P [133] Bill NO. C/200/Pub. 13/10/72 Df. 17.11.72 (38) Reprinted from Research and Industry, 1971, Vol. 16. No. 3, pp. 181, 182 for Ro. 13=06 LR-CP 133 810.181 Reprinted from Research and Industry, 1971, Vol. 16. Modified Lacs as 0000 fries Compounding Ingredients for Styrene-Butadiene Rubber: Part V-Mechanism of Reinforcement

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The mechanism responsible for the greater improvement in the mechanical properties of styrene-butadiene rubber brought about by modified lacs (lacs treated with epoxy resin or ethylene glycol) compared to straight lac has been investigated. The superior performance of modified lacs has been found to be due to less of interference in vulcanization by them as compared to straight shellac.

T was reported in earlier communications<sup>1-4</sup> that modified lacs, such as those obtained on treating lac with epoxy resin or ethylene glycol improve most of the mechanical properties of styrene-butadiene rubber (1502) to a greater extent than straight shellac. This paper gives the results of a study on the mechanism of the resulting reinforcement by determination of the crosslink density from equilibrium swelling and estimation of the free sulphur left after vulcanization when shellac or modified lacs are incorporated.

#### Experimental procedure

The composition of the base mix was: Styrene-butadiene rubber ( 502), 100; zinc oxide, 4; sulphur, 2; stearic acid, 1; phenyl  $\beta$ -naphthylamine (PBNA), 1; and cyclohexyl benzthiazyl sulphenamide (CBS), 1.5 parts/100 parts rubber. Shellac or modified lac was used in the proportion of 0, 2.5, 5 and 10 parts/100 parts rubber. The methods employed for mixing and vulcanization were the same as in the earlier study<sup>1</sup>.

Free sulphur was estimated according to BSI method BS 903  $(1958)^5$  and the crosslink density by the method of equilibrium swelling in pure benzene using the equation of Flory and Rhenner as described by Jose and Banerjee<sup>6</sup>.

## **Results and discussion**

The variation in free sulphur content and the number of crosslinks using various types of lac at two concentrations, viz. 5 and 10 parts/100 parts rubber is shown in Fig. 1 (A,B). It is seen that the amount of free sulphur at a particular cure time is more in samples in which shellac is used than in samples without any shellac. Also, at that cure time, for increased amount of shellac, the free sulphur content also increases, indicating that shellac interferes in the reaction of sulphur with rubber. However, the interference is less with both types of modified lacs, viz. epoxy resin and ethylene glycol modified lacs, the last one giving the best results in this respect.

The mode of variation of crosslink density is in agreement with that of free sulphur content and samples which do not contain shellac give higher crosslinks than samples having any type of shellac. Out of three types of lac incorporated, ethylene glycol modified lac again gives the best results followed by epoxy resin modified lac; straight shellac comes last.

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Fig. 1 — Variation in the free sulphur content and number of crosslinks in styrene-butadiene rubber containing different types of lac with period of cure [Proportion of lacs: (A) 5 parts/100 parts rubber; and (B) 10 parts/100 parts rubber]

As reported earlier<sup>1-4</sup>, modified lacs improve most of the mechanical properties of styrene-butadiene rubber (1502) to a greater extent than straight shellac. The results of the present study show that it is so because the interference in vulcanization due to shellac can be overcome to a great extent by its modification. This may be due to the fact that the modification of lac results in lowering the acid value (the values being 40.0 for epoxy resin modified lac<sup>1</sup>, 32.0 for ethylene glycol modified lac<sup>3</sup> and 70-72 for straight shellac<sup>7</sup>).

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