfur, % of stock	Cure time, min.	Combined S, % of stock	Levulinic acid, % C skeleton	Acetic acid, % C skeleton	Formic acid, % C skeleton	Carbon dioxide, % C skeleton		Total C, % C skeleton		Sulfuric acid, % of combined S	Insoluble fraction, % of stock
						Exptl.	Calcd.	Exptl.	Corr. for CO ₂		
0 (natural rubber)	—	—	23.26	32.17	5.19	1.01	8.04	61.63	68.66	—	—
2.92	50	2.56	18.41	11.13	3.19	1.20	2.80	33.93	35.53	39.08	50.03
	200	2.79	16.62	4.61	1.23	1.54	1.20	24.20	23.86	40.65	75.60
	300	2.90	16.06	7.96	1.31	1.07	2.00	26.40	27.33	35.87	19.10
5.89	20	2.70	8.13	12.68	5.02	1.06	3.17	26.89	29.00	35.1	19.32
	45	4.89	14.68	6.17	2.02	0.99	1.54	23.86	24.41	19.3	26.34
	80	5.10	11.55	5.15	1.70	0.64	1.29	19.04	19.69	27.0	30.14
12.46	20	4.08	10.39	2.50	—	0.38	0.60	13.27	13.49	6.01	79.93
	70	9.52	4.42	3.95	—	0.24	1.00	8.61	9.37	6.60	83.66
	150	9.42	6.22	3.50	—	0.13	0.60	8.85	9.32	8.30	88.39
25.0	30	10.40	5.68	1.24	—	1.85	0.31	8.77	7.23	1.86	80.25
	80	24.80	9.62	1.31	—	1.65	0.33	12.58	11.26	2.23	85.52
	200	26.16	7.19	1.22	—	1.47	0.40	10.88	8.81	2.23	89.78
	450	23.48	6.34	—	—	0.42	—	6.76	—	2.14	91.11
33.9	50	33.58	2.68	1.48	—	0.33	0.37	4.49	4.53	2.79	90.14
	150	27.15	6.07	—	—	0.07	—	6.14	—	1.82	90.60
	300	26.73	2.48	—	—	0.30	—	2.78	—	2.1	91.72

estimation of the reference acids (levulinic, acetic, and formic acids) by the chromatographic technique was therefore studied (Fig. 5). As the amount of sulfuric acid increases the quantitative significance of the estimation of

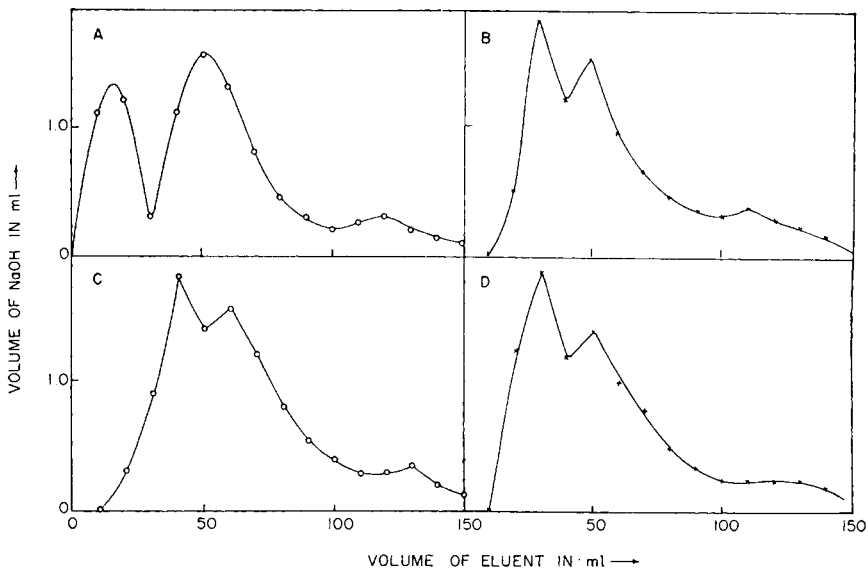


Fig. 5. Effect of sulfuric acid on the separation of reference acids: (A) without sulfuric acid; (B) 0.1 ml. of 0.05N H_2SO_4 ; (C) 0.3 ml. of 0.05N H_2SO_4 ; (D) 0.5 ml. of 0.05N H_2SO_4 .

