

## The Effect of Extraction and Rubber Purity on the Stress Relaxation of Dicumyl Peroxide Vulcanizates

J. R. DUNN,\* *The Natural Rubber Producers' Research Association, Welwyn Garden City, Herts., England*

The thermal stress relaxation of dicumyl peroxide and radiation vulcanizates in air has been found in some laboratories to give an autocatalytic relationship between  $\log f/f_0$  and time,<sup>1,2</sup> whereas other workers have found an approximately linear relationship.<sup>3</sup> The vulcanizates have been extracted with hot acetone in all these investigations, but it appears that the rubbers which did not degrade autocatalytically were not extracted before curing.<sup>4</sup> The effect of the purity of the unvulcanized rubber upon the rate of oxidative stress relaxation at 100°C. and the form of the curves obtained has therefore been studied.

### EXPERIMENTAL

The grades of rubber used were (a) No. 1 Ribbed Smoked Sheet, (b) sole crêpe, and (c) "highly purified" rubber (U. S. Rubber Co.). Vulcanizates were prepared from these rubbers both with and without 24 hrs. of prior extraction with hot acetone under nitrogen. Vulcanization was effected by heating at 140°C. with 3 phr dicumyl peroxide for 35 min. between plattens spaced to yield sheets 15 × 15 × 0.02 cm. Further vulcanizates were prepared by compounding each of the unextracted rubbers with 1% phenyl-β-naphthylamine (PBN) as well as dicumyl peroxide and vulcanizing as

TABLE I

Rubber	PBN, phr	Code name	V <sub>r</sub>
Unextracted smoked sheet	—	RSSU	0.246
Unextracted smoked sheet	1	RSSU/PBN	0.235
Extracted smoked sheet	—	RSSE	0.285
Unextracted sole crêpe	—	CU	0.247
Unextracted sole crêpe	1	CU/PBN	0.225
Extracted sole crêpe	—	CE	0.270
Unextracted purified rubber	—	HPU	0.261
Unextracted purified rubber	1	HPU/PBN	0.214
Extracted purified rubber	—	HPE	0.253

\* Present address: R. and D. Division, Polymer Corporation, Sarnia, Ontario.

before. The code names used for the various vulcanizates are listed in Table I.

Stress relaxation was measured in a manner described elsewhere.<sup>5</sup>

## RESULTS

The degree of swelling of the vulcanizates in *n*-decane at 25°C., expressed as values of  $V_r$ , is shown in Table I.  $V_r$  values for RSSE and CE are greater than those for RSSU and CU, owing to the removal of natural inhibitor before cure. In the presence of PBN the degree of crosslinking was appreciably reduced.

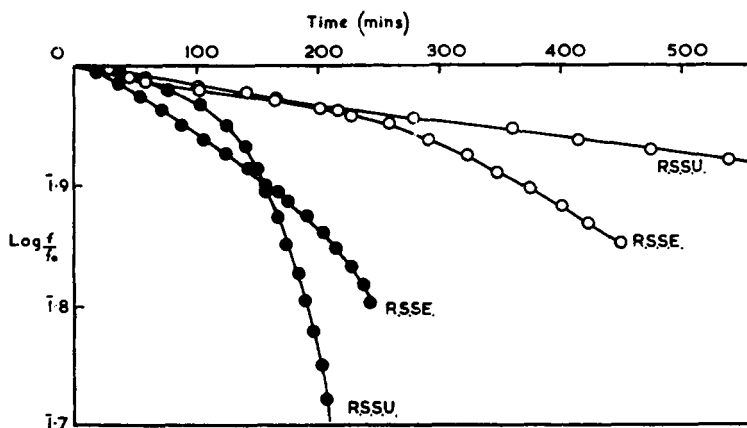


Fig. 1. Stress relaxation at 100°C. in air, of dicumyl peroxide vulcanizates of RSSI both with and without extraction before and after vulcanization: (●) not extracted after cure; (○) acetone-extracted after cure.

