UNIVERSITY OF LONDON

Thesis

Submitted for the Degree

of

Doctor of Philosophy

by

Dasarathi Banerjee.

TITLE

"THE MECHANISM OF THE VULCANISATION OF RUBBER AND THE STRUCTURE OF THE VULCANISATE, AS SHOWN BY A STUDY OF THE APPARENT UNSATURATION OF VULCANISED RUBBER UNDER VARYING CONDITIONS."

ABSTRACT.

An analytical method of determining true iodine indices of vulcanised rubber has been developed. Iodine chloride reacts with a small proportion of combined sulphur in vulcanised rubber. The amount of this halogen-reactive sulphur is approximately 3% in soft rubber, and with ebonite it increases to approximately 5.5%. The types of sulphur linkages in vulcanised rubber have been suggested. Additional evidence to justify the suggested types of sulphur linkage has been obtained from

the reaction of iodine chloride on known sulphur compounds. Structure

$$\begin{matrix} -C \\ -C \end{matrix}\!\!>\!S \quad \text{(I)} \quad \text{and} \quad \begin{matrix} -C-C- \\ \quad | \quad \\ -C-C- \end{matrix}\!\!>\!S \quad \text{(II)}$$

are suggested as the main reactions in soft vulcanisation resulting in a rapid fall in unsaturation at the initial stages. Structures

$$\begin{matrix} -C-C- \\ S \quad\quad > \\ -C-C- \end{matrix}\!\!>\!S \quad \text{(III)}$$

and some substitution are considered to constitute the ebonite reaction. The rate of saturation decreases during theebonite reaction.

Unsaturation of vulcanised rubber has been followed by ozone. An organic acidic thio-compound has been isolated from the ozonolysis products of vulcanised rubber. The amount of this compound increases with progressive vulcanisation. Laevulinic aldehyde and volatile fatty acids are obtained in proportions dependent on the state of vulcanisation of the original rubber. Sulphuric acid is another constituent of the reaction products.

The effect of ozone on stretched rubber is chemical. It attacks part of the combined sulphur in vulcanised rubber producing H_2SO_4. The chain is broken into smaller units still unsaturated and these are capable of forming addition compounds with bromine. The

tensional force in stretched rubber as distinct from mere elongation has been shown to be essential in the developing of surface-cracks in ozone. It is demonstrated that great elongation of rubber renders it more resistant to physical break-down in ozone, although the degree of chemical attack is increased.

The addition of sulphur monochloride to rubber, under varying conditions, has been studied. The importance of the tensional force in stretched rubber in attributing a greater reactivity to the rubber has been confirmed. Maximum chemical combination of S_2Cl_2 by stretched vulcanised rubber is 19%. With rubber in solution a maximum of 20% has been attained. The sulphur and chlorine contents are in indefinite ratio. The addlication of the rubber molecules on stretching has been demonstrated by the fibrous character of the cold-vulcanised products.

The reactions of neoprene are compared with those of rubber under similar conditions.
