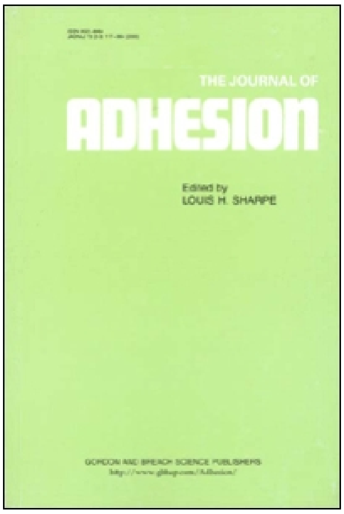

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The Influence of the Cation in Organometallic Boroacylate Adhesion Promoters on the Adhesion Between Steel Cord and Skim Rubber Compound

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The influence of transition metal cations (cobalt, nickel and zinc ion) associated with organometallic boroacylate adhesion promoters on the adhesion between brass-coated steel cord and rubber skim compound under the influence of various environments, which simulate tyre service conditions, has been studied.

Incorporation of adhesion promoters individually in the steel cord-skim formulation leads to increase in crosslink density, Young's modulus and cord pull-out force. The adhesion energy is enhanced significantly with the addition of cobalt adhesion promoter. The performance of the promoter is influenced by the ease of dissociation of the transition metal ion from the promoter, its participation in the rubber curing and the modification of the interfacial film responsible for adhesion. During aerobic ageing, cobalt followed by nickel is found to be effective, whereas cobalt and, partially, zinc salts offer certain resistance to thermal ageing. Against salt and steam ageing, cobalt boroacylate is very effective followed by zinc salts. The influence of the variation of concentration of zinc ion on adhesion energy is not appreciable. The study points towards the supremacy of cobalt ion among the cations studied, considering its overall good performance and the protection offered against various hostile environments.

KEY WORDS: Steel cord; brass coating; organometallic boroacylate salts; cobalt; zinc; nickel; adhesion; adhesion promoters; rubber; effects of environmental ageing.

INTRODUCTION

The effectiveness of brass-coated steel cord reinforcement in enhancing tyre performance depends directly on the strength of the cord-rubber adhesion attained during tyre vulcanisation and on its durability in service on the road. Two main groups of adhesion promoters, a resin former (SRH-Silica, Resorcinol and Hexamethyl melamine system) and an organometallic adhesion promoter (mainly organic cobalt salt), either individually or jointly, are used in the rubber compound in order to

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*Corresponding author.

obtain adequate adhesion and reduce the deleterious effects of corrosion process encountered by the brass coating under different hostile environments.[1-7] Better bonding and durability are achieved when both systems are used simultaneously.[8,9]

Incorporation of cobalt promoter greatly enhances the adhesion energy, influences the compound properties, crosslink density, vulcanisation kinetics and rheological behaviour of standard steel cord formulation.[10-13] Several authors[14-18] studied the influence of these popular systems on the static and dynamic adhesion between rubber and brass-coated steel cord. The use of these cobalt salts has increased rapidly due to increased production of steel-cord-reinforced radial tyres and also to the wider acceptance of this system because of improved performance which it imparts to tyres. This has caused concern over the continuity of the supply of the cobalt adhesion promoter and its price stability. Because of this, it is necessary to seek actively suitable alternatives for cobalt adhesion promoter.[19] Replacing the cobalt resin system by chlorotriazines[20,21] or partial replacement of cobalt by post-vulcanisation stabilisers[22] have been pursued. Another direction is to replace these cobalt salts partially or completely by other organometallic complexes of similar transitioin metals. Metals which have attracted interest include nickel, zinc, zirconium, tin, iron and manganese.[19] The effect of these systems on the static adhesion between brass-coated steel cord and rubber was investigated mainly using the ASTM D 2229 pull-through test.[23] The major disadvantage with this test method is that the rubber is largely sheared between the central cord and an external clamp or holder and no part of the rubber block is subjected to simple extension. Moreover, the initial site and mode of propagation of a debond are not well defined. Failure initiates at either end of the cord and propagates inwards by cracking of the matrix or by a complex process.[10,24] Survey of the literature revealed that no systematic study had been carried out on the influence of the cation in organometallic boroacylate (among all the anions, boroacylate established its supremacy)[10] on the static adhesion between steel cord and rubber skim formulation. The objective of this article is to examine these effects on adhesion energy between brass-coated steel cord and rubber compound under different ageing conditions using the "Tire Cord Adhesion Test (TCAT)" method. The TCAT-method is chosen for energy calculation due to its simplicity, reproducibility and fundamental nature and for the fact that it offers a useful method for determining the interfacial energy of a given cord-rubber system.[25-27]

THE ORETICAL CONSIDERATIONS

Gent *et al.*[27] and Fielding-Russell *et al.*,[25,26] observed that the cord pullout force (F) of a TCAT-test specimen is directly proportional to the Young's modulus (E) of the rubber, the cross-sectional area of the specimen (A), the radius of the cord (r) and the adhesion energy (G_a), *i.e.* the energy required to fracture unit area of the rubber-cord interface. The cord pullout force, F, is governed by the following equations:

$$F = (4\pi r\, E\, A\, G_a)^{1/2} \tag{1}$$

or

$$G_a = \frac{F^2}{4\pi r\, E\, A} \tag{2}$$

Equation (2) is based on the assumptions that the cords are inextensible, the rubber block follows a simple stress-strain relation in extension, the cross-sectional area of the cord is small in comparison with the rubber block and the cord embedment length is large. In our earlier communication, this equation has been successfully applied.[10]

The interfacial debonding energy is being considered in this paper since it is independent of the test piece parameter.[9]

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

The materials used for these experiments are presented in Table I.

TABLE I
Materials used for the study

Materials	Grade	Suppliers
Natural rubber	RMA-4	Kerala, India
Methylene donor	Cohedur-A	Bayer AG, Germany
Homogeneous solidified melt of resorcinol and stearic acid in the ratio of 2:1 (Methylene acceptor; Resorcinol component)	Cohedur-RS	-ditto-
N-phehyl-N′(1,3-dimethyl butyl)-p-phenylene diamine	Vulkanox-4020 (Antioxidant-6PPD)	-ditto-
N, N-dicylohexyl-2- benzothiazole sulphenamide	Vulkacit-DZ (Accelerator DCBS)	-ditto-
Hydrated silicon dioxide (Pptd. silica)	Ultrasil-VN3	Degussa AG, Germany
Octyl phenol formaldehyde resin		CECA, SA, France
Insoluble sulphur (20% highly non-staining naphthenic oil treated)	Crystex OT-20 OT-20	Kali Chemical, Germany

Organometallic Adhesion Promoters*

Name	Metal content (%)	Grade
Cobalt boroacylate	23.0	Manobond 680 C
Nickel boroacylate	6.0	Manocat NBA
Zinc boroacylate	16.0	EP 9165

Steel Cord
Style-7 × 4 × 0.2 mm** Tokyo Rope, Japan
Lay length (direction), mm-10S/14Z
Plating composition-67.5 ± 1.0% Cu; 32.5 ± 1% Zn
Plating density-6.0 ± 0.5 gm/kg
Nominal diameter-1.5 mm***

*All these organometallic promoters were supplied by Manchem Ltd. (UK)

**This cord is basically a commercial truck tyre cord. The convention used in wire and tyre industries is followed for writing construction.

