"INTRODUCTION"

Investigations of the course of vulcanization have mostly been conducted in the solid rubber-sulphur phase. Weber[6], who for the first time undertook such study, obtained results which showed that during vulcanization a continuous series of addition products of sulphur and the rubber hydrocarbon were being formed. Spence and Young[15] later thoroughly investigated the course of vulcanization again in the solid phase. They vulcanized acetone-extracted para-rubber with 10 parts of sulphur at 135° and 155° C respectively. Values for combined sulphur obtained after 2 hour intervals gave a non-hyperbolic curve free from breaks, unlike that obtained by Weber.

If during the process of vulcanization, compounds were being formed between sulphur and rubber hydrocarbon, it should be possible to test the homogeneity of the product by fractional peptization. The different fractions should have percentages of sulphur that differ from those which follow. It should also be possible to separate vulcanized products from unattacked raw rubber.

Bacon[42] vulcanized a sample of crepe rubber to the extent of 0.1% combined sulphur. It was placed in a Soxhlet apparatus and subjected to pepitzation by hot benzine[2]. Various fractions were obtained and sulphur content in each was determined. Some of his results are:

	Gms.	Gms.	Gms.	Gms.
Weight of sample analysed -	3.9250	3.6072	3.7638	4.4677
Combined sulphur %	0.091	0.09	0.08	0.085

It appears that there was homogeneity as far as sulphur content

was concerned.

Midgley[49] and co-workers, however, arrived at a different conclusion. Pure sol-rubber hydrocarbon was mixed with tetramethyl thiuram disulphide and zinc stearate till the combined sulphur was approximately 0.06%. The material was subjected tofractional peptization and three successive components were thus isolated with sulphur content respectively of 0.058 ± 0.003%, 0.116 ± 0.003%, 0.179 ± 0.003%

Williams[50] attempted to show that rubber was not homogeneous in regard to the distribution of combined sulphur. He was able to peptise well vulcanized rubber in aromatic solvents containing piperidine at temperature below 100° C. The peptised solutions were sufficiently fluid to be filtered through paper and fractionation of the filtrate was carried out by ethyl alcohol.

An unaccelerated mixture of 100 parts of rubber and 10 parts of sulphur vulcanized at 148° C for 120 minutes gave rise to nine fractions. The properties of the various fractions and the distribution of sulphur were determined.

Lewis[69] and co-workers obtained a different degree of vulcanization for parts of rubber located near the centre of a mix. Uncured mix was sheeted out on the mill to 0.03 inch and cut into discs of 1.5 inches diameter. Each disc was protected from the other by a sheet of aluminium foil and all were vulcanized in a sandwich fashion in a mould, so that there were seven layers of rubber separated by thin foil. Combined sulphur was determined in each layer. The central layer always had a higher percentage of combined sulphur.

One can conclude from these observations that in these experiments vulcanization in the solid phase was not a homogeneous reaction. One can never know under which conditions Bacon[42] obtained results which showed homogeneity of vulcanizates, even when the combined sulphur was 0.1%.

What could be the reasons for such heterogeneity in a chemical reaction of rubber and sulphur? Kemp[51] and co-workers made a thorough investigation of the solubility of sulphur and other ingredients in rubber. They have shown that the limited solubility of sulphur, many accelerators and zinc soaps in rubber leads to the presence of these substances partly in solution and partly in the dispersed state at the start of vulcanization. Local high concentration of these substances occur in solution around the dispersed phase owing to their increased solubility which results from the temperature rise during vulcanization coupled with their slow rate of diffusion through rubber. It is apparent therefore that heterogeneous vulcanization will result from such non-uniform dispersion. Heterogeneous or spotty vulcanization could be more common in high sulphur stocks where most of the sulphur exists as a solid dispersion in the rubber.

In order, therefore, to study vulcanization under homogeneous conditions one must start with solutions of rubber and the other ingredients. Stern[70] tried to employ quantitative physical measurements in the study of vulcanization using naphthalene as a suitable solvent for both rubber and sulphur. However, the changes in physical properties were too small to permit definite conclusions.

Later, he tried to obtain information about the course of the vulcanization process by pouring the reaction mass in acetone and thus precipitating the vulcanized rubber and determining the combined sulphur in the extracted residue. Though he believed in Ostwald's[10] absorption theory of vulcanization, later discarded, he was the first to use solutions for the study of the vulcanization reaction.

Boiry[71] used solvents such as petrol, nitrobenzene, thymol, aniline. Since now it is definitely established that solvents like aniline, nitrobenzene have a definite accelerating effect in the course of vulcanization, much reliance cannot be placed in his results.

Since rubber is an unsaturated hydrocarbon and is therefore readily attacked by sulphur, the solvent should be a saturated hydrocarbon (unlike naphthalene used by Stern) so that there is no possibility of sulphur attacking the solvent. Moreover, if the vulcanization is to be studied at high temperatures the solvent should have a boiling point which far exceeds the vulcanization temperature.

In the present investigation, therefore, decalin was chosen as the right kind of a solvent. The boiling point of this saturated hydrocarbon is 185.5° C (trans-form) 194.6° C (cis-form) and can thus be used for vulcanizations up to 160° C. Moreover the solubility of respectively rubber and sulphur in decalin (described later) was such that this solvent was the right one to choose.

Substances Influencing Vulcanization

Crude rubber as it is received contains so-called resins and

protein matter in addition to the rubber hydrocarbon.

Examination of resin which constitutes on an average 2.8% of the weight of the raw rubber in the form of latex crepe or sheet has approximately the composition shown in the following table:[72]

	%
A phytosterol ester	0.075
Sitosterolin	0.175
A phytosterol	0.225
d-valine	0.015
Quebrechitol	very small
Stearic acid	0.15
Oleic acid, Linoleic acid	1.25

It has been shown by various workers that the resin contituents of raw rubber act as accelerators of vulcanization. The raw rubber vulcanizates therefore are superior in physical properties than the extracted rubber.

Whitby and Greenburg[72] gave the following figures in illustration of this:

Basal Stock:

Rubber	100	Vulcanized at 150° C for 30 and 50 minutes
Sulphur	5	
Zinc oxide	5	
Accelerator	5	

Unextracted Mix			Extracted Mix		
$T_{600\%}$	T_B	E_B	$T_{600\%}$	T_B	E_B
128.5	250	716	57.5	168	798
155	250	696	62.5	163	794

T_{600} T_B = Tensile strength in kilograms per square centimeter at 600% elongation and elongation at break of the test pieces.

E_B = Elongation at break of the test pieces.

It should therefore be necessary that, for a scientific study of vulcanization reaction between rubber hydrocarbon and sulphur, these resin contituents should be taken out of the pale crepe.

Recent studies of the vulcanization reaction have revealed that the primary stages of vulcanization are really the most important ones. Brown and Hauser[59] have shown that the desirable physical properties of the vulcanizates are conferred before any serious diminution in the unsaturation of the rubber has occurred or any large proportion of what has become chemically combined.

It is therefore very essential that the progress of vulcanization should be followed at frequent intervals from the beginning.

Therefore the experimental work was planned as follows:-

(1) Purify the pale crepe of the resin contituents without doing much harm to the physical state of the hydrocarbon.

(2) Make a suitable dispersion of the purified pale crepe in decalin.

(3) Study the progress of vulcanization reaction at various

temperatures by analysing the vulcanizates at 15 minute intervals.