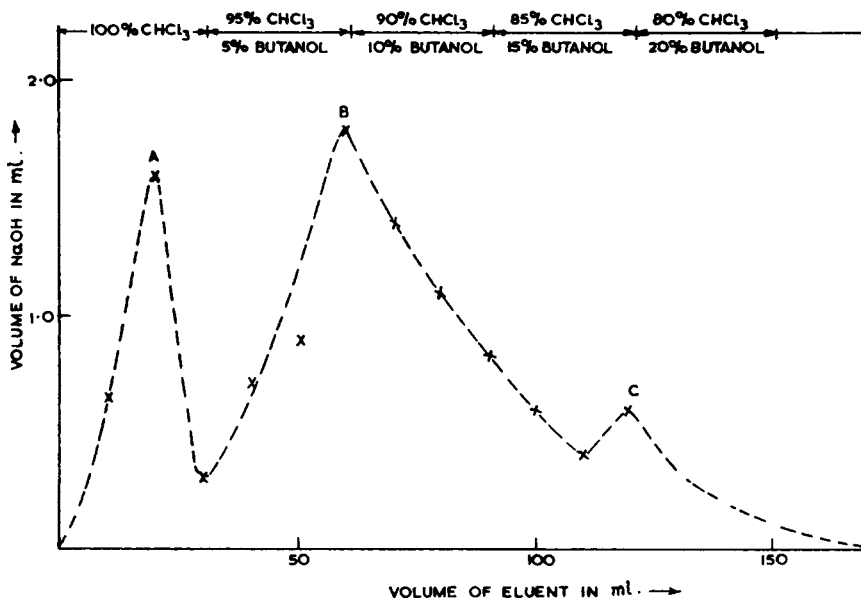


Fig. 6. Separation of reference acids: (A) levulinic acid; (B) acetic acid; (C) formic acid; (D) sulfuric acid (precipitated out with $BaCl_2$).