***The "Effective Cord Diameter" of the multifilament cord was measured using micrometer, assuming close packing as shown in Figure 1.

Other chemicals, not included in the Table, were received from the standard Indian Suppliers. A complete list of the rubber mixes used in the present investigations along with their Mooney viscosity, cure characteristics and the physical properties are shown in Table II.

Mixing and Processing

Mixing was carried out in three stages using a Laboratory Banbury of capacity 1.2 kg (batch weight) from Stewart Bolling, USA, having a 2-wing rotor (model # 00). All ingredients except the organometallic adhesion promoter, methylene donor and vulcanising agents were mixed in the masterbatch stage. In the next stage, these batches were remilled in the Banbury. The remaining ingredients were added in the final stage. The batches were sheeted out using a laboratory 2-roll mixing mill and covered with polyethylene film. The laboratory Banbury mixing conditions are shown in Table III.

Cure characteristics of the specimens were studied using a Rheometer (Monsanto MDR-2000) at a temperature of 141°C. Mooney viscosity (ML_{1+4} at 100°C) was determined using a Monsanto Mooney viscometer (MV-2000) as per ASTM D 1646.

TABLE II
Formulations and characterisation of mixes

Ingredients (parts of metal ion per hundred parts of rubber)	Mix Number							
	A	A′	B	C	D	D_1	D_3	D_4
Cobalt boroacylate	—	—	0.25	—	—	—	—	—
Nickel boroacylate	—	—	—	0.25	—	—	—	—
Zinc boroacylate*	—	—	—	—	0.25	0.15	0.35	0.45
Properties								
Mooney viscosity (ML_{1+4} at 100°C)	85.3	73.9	89.3	77.2	83.9	84.7	83.8	84.4
Scorch time (t_2), min	5.5	6.8	5.2	6.3	6.2	5.9	6.5	6.8
Optimum cure time (t_{90}), min	38.6	34.7	28.7	35.0	40.4	38.9	41.3	42.6
Reversion (t_{98}) (after crossing maximum), min	>120	86	75	77	95	99	93	91
Cure rate, dN.m/min	0.72	0.72	1.20	0.92	0.75	0.78	0.74	0.71
V_r	0.286	0.269	0.299	0.302	0.303	0.299	0.303	0.302
Young's modulus (MPa)	7.0	5.9	7.4	8.4	7.3	7.3	7.5	7.6
Energy to break (KJ/m^2)	22.4	27.5	14.1	16.9	24.0	25.0	21.7	21.0

All mixes contain (in phr), NR-100; Peptiser (activated PCTP)-0.1; carbon black (HAF, N330)-60; Aromatic oil-6; Cohedur RS-3.5; PPtd. silica-10; ZnO-10; Stearic acid-0.25; 6 PPD-2.0; P.F. resin-2.5; Insoluble sulphur-6.0; DCBS-1.0; Cohedur-A 2.25; except A′, which do not contain Cohedur-RS; pptd. silica and Cohedur-A, *i. e.*, SRH-system and in addition, in case of A′ the stearic acid dosage is 1.4 (considering the stearic acid contribution from Cohedur-RS in other formulations).

*Concentration of Zn-ion throughout the text will signify the concentration of Zn-ion contributed by Zn-boroacylate by Zn-boroacylate only

TABLE III
Mixing parameters

Mixing Parameters	Master	Remill	Final
Mastication time. (min)	1.0	—	—
Temperature control unit setting, (°C)	90	90	70
Rotor speed (rpm)	30	30	30
Ram pressure (MPa)	0.5	0.5	0.5
Ram scraping (kWh)	0.1, 0.2, 0.3	0.05	0.12
Power integrator setting for dumping (kWh)	0.42	0.12	0.18

Moulding and Ageing of TCAT-Specimen

The different rubber mixes shown in Table II were utilised for preparing "Tire Cord Adhesion Test (TCAT)" specimens having dimensions 10.0 mm × 12.0 mm × 50.0 mm (Fig. 2) by a compression-moulding technique, in a specially-designed six-cavity mould.

In our earlier work,[10] pullout force was measured after random variation of the cord embedment length in a control rubber compound with the SRH-system. The pullout force (F) and the adhesion energy (G_a) were found to be almost independent of embedment length (l) at lengths above about 20 mm. Below 20 mm, however, the pullout force increased with increase in the embedment length due possibly to higher volume of the rubber deformed and, hence, larger dissipation of energy. To overcome those problems of dependence of pullout force and adhesion energy on cord embedment length, the latter was kept at 21.0 mm throughout the experiment.

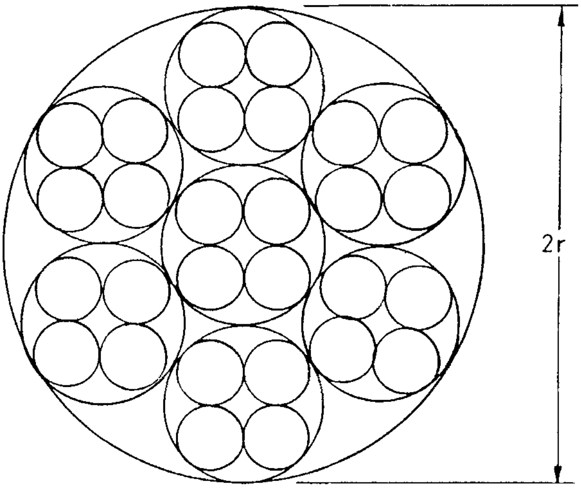


FIGURE 1 Diagram illustrating cord diameter (2r).

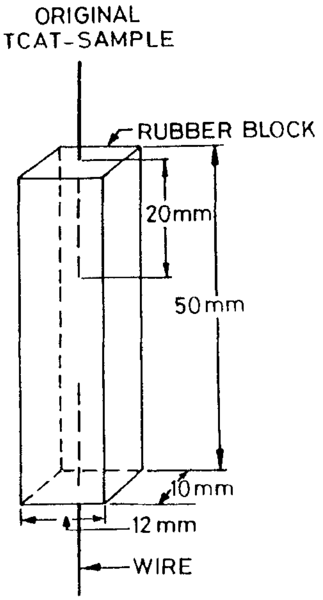


FIGURE 2 TCAT pullout test specimen.

TABLE IV
Different ageing conditions and their simulated effects

Parameter combination	Test	Test conditions	Simulation of
Time and temperature	Thermal ageing (i e.. anerobic ageing)	Curing TCAT samples at 141°C for 2, 4, 8 and 16h	Ageing of steel cord skim compound during service
Time, temperature and air	Heat ageing in presence of air (aerobic ageing)	Heat ageing in a multicell ageing oven at 70°C for 1, 2, 3 and 4 weeks	Proceeding of ageing during tyre service and retreading
Time, humidity and temperature	Steam ageing	Ageing in presence of steam having 0.3 MPa pressure at 120°C for 8 h in an autoclave	Humid conditions during tyre service
Time, humidity and aggresive media	Salt ageing	TCAT samples were immersed in 10% NaCl solution for 14 days at 25 ± 2°C temperature	Winter road conditions

For aerobic, salt and steam ageing TCAT-samples cured at 141°C for 2 h were considered.

