Characteristics of sulphur vulcanisation of nitrile rubber in contact with metals

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INTRODUCTION

During sulphur vulcanisation of rubbers on metals complex processes take place in the adhesive contact zone. The first of these that should be mentioned are the transformations involving the sulphur in the crosslinking of the rubber and the sulphidised substrate. Since these transformation occur in parallel, the degree of vulcanisation of the rubber in the layer immediately next to the substrate is normally differentiated from the degree of vulcanisation in the remaining volume of the rubber [1 – 3]. In turn the sulphidisation of the metal changes the rheological conditions for the formation of contact between the materials being bonded and the strength properties of the surface layer of the substrate, and this leads to a change in the adhesion or strength of bonding of the components. It has been assumed [4 – 6] that the anomalously high adhesion of sulphur vulcanisates to brass is due to the mechanical bonding of the rubber in the sulphide film formed on the surface of the substrate.

It should be noted, however, that the data available in the literature are very varied and in fact not one of the published studies examines the participation of sulphur in the reactions of sulphidisation of the metal and crosslinking of the rubber from the perspective of overall consumption of the sulphur. Studies of this kind are extremely important, since even today there is no single accepted opinion regarding the mechanism of formation of adhesion contact or the factors determining the strength of adhesive bonds of sulphur vulcanisates with brass.

EXPERIMENTAL

For our experiments we used an industrial rubber compound based on butadiene-acrylonitrile rubber (Technical Spec. 38.102.1082-86), which was vulcanised in contact with various metal substrates. The thickness of the rubber layer in the adhesive bonds was 0.1 mm. The substrates employed were sheet consisting of L62 brass (State Standard 2208-75) and components of an alloy of copper M1 (State Standard 5638-75) and zinc (State Standard 18846-73). Before applying the rubber mix the substrates were carefully cleaned with acetone. After vulcanisation the specimens were removed from the press and cooled to room temperature.

The part played by the sulphur in the crosslinking of the rubber was evaluated from the degree of swelling of the vulcanisate in a boiling reactive fuel (State Standard 16564-71) for 6 h.

Experiments were carried out to assess the rate of sulphidisation of the substrate. For this the rubber mix was modelled by an emulsion of sulphur in benzene (sulphur content 4% by mass). The sulphidisation was effected by placing a metal sheet in the emulsion, which was heated to the required temperature. The amount of precipitated sulphur was determined from the change in mass of the specimen, and as a characteristic of sulphidisation we used the surface density of the precipitated sulphur.

The formation of a sulphide film directly under the layer of vulcanisate was assessed by the presence of residues of this film on the surface of the vulcanisate after breakdown of the adhesive bond. For this purpose after separation of the adhesive bond the rubber was reduced to an ash, and from the ash we prepared working solutions in which the content of metal-substrate was determined by polarographic analysis [7]. In the experiments we assessed only the copper content, since the residues of zinc sulphide on the failure surface cannot be determined owing to the high content of zinc oxide in the rubber.

Adhesion of the vulcanisate to the substrate was characterised by the peeling resistance of the metal sheet from the rubber layer. Separation was carried out at an angle of 180° and at a speed of 90 mm/min.
Figure 1 shows data on the change in swelling of the vulcanisate as a function of its time of vulcanisation in contact with the substrates. It is clear that the difference in degrees of crosslinking of the vulcanisates is fixed already at the start of vulcanisation. For this stage the activity of the substrates on the crosslinking of the rubber as assessed from the rate of decrease in swelling of the vulcanisate decreases in the order: brass > zinc > copper. During subsequent vulcanisation the zinc and brass change places in their order of activity (see Figure 1).

RESULTS

It may be assumed that the higher the rate of sulphidisation of the metal substrate the lower is the rate of contact vulcanisation of the rubber on the metals, apparently because of the fact that the sulphur varies in its participation in the sulphidisation of the substrates. However, the total consumption of sulphur in the rubber mixes vulcanised on different substrates should remain constant.