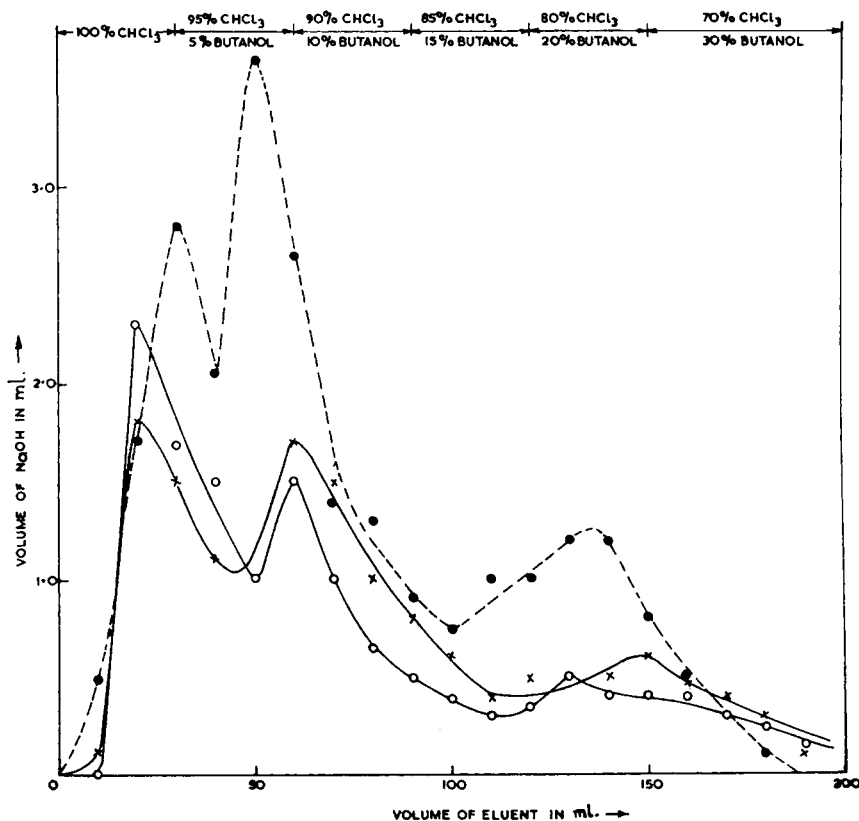


Fig. 7. Chromatographic separation of acids from natural rubber vulcanizates (cure temperature $160^{\circ}\text{C}.$): (○) 50 min.; (×) 200 min.; (●) 300 min. Composition of stock: rubber 97.08%; sulfur 2.92%.

other organic acids becomes less and less, and when 0.5 ml. of 0.05*N* sulfuric acid was added to 0.1*N* solution containing the mixture of reference acids the peak corresponding to formic acid is totally absent.

A number of processes for the separation of organic acids in presence of sulfuric acid was found in the literature.¹³⁻¹⁵ However, such methods when applied to the present system failed to give desirable separation. A combination of chemical and chromatographic techniques was therefore attempted to achieve the separation. This consists in precipitating out the sulfuric acid as barium sulfate and addition of the whole solution, with the precipitate, to the chromatographic column containing silica gel, the sulfuric acid being separately estimated outside the column with another portion of the solution. Satisfactory separation was obtained, as is evident in Figure 6.

Disappearance and Formation of Different Species in the Vulcanization Reaction. Having established the method for the separation and estimation of the reference acids in the presence of sulfuric acid, experiments were

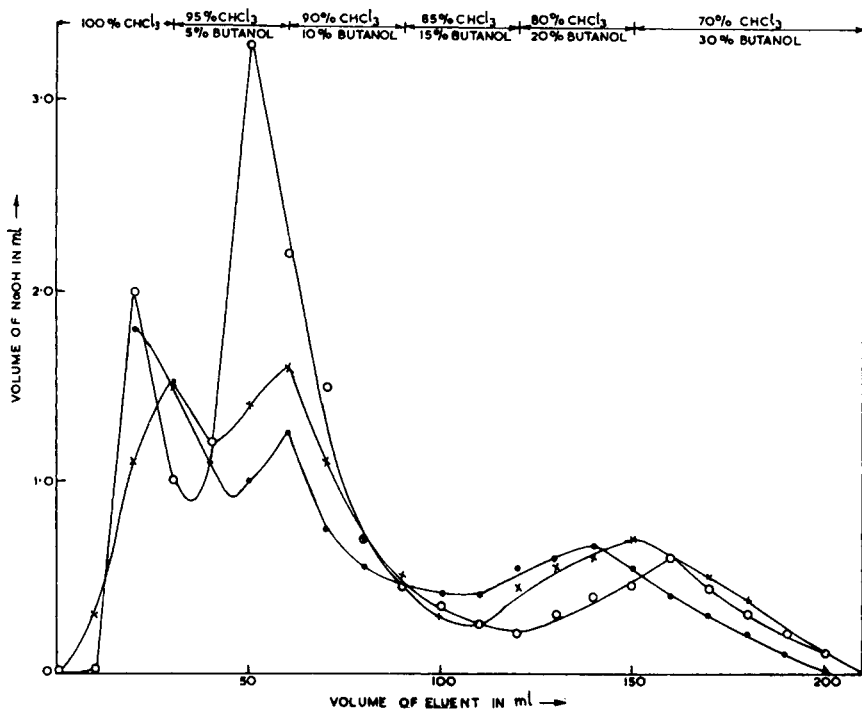


Fig. 8. Chromatographic separation of acids from natural rubber vulcanizates (cure temperature 160°C .): (O) 20 min.; (X) 45 min.; (●) 80 min. Composition of stock: rubber 94.11%, sulfur 5.89%.