TCAT-specimens were cured at 141°C and 15MPa pressure for 2, 4, 8 and 16hrs to simulate the ageing of the steel cord skim rubber compound in a tyre under anaerobic conditions.

To see the deleterious effect of different ageing environments on the rubber-to-steel-cord interface, TCAT-specimens were subjected to different environments (Table IV). The parameters involved in tyre ageing simulation testing were temperature, time and presence of aggressive media.

Details of mixing and moulding of TCAT-specimen were described in our previous publication.[10]

Testing

Young's modulus Young's modulus of the rubber compounds cured to different extents was determined from the slope of the initial linear portion of the stress-strain curves obtained using a Zwick Universal Testing Machine (model 1445) at a crosshead speed of 50 mm/min at 25 ± 2°C.

Mechanical properties and volume fraction of rubber Compound rupture energy or energy to break was determined from the area under the stress-strain curve at a crosshead speed of 50 mm/min at 25 ± 2°C using the Zwick Universal Testing Machine. Vr (volume fraction of rubber in the swollen vulcanisate) was considered as a measure of crosslink density and calculated using the method described by Ellis and Welding.[28] The swelling measurement was carried out in toluene at 25°C for 72hrs, when equilibrium was attained using the procedure described earlier.[11]

Adhesion testing For measurement of the pullout force, the two opposite axial free cord ends of the TCAT-samples were clamped in a Zwick Universal Testing Machine and pulled at a rate of 50 mm/min at 25 ± 2°C. Initially, only the block deformed but, at a critical load, one of the cords was pulled out. The pull-out force was the maximum value obtained during testing, which occurred in a short, approximately constant, region before the force dropped rapidly to zero. Each value reported was the average of six specimens. In order to check the reproducibility, statistical analysis of the data was carried out. The values of pull-out force for the samples A, A′, B, C and D are given in Table V. Each set consisted of six readings

TABLE V
Typical pull-out force data

	Mix Code				
No. of obs.	A	A′	B	C	D
1	735	629	832	760	736
2	727	634	820	757	730
3	730	627	816	770	742
4	737	630	831	761	745
5	733	636	826	765	741
6	730	630	819	765	740
Mean pull-out force, F(N)	732	631	824	763	739
Standard deviation (S)	3.37	3.06	6.08	4.20	4.83
Coefficient of variation (C.O.V. = S/F × 100)	0.460	0.485	0.738	0.550	0.654
Minimum	727	627	816	757	730
Maximum	737	636	832	770	745
Range of pull-out force	10	9	16	13	15

Compound curing temperature = 141 °C, Cure time = 2.0 h, Cord embedment length = 20 mm.

and was considered representative. The mean values of pull-out force (F), the standard deviation (S) and the coefficient of variation are also summarised in the table. The coefficient of variation ($V = 100\ S/F$) is reasonably low and the reproducibility of the data is quite good.

RESULTS AND DISCUSSION

Characterisation of Compounds

The properties of the formulations used in this study are shown in Table II. The incorporation of the SRH-system in the skim formulation has drastically increased the compound's Mooney viscosity (Mix Nos. A and A'). The SRH-system, forming a polar resin, presumably is mainly responsible for this.[8] A mixed action of organometallic adhesion promoter on Mooney viscosity is observed.

The presence of the SRH-system enchances the Vr values substantially. They are further boosted by the boroacylate salts. The extent of the increase is highest with Zn-ion (well known for its accelerator activating effect in sulphur vulcanisation systems) followed closely by nickel and cobalt ion.

The mechanical properties are also affected to various extents by these promoters. For example, Young's modulus shows about a 5–20% increase. These data will be discussed later to explain the adhesion results.

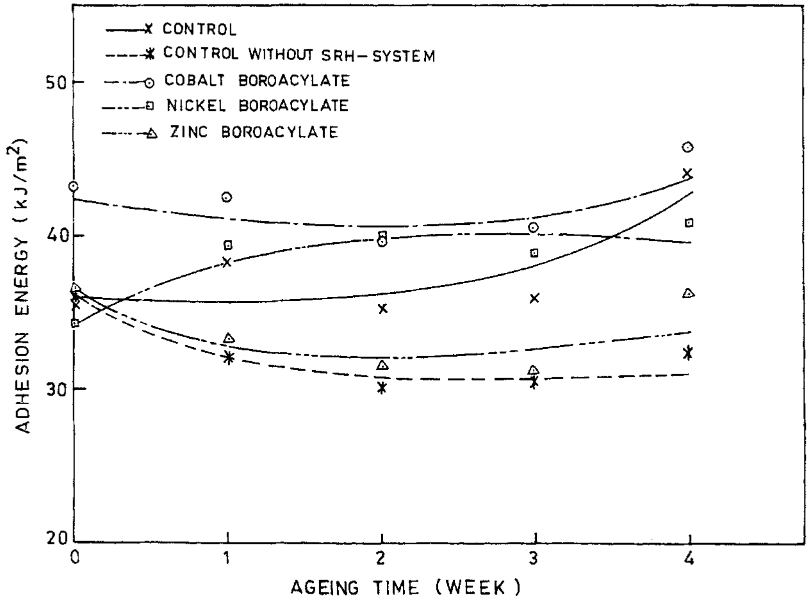
Adhesion Energy

Adhesion energy of various joints and the effect of aerobic ageing The influence of aerobic ageing on the adhesion energy of the vulcanisate without and with the SRH-system in the absence or presence of organometallic boroacylate with different cations is shown in Figure 3a.

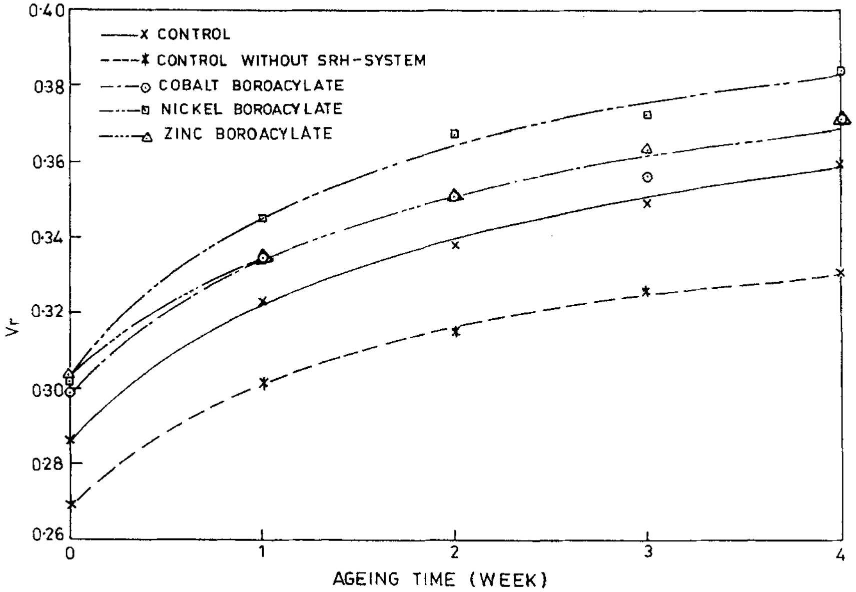
With the incorporation of adhesion promoters the extent of changes in adhesion energy for the unaged samples are comparable except with cobalt boroacylate. Incorporation of cobalt promoter has increased the adhesion energy substantially.