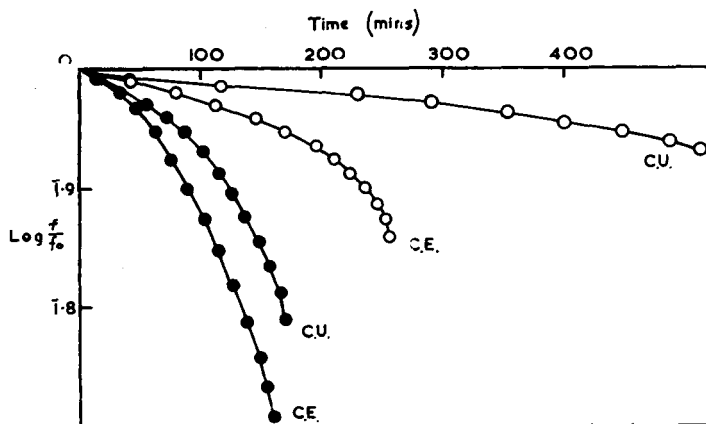


Fig. 2. Effect of extraction before and after dicumyl peroxide vulcanization on the aging of pale crêpe vulcanizates at 100°C. in air: (●) not extracted after cure; (○) acetone-extracted after cure.

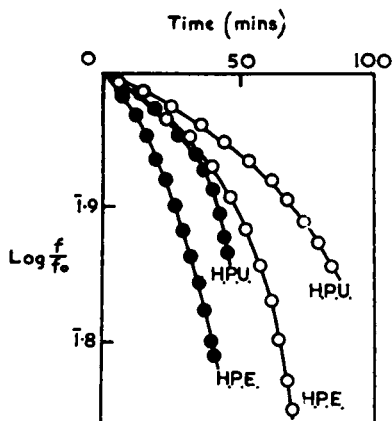


Fig. 3. Effect of extraction before and after vulcanization on the stress relaxation of highly purified rubber vulcanized with dicumyl peroxide: (●) not extracted after cure; (○) acetone-extracted after cure.

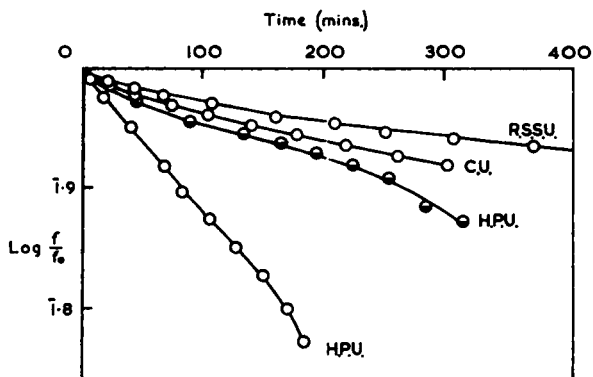


Fig. 4. Stress relaxation at 100°C. in air, of extracted dicumyl peroxide vulcanizates of various types of natural rubber compounded with 1% PBN: (○) continuous relaxation; (●) intermittent relaxation.

The stress relaxations of smoked sheet (RSS), sole crêpe (C) and highly purified rubber (HP) vulcanizates are shown in Figures 1, 2, and 3, respectively. The vulcanizates extracted after curing relax more slowly than those aged without extraction, and vulcanizates derived from unextracted rubber relax more slowly than those prepared from extracted rubber. *Truly autocatalytic curves are only obtained from highly purified rubber.* Extracted vulcanizates compounded with PBN all initially yield linear  $\log f/f_0$  vs. time plots and the rate of relaxation increases in the order  $RSS < \text{crêpe} < \text{HP rubber}$  (Fig. 4). Intermittent relaxation of the HPU vulcanizate compounded with PBN is markedly slower than continuous.