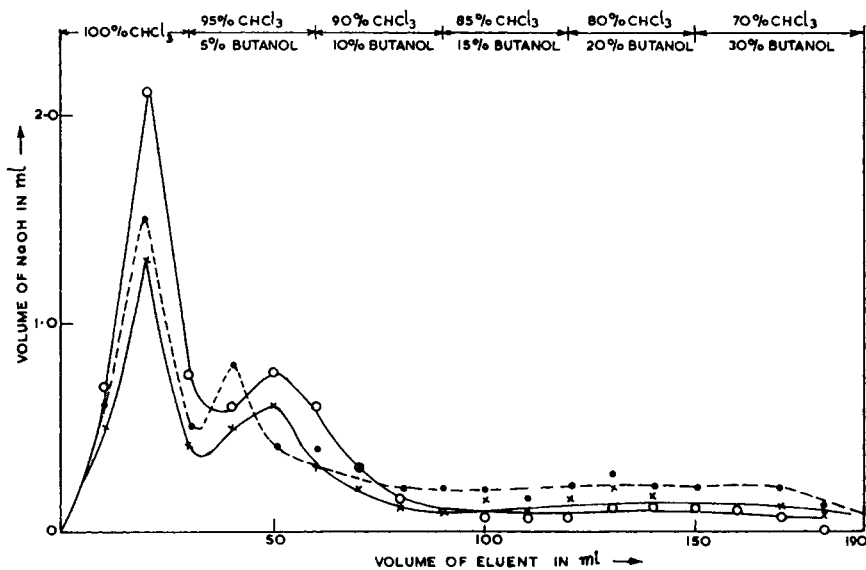


Fig. 9. Chromatographic separation of acids from natural rubber vulcanizates (cure temperature 160°C .): (O) 20 min.; (X) 70 min.; (●) 100 min. Composition of stock: rubber 87.56%, sulfur 12.46%.

conducted with samples obtained from vulcanizates containing increasing amount of sulfur. These are reported in Figures 7-11.

It is seen from Figures 7-11 and Table II that, as the proportion of sulfur in the compound is increased, the total amount of carbon skeleton

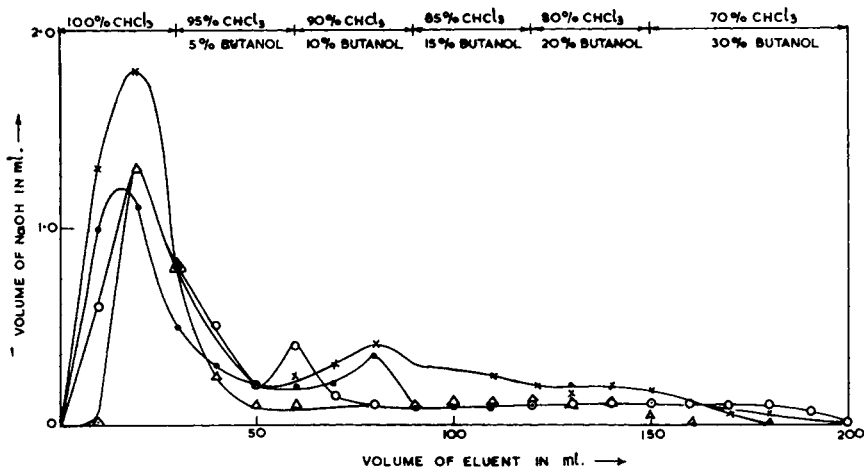


Fig. 10. Chromatographic separation of acids from natural rubber vulcanizates (cure temperature 160°C .): (O) 30 min.; (X) 80 min.; (●) 200 min.; (Δ) 450 min. Composition of stock: rubber 75%, sulfur 25.0%.