With ageing time, there is a tendency of the adhesion energy to increase at long times. With the zinc boroacylate system and the control without the SRH-system, the adhesion energy decreases marginally in the initial stages.

Vr of all the compounds increases gradually with ageing time (Fig. 3b). These values are higher in the presence of the SRH-system compared with the control without any promoter and are further increased when boroacylate salts are added. The highest increase is noticed in the presence of nickel salts followed by comparable values for cobalt and zinc. Comparatively higher values of Vr in the presence of promoter is due to the influence of these promoters on the crosslinking reaction. Young's modulus, a property dependent on Vr, behaves in a similar fashion (Fig. 3c). It is also observed that the adhesion energy (30 kJ/m^2 to 45 kJ/m^2) is much higher than the corresponding compound rupture energy (3 kJ/m^2 to 28 kJ/m^2) *i.e.*, the energy to break (Fig. 3a *vs*. Fig. 3d). As a result, during the cord pullout test cohesive failure of the rubber occurs. Hence, Young's modulus, Vr and pullout force



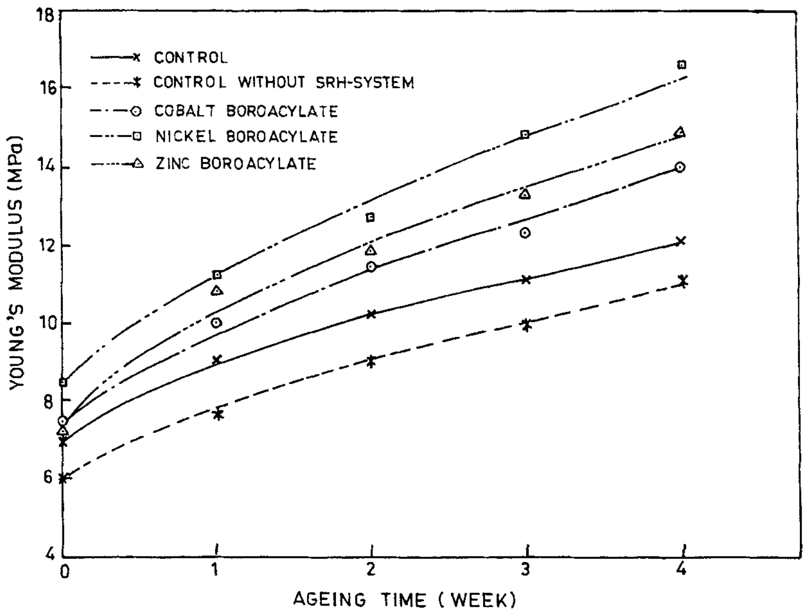
(3a)



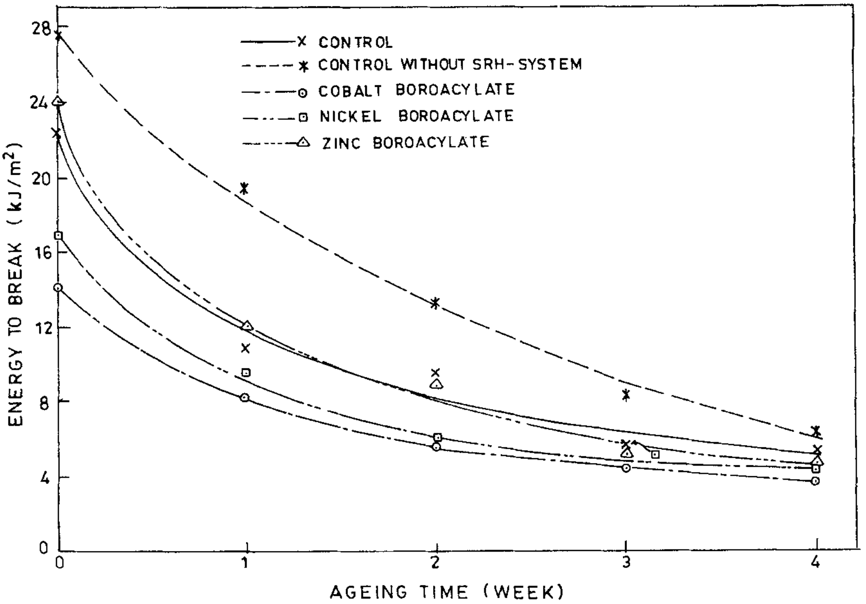
(3b)

all increase with ageing time in a similar fashion. However, due to disproportionate changes of the pullout force with Young's modulus, the nature of the variation of the adhesion energy with ageing time is different (*c.f.* Figs. 3a and 3e).

A plot of the cord pullout force against Young's modulus shows an almost linear relationship. A representative plot of pullout force against Young's modulus of the



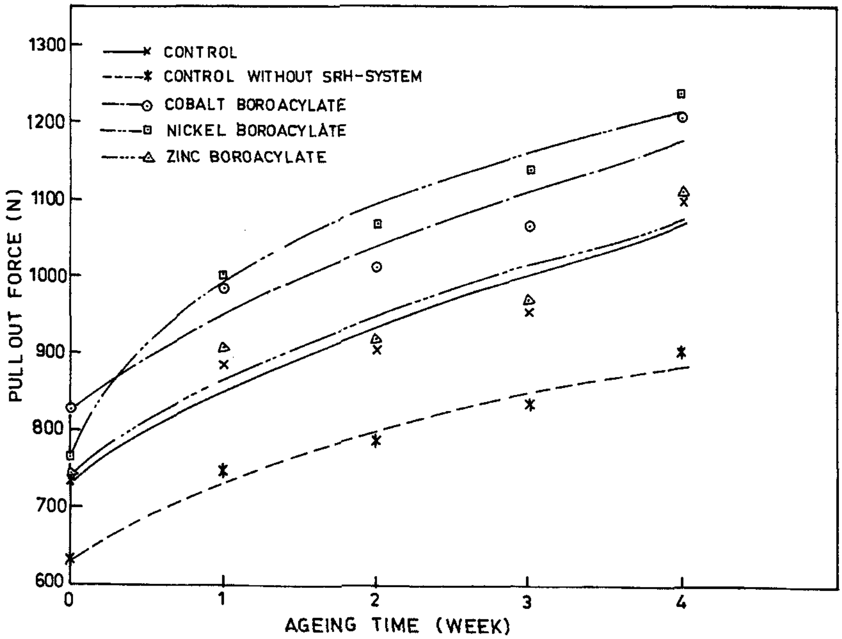
(3c)



(3d)

compound containing nickel boroacylate (Mix No. C) is presented in Figure 4. This correlation points towards cohesive rubber failure during the pullout test.