To confirm this theory we assessed the activity of sulphur in the sulphidisation of the different metals. As indicated above, the rubber mix was modelled by a suspension of sulphur in benzene. It is clear from Figure 2 that the rate of precipitation of the sulphur depends on the nature of the substrate. The sulphur is precipitated more rapidly on the copper (see Figure 2, curve 1), but in this case a thick and brittle film is formed which low mechanical strength and is easily separated from the substrate. In comparison with the copper the sulphidisation of zinc and brass takes place fairly slowly, and here the amount of sulphur precipitated (temperature of the emulsion 100°C) is practically unchanged with time (see Figure 2, curves 4 and 5). At a high precipitation temperature (boiling benzene, 137°C) there is a continual increase in mass of the sulphide layer (see Figure 2, curves 2 and 3). Irrespective of the temperature of sulphidisation the rate of precipitation of sulphur on zinc is higher than its rate of precipitation on brass. In order of decrease in the rate of sulphidisation the substrates can be ranked as follows: copper > zinc > brass. It is notable that it is in this same order that the activity of the substrates increases with regard to crosslinking of the rubber in the initial stage of vulcanisation (see Figure 1). Thus, the data obtained seem to show that during vulcanisation of rubber mixes on substrates of differing activity the total consumption of sulphur is the same: the greater the amount of sulphur that is expended on sulphidisation of the substrate, the smaller is the amount that participates in crosslinking of the rubber.

The sulphide layer formed in the emulsion is not very strong, and with repeated treatment (up to 10 min) in boiling benzene a significant proportion of the precipitated sulphur is washed off. For instance, in the sulphide layer on brass the amount of sulphur removed reaches 90%.
The differences in the rates of sulphidisation of the substrates under the layer of vulcanisate can be observed from the character of failure of the rubber-metal adhesive bonds. It has been shown that failure takes place in the sulphide layer forming during vulcanisation, and the surface of the vulcanisate shows traces of this layer. Figure 3 shows data on the change in surface density of copper on the vulcanisate as a function of the time and temperature of vulcanisation of the rubber mix on substrates of copper and brass. The dependences take the form of curves with saturation. The content of copper on the surface of the rubber vulcanised in contact with the copper substrate is higher than it is on the surface of the rubber in contact with brass. As the temperature of vulcanisation is reduced the amount of copper remaining on the surface of the rubber decreases, but in order of activity in the process of sulphidisation the relative positions of the substrates (copper and brass) are retained.

It is noteworthy that in terms of the rate of sulphidisation the brass substrate does not occupy an intermediate position between the copper and zinc (components of brass); it appears that the sulphide layer on the brass is formed anomalously.

Also anomalous is the change of adhesion during vulcanisation of the rubber in contact with brass. The curve of the separation resistance of the bond between the rubber and brass vs time of vulcanisation (100°C) shows a clear maximum with an absolute value in the region of 5–6 kN/m (see Figure 3, curve 5). By the time of completion of vulcanisation he adhesion of the rubber to the brass stabilises at a value of about 1 kN/m. Under the same conditions the adhesion in bonds based on copper and zinc does not exceed 0.5 kN/m. The anomalous increase in adhesion in bonds of rubber with brass is found only in a limited range of vulcanisation temperatures. For instance, in bonds between rubber and brass formed at 150°C the adhesion is low, and at all stages of vulcanisation it is intermediate between the adhesion in bonds of rubber to copper and zinc (see Table 1). Additional research is required to elucidate this phenomenon.

![Figure 3](image)

**Figure 3** Dependence of (a) the surface density of copper and (b) of the adhesion on the time of vulcanisation of the rubber mix on copper (curves 1, 2 and 7), brass (curves 3-5) and zinc (curve 6) substrates at temperatures of 100 (curves 2, 4 – 7) and 150°C (curves 1 and 3)

### REFERENCES

1. V.P. Zakharov et al., Kauch. i Rezina, No.11, 1987, p.31.

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<th>Substrate</th>
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