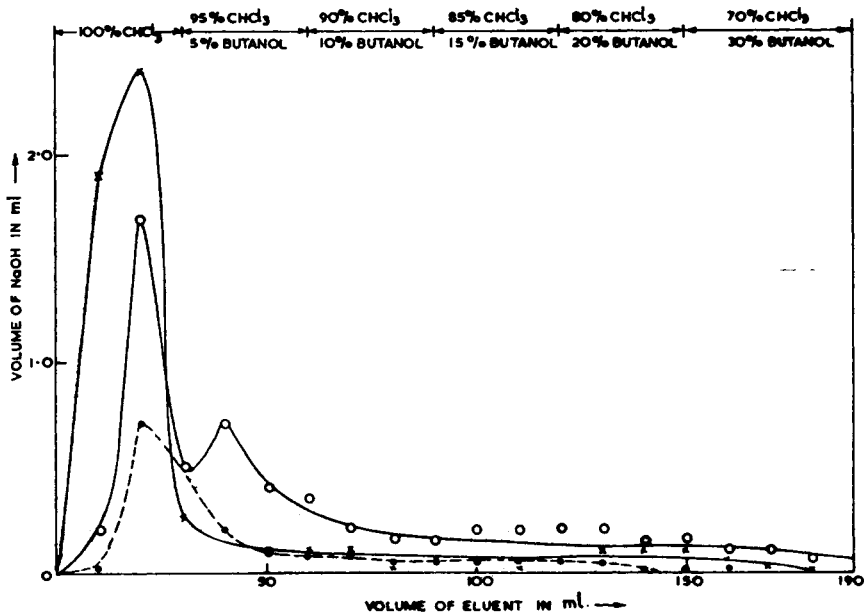


Fig. 11. Chromatographic separation of acids from natural rubber vulcanizates (cure temperature 160°C .): (O) 50 min.; (X) 150 min.; (●) 300 min. Composition of stock: rubber 66.1%, sulfur 33.9%.