That the failure is mainly cohesive in nature is further supported by a SEM study conducted in our earlier work.[10,17] Cobalt boroacylate (Mix No. B) was selected as



(3e)

FIGURE 3 Influence of aerobic ageing on vulcanisates without and with SRH-system in absence or presence of organometallic boroacylate with different cations. (a) Adhesion energy; (b) degree of crosslinking, Vr; (c) Young's modulus; (d) Energy to break and (e) pullout force.

being representative of the other promoters and the fracture features were compared with the corresponding reference compund (Mix No. A). The SEM study clearly indicates that the failure was mainly cohesive and random in nature.

The observed effects of these adhesion promoters depend on the following major factors:

* Migration of polar SRH-systems to the brass surface, which affects bonding by influencing the sulphidation reaction.[8]
* The stability of the organometallic adhesion promoter and release of the transition metal ion from the promoters. This may depend on the atomic/ionic radii of the metal.
* Participation of the transition metal of the organometallic adhesion promoter in different steps of the cure reaction. Its reactivity depends on the electron distribution in the d-orbital.
* The changes in properties of the rubber compounds.
* The modifications of the interfacial film of reaction products.
* In addition to the above, the zinc ion already present in the matrix is playing its usual role.[12]

The poorest performance of the zinc ion may be related to its accelerator activating effect which is well known, especially in sulphur vulcanisation systems. During vulcanisation, the zinc ion reacts with the sulphur, accelerator and stearic acid to aid

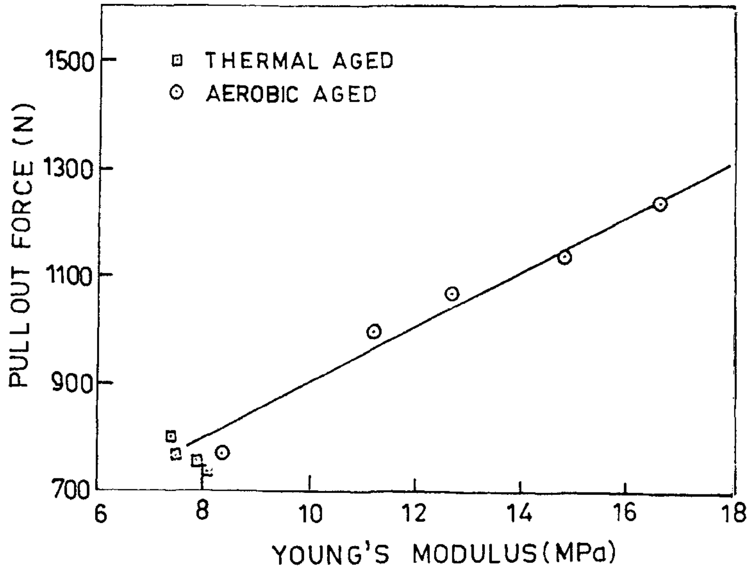
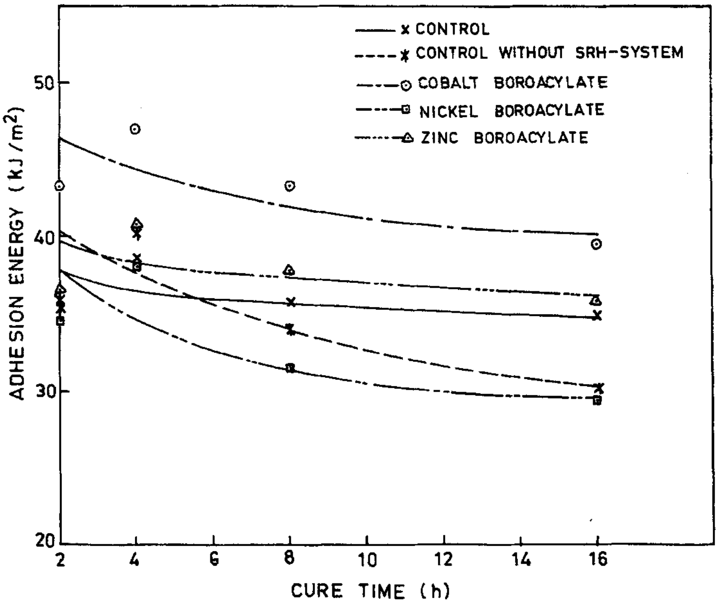


FIGURE 4 Relationship between cord pull out force and Young's modulus of aerobic and thermal aged compounds containing nickel boroacylate.

in the formation of crosslinks. As a result, the sulphur and the promoter are possibly used more efficiently for modification of the rubber rather than for the interfacial film on the brass.

Effect of thermal ageing The effect of overcuring or anaerobic aging on the adhesion energy is shown in Figure 5a. The adhesion energy decreases continuously with overcuring. However, the reduction in adhesion energy is very fast in the case of the reference compound without the SRH-system. The compound containing the SRH-system and the organometallic promoter individually or jointly offers a certain degree of protection against deterioration of adhesion owing to the overcuring. Nickel boroacylate behaves similarly to the reference compound without any SRH-system, due to the reasons described in the following sections.

Vr of all the compounds and Young's modulus, a property dependent on Vr, show similar behaviour (Figs. 5b and 5c). These properties are reduced rapidly in the initial stages. The pullout force of the compounds is reduced slowly with cure time (Fig. 5d). The lowest pullout force is noticed in the case of the reference compound without any type of promoter. The presence of both the SRH-system and organometallic adhesion promoter offers the lowest drop in the pullout force even on prolonged curing. The highest pullout force is observed in the presence of boroacylate salts of cobalt followed by nickel and zinc. The changes in these properties (*e.g.* Vr., Young's modulus and pullout force) with cure time are similar, although the reduction of Vr and Young's modulus with cure time is found to be relatively high when compared with the corresponding reduction in the pullout force with overcuring. As a result, the pullout force does not maintain a linear relationship



(5a)

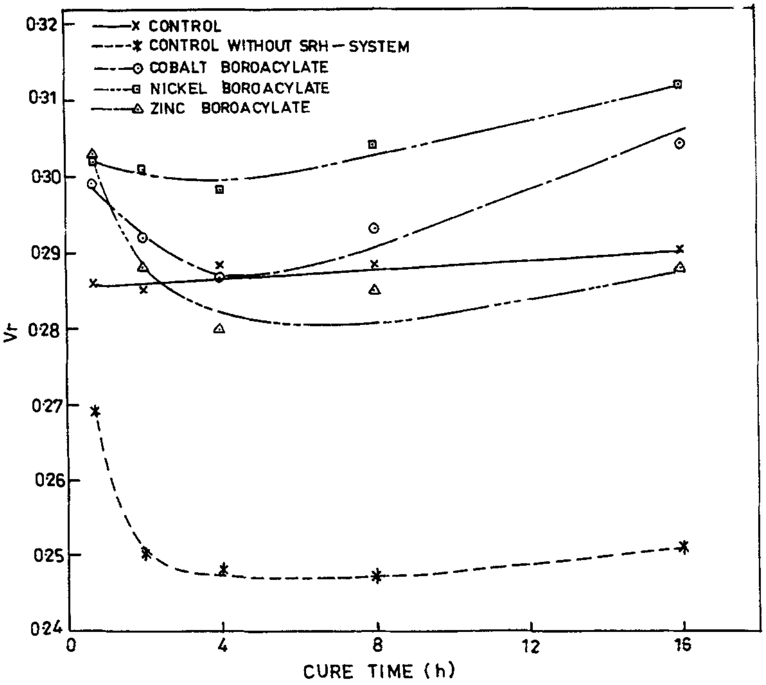
with Young's modulus as observed in the case of aerobic ageing (Fig. 4). Consequently, adhesion energy shows the behaviour in Figure 5a. However, such a relationship would be expected in the case of 100% cohesive rubber failure.