## DISCUSSION

In the absence of PBN, extraction after vulcanization reduces the rate of oxidative relaxation, presumably through removal of residual dicumyl peroxide. In practice, prolonged cure is sufficient to ensure that no unreacted peroxide remains; the remaining discussion is confined to vulcanizates extracted before relaxation. Invariably, extraction before curing yields vulcanizates which age more rapidly than those derived from unextracted rubbers. RSSU and CU vulcanizates show no sign of autocatalysis, but HPU vulcanizates age autocatalytically. This may be put down to the very low content of nitrogenous antioxidant in HP rubber even before extraction. All the vulcanizates compounded with PBN relaxed without autocatalysis, and it is concluded that nitrogenous materials present before vulcanization are difficult to remove afterwards, and may function as antioxidants. HPU vulcanizates compounded with PBN exhibited a more marked contrast between the rates of continuous and intermittent aging than is commonly found for extracted peroxide vulcanizates of purified rubber. This suggests that a crosslinking reaction occurs which is independent of the oxidative degradation during the aging of carbon-carbon crosslinked natural rubber.

## CONCLUSIONS

Information on the aging of rubber networks free of natural or added antioxidant can be obtained only by the use of extracted rubbers of high purity. It is not sufficient merely to extract the vulcanizates.

## References

1. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **55**, 667 (1959).  
Dunn, J. R., *Kautschuk Gummi*, **14**, WT 114 (1961); *Rubber Chem. Technol.*, **34**, 910 (1961).
2. Ore, S., *On the Oxidative Stress Relaxation of Natural Rubber Vulcanized with Di-tertbutyl Peroxide*, Oslo Univ. Press, 1958.
3. Mercurio, A., and A. V. Tobolsky, *J. Polymer Sci.*, **36**, 467 (1959).
4. Mercurio, A., Thesis, Princeton, Univ., N. J., 1960.
5. Dunn, J. R., and J. Scanlan, *J. Appl. Polymer Sci.*, **4**, 34 (1960).

## Synopsis

The oxidative stress relaxation of peroxide vulcanizates of various grades of natural rubber has been investigated at 100°C. The rubbers were examined both with and without hot acetone extraction before or after cure. Highly purified rubber vulcanizates exhibited autocatalytic relaxation, but those based on crêpe or smoked sheet did not, because they retained natural antioxidant even after extraction. Autocatalysis was no longer found in extracted purified rubber vulcanizates if these were prepared from a mix containing phenyl- $\beta$ -naphthylamine. The presence of such an antioxidant reduced network scission but had less effect upon the amount of crosslinking taking place during aging.

### Résumé

On a étudié la relaxation oxydante à 100°C de la tension du caoutchouc naturel, vulcanisé à divers degrés par les peroxydes. On a examiné les caoutchoucs avant et après avoir subi l'extraction à chaud par l'acétone, avant et après le traitement. Les vulcanisats de caoutchouc fortement purifié présentent une relaxation autocatalytique, mais non ceux exécutés sur du crêpe ou de feuilles de caoutchouc, parce que ceux-ci retiennent les antioxydants naturels, même après extraction. On ne trouve plus d'autocatalyse dans les vulcanisats de caoutchouc purifié, s'ils sont préparés à partir d'un mélange contenant de la phényl- $\beta$ -naphthylamine. La présence d'un antioxydant comme celui-ci réduit la scission du réseau, mais a moins d'effet sur le taux de pontage qui a lieu au cours du vieillissement.

### Zusammenfassung

Die oxydative Spannungsrelaxation von Peroxydvulkanisaten verschiedener Naturkautschukproben wurde bei 100°C untersucht. Die Kautschuke wurden sowohl mit als auch ohne Extraktion mit heissem Aceton vor und nach der Vulkanisation geprüft. Vulkanisate aus hochgereinigtem Kautschuk zeigten autokatalytische Relaxation, jedoch nicht solche aus Crepe oder Smoked Sheets, da diese auch nach der Extraktion noch natürliche Antioxydantien enthielten. Bei extrahierten Vulkanisaten aus gereinigtem Kautschuk trat dann keine Autokatalyse auf, wenn sie aus einer Phenyl- $\beta$ -Naphthylamin enthaltenden Mischung dargestellt worden waren. Die Gegenwart eines solchen Antioxydans setzte die Netzwerkspaltung herab, hatte aber weniger Einfluss auf das Ausmass der Während der Alterung stattfindenden Vernetzung.

Received March 6, 1962