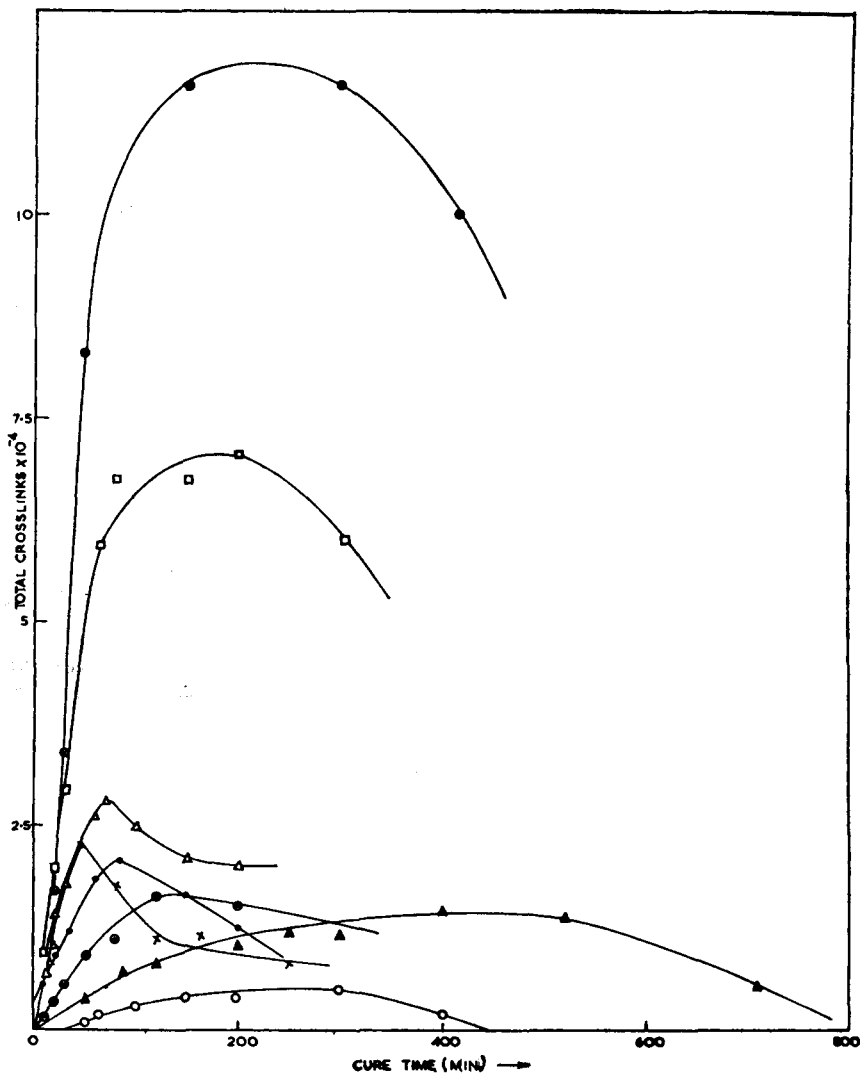


Fig. 12. Variation of total crosslinks with cure time and temperature: (○) 2.92% S, 160°C.; (×) 5.89% S, 160°C.; (●) 9.37% S, 160°C.; (Δ) 12.46% S, 160°C.; (□) 25.0% S, 160°C.; (⊗) 33.9% S, 160°C.; (⊙) 5.89% S, 150°C.; (▲) 5.89% S, 140°C.

not undergoing sulfuration decreases, indicating more and more formation of insoluble fraction including those containing the crosslinks. This is what can be expected, as it is known that as the proportion of sulfur is increased total amount of the hydrocarbons reacting with sulfur either to form crosslinks or cyclic compounds would increase. This is also in agreement with Figure 12, where it is shown that as the proportion of sulfur in the compound increases the number of total crosslinks increases thereby immobilizing an increasing proportion of the hydrocarbon chain.

The above observation can be confirmed from the results in Table II where it may be seen that as the proportion of sulfur increases the yield of insoluble fraction in the degraded vulcanizate increases. Table II also shows that as the time of cure of each compound is increased, the proportion of hydrocarbon residue decreases and the insoluble fraction increases. This also supports the conclusion above.

Another pertinent observation is the proportionally high yield of hydrocarbon acids and low yield of insoluble fraction in 5.89% sulfur stocks compared to the 2.92 S stocks: In the former, the proportion of sulfur is double, the yield of hydrocarbon portion is almost the same, and that of insoluble fraction is lower. This again lends further support to the idea that this composition is within the range of "rotten rubber stage" which is very susceptible to oxidative breakdown of the main chain during vulcanization. This amounts to a decrease of molecular weight of the backbone chain. Consequently, more sulfur will be necessary to effect crosslinking or immobilization. Conversely, more hydrocarbon residue will escape immobilization and would increase the proportion of hydrocarbon portion.

After 25% sulfur, which is in the range of hard rubber composition, the yield of hydrocarbon portion is very small and that of insoluble fraction very large, showing that in the hard rubber stage almost all the hydrocarbon chains are immobilized due to combination with sulfur.

It may be observed in Table II that yield of acetic acid in the uncompounded rubber is much higher than that of levulinic acid, showing the prominence of secondary degradation of the backbone chain, but in the vulcanized compounds this is reversed and the proportion of acetic acid progressively decreases (Figs. 7-11) as the percentage of sulfur in the compound is increased. This may be due to the protective action afforded by the increasing amounts of oxidized sulfurated structures as vulcanization progresses or sulfur in the compound is increased. Such a protective action of oxidized sulfur compounds on olefinic structures was also described by Barnard.¹⁶

It may also be observed (Table II and Figs. 7-11) that the amount of formic acid progressively decreases on vulcanization, and vanishes at 12.46% sulfur in the stock, possibly due to the blocking of the 3,4 structures from which it arises. However, the rate of blocking by sulfur seems to be almost the same both in the side chain and in the main chain, since the ratio *acetic/formic* in the case of vulcanized stocks is almost the same with two exceptions. Such disappearance of formic acid can not be due to the simultaneous presence of sulfuric acid since the mineral acid was previously removed by precipitation. Also in the high-sulfur stocks, the yield of sulfuric acid is proportionately small.