It is observed that the adhesion energy of the compound (30 kJ/m^2 to 48 kJ/m^2) is appreciably higher than the corresponding compound rupture energy (9.5 kJ/m^2 to 27.5 kJ/m^2) under similar conditions (Figs. 5a and 5e). This, inturn, should lead to cohesive failure of the compound during pullout, However, compared with aerobically-aged samples, the corresponding compound rupture energies are always much higher in the case of thermally-aged samples. Possibly this has shifted 100% cohesive failure of rubber to other of the following possible modes of failure as suggested by Van Ooij *et al.*[14]:

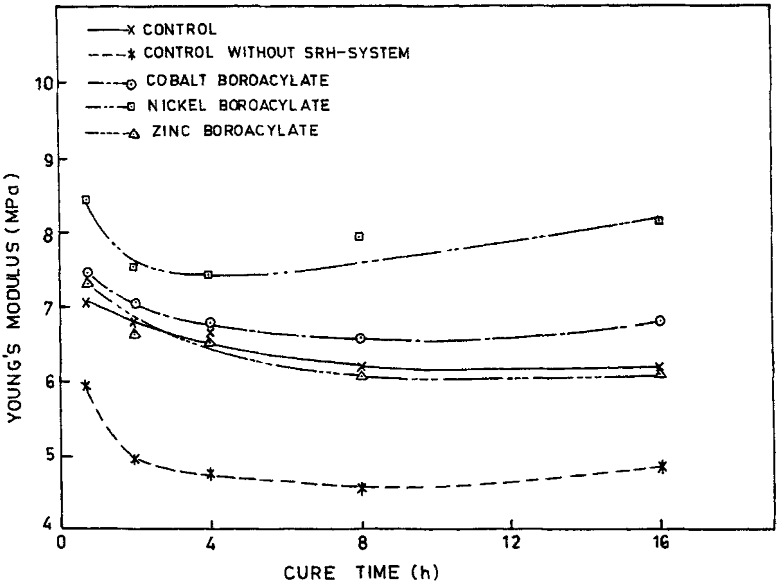
— cohesive failure of the rubber
— adhesive failure of the sulphide-rubber interface
— cohesive failure of the sulphide layer
— adhesive failure at the sulphide-ZnO interface
— adhesive failure of the ZnO-metal interface

That the failure at the brass-rubber interface is higher in the case of thermally-aged samples was also noticed during our earlier work on steel cord-rubber adhesion both under static and dynamic conditions[10,16] and in SEM studies of the failed steel cord-rubber interface.[17]

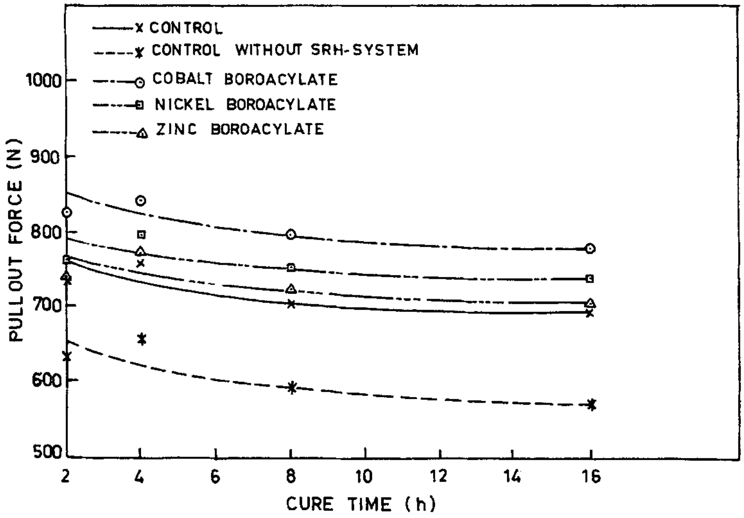
The highest adhesion energy is noticed in the presence of the cobalt system and lowest in the presence of the nickel system. The above observations can be explained on the basis of previous XPS studies of the failed rubber-metal interface.[4,15] The


CONTROL
CONTROL WITHOUT SRH—SYSTEM
COBALT BOROACYLATE
NICKEL BOROACYLATE
ZINC BOROACYLATE
Vr
0·32
0·31
0·30
0·29
0·28
0·27
0·26
0·25
0·24
0
4
8
12
16
CURE TIME (h)

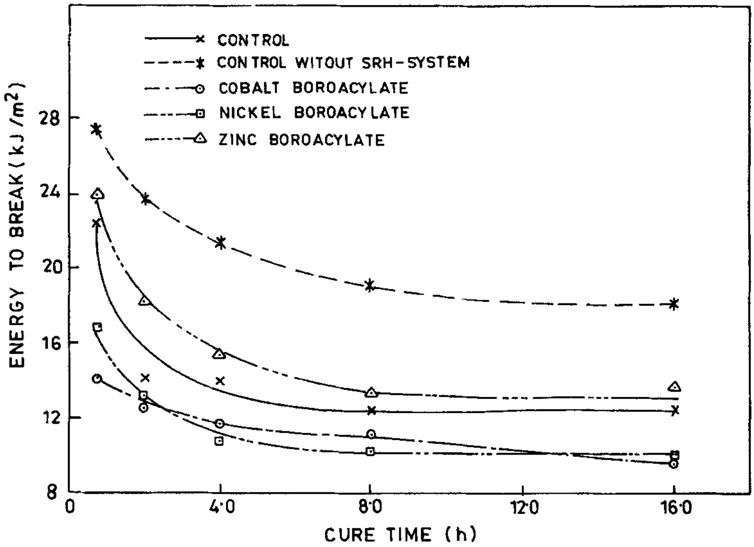
(5b)


CONTROL
CONTROL WITHOUT SRH-SYSTEM
COBALT BOROACYLATE
NICKEL BOROACYLATE
ZINC BOROACYLATE
YOUNG'S MODULUS (MPa)
10
9
8
7
6
5
4
0
4
8
12
16
CURE TIME (h)

(5c)



(5d)

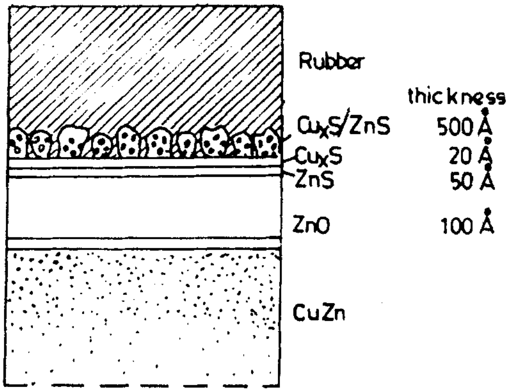


(5e)

FIGURE 5 Influence of thermal ageing on vulcanisates without and with SRH-system in absence or presence of organometallic boroacylate with different cations. (a) Adhesion energy; (b) Degree of cross-link, Vr; (c) Young's modulus; (d) Pull out force; and (e) Energy to break.

interface is assumed to consist of layers of the following: Cu/Zn, ZnO (~100 Å), ZnS (~50 Å), Cu_xS (~20 Å), Cu_xS/ZnS (~500 Å) and rubber, respectively (Scheme 1).

It has been reported that there is a minimum critical thickness of Cu_xS for maximum adhesion as well as a maximum thickness above which the adhesion strength begins to drop. The nature of the brass-rubber interface does not differ



SCHEME 1 Schematic of rubber to brass interface (Refs. 4, 15).

much with the addition of the boroacylate salts to the reference compounds. The organomatallic complex dissociates to form M^{2+} ions at the interface during curing and affects the Cu_xS layer formation during vulcanisation. The ease with which this happens depends on the type of the complex. This is directly related to the efficiency of the adhesion promoter and dictated by the interplay of the factors already mentioned during discussion of the influence of aerobic ageing. During our XPS studies,[15] we noticed that the ratio of Cu to Zn increased in the presence of cobalt promoter. This clearly indicates that cobalt salts act to inhibit or retard the formation of ZnS at the cord interface and rapid formation of Cu_xS is, therefore, stimulated. Cobalt is presumbly present as Co^{3+} in a ZnO lattice and reduces electrical conductivity and the diffusion rate of Zn^{2+} ions through the semiconducting film, *i.e.* the migration of these ions to the surface may be retarded. Consequently, once the cobalt salt is used up, the initial formation of ZnS at the cord surface is suppressed and the rapid formation of Cu_xS is stimulated. Cobalt may also act to increase the surface area of the copper inclusions. All these are in favour of the better bonding which normally takes place in the presence of cobalt promoters.[10]

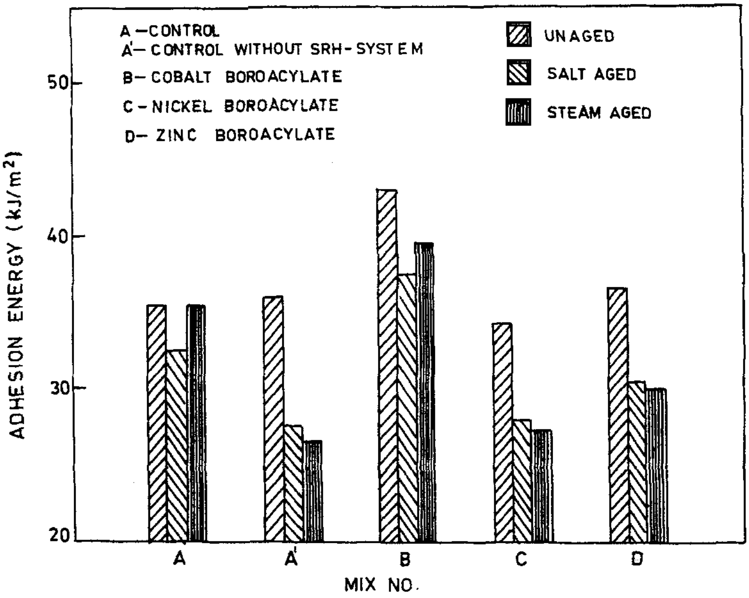
Basically, nickel and cobalt, both being members of the transition metal group, are expected to behave in the same fashion. Even the presence of Ni^{3+}, like Co^{3+}, is found in the same layer of Cu/CuO and ZnO/ZnS at the steel cord-rubber interface. However, the presence of nickel discourages the sulphidation reaction, leading to a thicker ZnO layer.[15] This ZnO layer is of paramount importance, in the sense that this layer determines the interfacial reactions as well as modifies its defect structures. ZnO, being a weak boundary layer, leads to poor adhesion when the thickness is large.[4,29]

Zinc ion plays an important role in the adhesion of rubber to brass. Normally 10 phr of ZnO is suggested to achieve optimum adhesion.[30,31] As more ZnO is available (up to a certain optimum level), the attack of the vulcanising agents on the ZnO of the brass-coated steel cord is reduced and the adhesion is improved. After the optimum dosage, probably the ZnO layer on the brass-coated steel cord is overgrown which is detrimental for adhesion. In the presence of this 10 phr of ZnO loading in the formulations in our study, the Zn^{2+} ion from zinc boroacylate has an intermediate influence on the formation of the Cu_xS layer, leading to an adhesion energy in between cobalt and nickel-based boroacylate salts. Basically, the M^{3+} ions from organometallic boroacylates have an effect on the amount of Cu_xS formed during rubber cure. As a result, the Cu/Zn ratio changes when we go deeper down from the steel cord surface and it is different for promoters containing different cations.

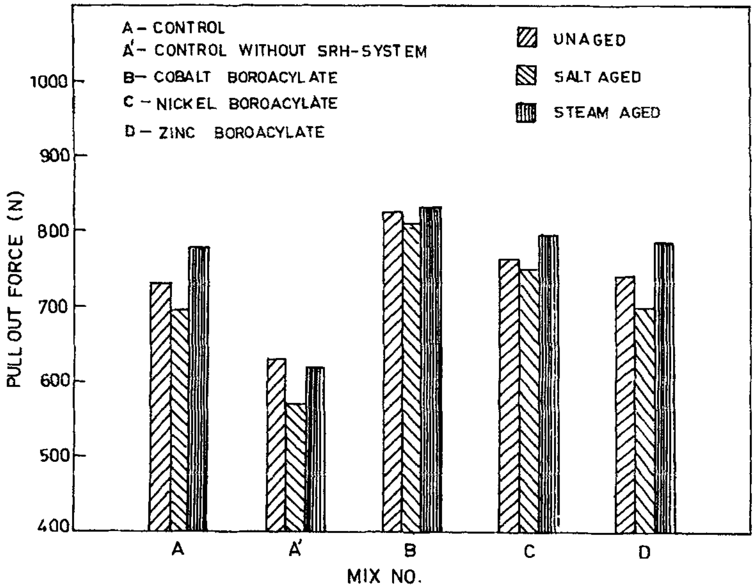
Now, it appears quite reasonable that out of the CoS, NiS or ZnS layer formed (due to the presence of corresponding boroacylate salt) at the rubber-metal interface (which is absent in the reference compounds), the CoS formation offers the highest protection of the Cu_xS layer from further degradation during thermal ageing.