It may be seen in Table II that the proportion of sulfur going to form sulfuric acid is much higher in the two low-sulfur stocks than those containing higher proportions of sulfur. This shows that particular sulfur links in the low-sulfur stocks are ozone-reactive and may be ascribed to the preponderance of polysulfide crosslinks. The yield of sulfuric acid is very

small in the two hard rubber compounds (25 and 33.9% S), which are known to consist of predominantly intramolecular cyclic structures containing one or two sulfur atoms. This also fits in with the picture as described above and agrees with the observation of Banerjee.¹²

The value obtained in estimation of carbon dioxide is considerably lower than that expected by theory, as has been discussed above.

CONCLUSION

The present work on ozonolysis of natural rubber and unaccelerated vulcanized samples of different sulfur concentration coupled with the chromatographic separation, identification, and estimation of the degraded products improves the quantitative correspondence between the mass of the initial polymer sample and the products obtained therefrom. However, the results show that the estimation of carbon dioxide is in error as it gives very low value compared to the theoretical, and the quantitative correspondence is still very poor. The present work shows that the attachment of the isoprene molecule in natural rubber is almost 95% *cis*-1,4.

About 5% of 3,4 addition units containing vinyl side groups which give rise to formic acid is also present. Results for the vulcanized samples show how with increasing proportion of sulfur, increasing amounts of polymer are immobilized and substantiates the present concept of vulcanization as a crosslinking process. The analysis of the result gives an idea of the transitions taking place as the proportion of sulfur in the compound is increased. Intermolecular reaction first gives place to the degradation reactions in the vulnerable rotten rubber stage, which in turn is overshadowed by the intramolecular cyclization process as the proportion of sulfur attains that corresponding to the hard rubber stage.

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Résumé

On présente un rapport relatif à la caractérisation quantitative du caoutchouc naturel, le polymère de départ et d'échantillons de vulcanisats dépourvus d'accélérateurs, contenant différentes proportions de soufre, et variant de caoutchoucs moux à des caoutchoucs durs. En supposant que l'acide lévulinique est le seul produit de dégradation, on peut rendre compte de 86% des chaînes, alors que Harries n'en avait trouvé que 37%. Environ 5% de la chaîne se présente dans la structure 3,4, qui donne lieu à la formation d'acide formique par dégradation. Une faible quantité d'acide sulfurique est présente dans le produit de dégradation des échantillons vulcanisés; elle décroît avec une augmentation du pourcentage en soufre dans le matériau ainsi qu'avec la durée du recuit. On décrit une technique chromatographique permettant la séparation des acides lévulinique, acétique et formique en présence d'acide sulfurique. Lorsque la proportion de soufre augmente, la quantité totale du squelette carboné, qui échappe à la sulfuration, décroît tandis que la quantité de fraction insoluble augmente.

Zusammenfassung

Eine quantitative Charakterisierung von Naturkautschuk, sowohl des Polymergrundstoffes als auch von ohne Beschleuniger vulkanisierten Proben mit verschiedenem Schwefelgehalt vom Weichgummi-bis zum Hartgummizustand wird gegeben. 86% der Ketten von Naturkautschuk, gegen 37% nach Harries, konnten unter der Annahme erfasst werden, dass Lävulinsäure das einzige Abbauprodukt ist. Etwa 5% der Ketten sind als 3,4-Struktur vorhanden und liefern Ameisensäure im Abbauprodukt. Im Abbauprodukt der vulkanisierten Proben findet sich eine kleine Menge Schwefelsäure, welche mit Zunahme des Schwefelgehalts in Vulkanisat und mit der Vulkanisationsdauer abnimmt. Ein chromatographisches Verfahren zur Trennung von Lävulinsäure, Essigsäure und Ameisensäure in Gegenwart von Schwefelsäure wird angegeben. Mit Zunahme des Schwefelgehaltes im Vulkanisat wird der Anteil des nichtschwefeligen Kohlenstoffskeletts geringer und der der unlöslichen Fraktion höher.

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