Salt and steam ageing The adhesion energy of different formulations after salt and steam ageing is compared directly with that of the unaged sample. The results are presented in the form of a bar graph in Figure 6a. Incorporation of cobalt boroacylate has markedly improved the initial adhesion; the reason has already been discussed earlier. However, this improvement is unable to prevent degradation due to salt and steam ageing. Salt and stream ageing have comparable effects except in the case of the reference compound with the SRH system in the absence and presence of cobalt boroacylate. In the latter two cases, salt ageing is more detrimental than steam ageing. This behaviour will be well understood if we analyse the corresponding pullout force (Fig. 6b), Young's modulus and Vr (Figs. 6c and 6d). However, no direct correlation is noticed between the pullout force and other physical properties. This is basically due to a mixed mode of failure as a consequence of the dezincification reaction and its effect on adhesion energy *vis-a-vis* the influence of salt and steam ageing on the rupture energy of the rubber compound (Fig. 6e).

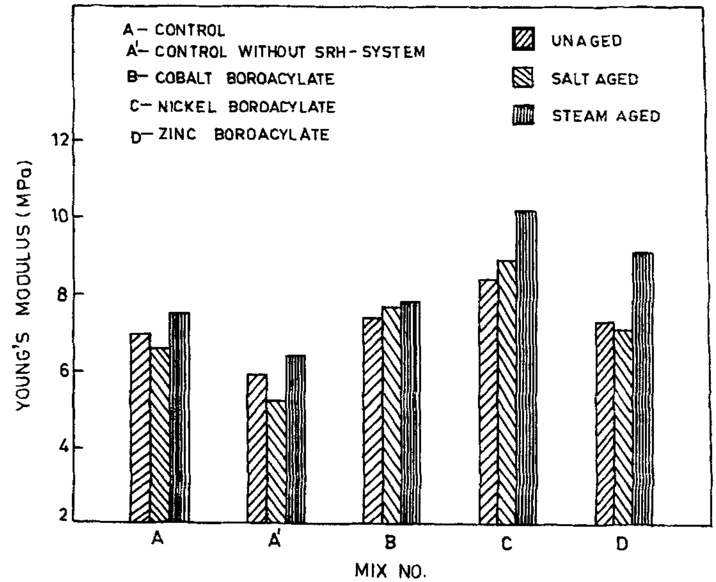
The higher pullout force in the presence of the polar SRH-system is due to the increased stiffness and Young's modulus of the compound and not to increased



(6a)



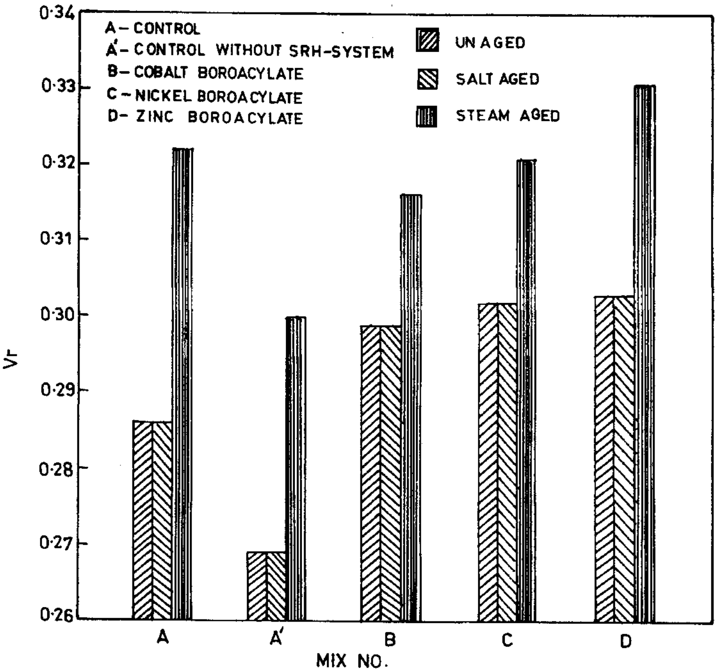
(6b)



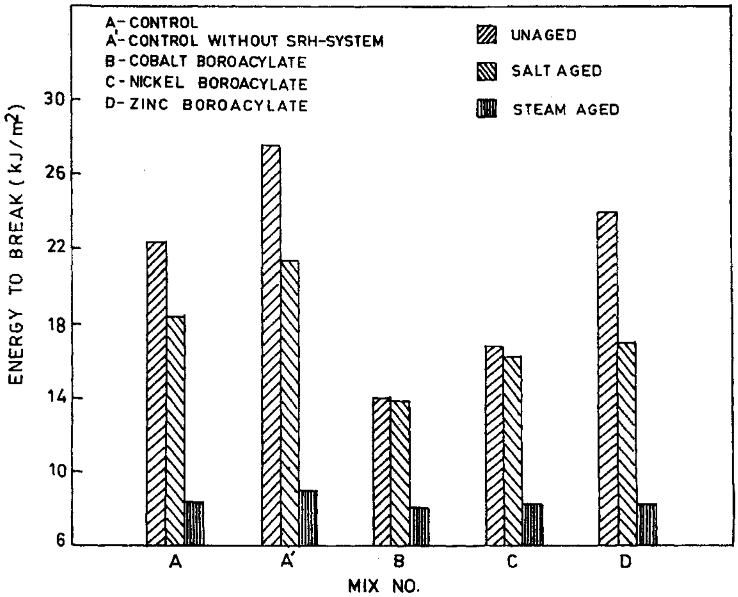
(6c)

brass-rubber adhesion. However, the SRH-system partially resists the degradation in the presence of salt and steam ageing. Perhaps a resin-rich layer near the brass-rubber interface provides a barrier to the moisture attack of this region.[8]

Steam ageing leads to the formation of $ZnO/Zn(OH)_2$ and a Cu_xS layer at the metal-rubber interface without any ZnS (Fig. 7).[9,10] With the increase in the thick-



(6d)



(6e)

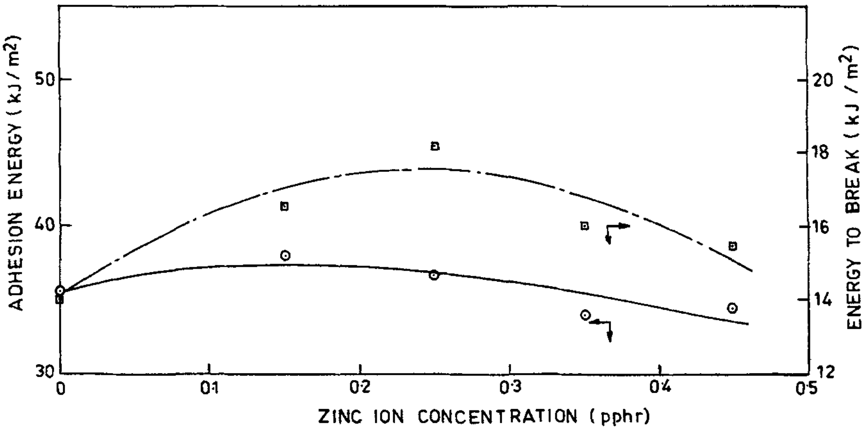
FIGURE 6 Influence of salt and steam ageing on vulcanisates without and with SRH-system in absence or presence of organometallic boroacylate with different cations. (a) Adhesion energy; (b) Pull out force; (c) Young's modulus; (d) Degree of crosslink, Vr; and (e) Energy to break.

FIGURE 7 Schematic presentation of interfacial film formed between rubber and brass due to steam ageing.

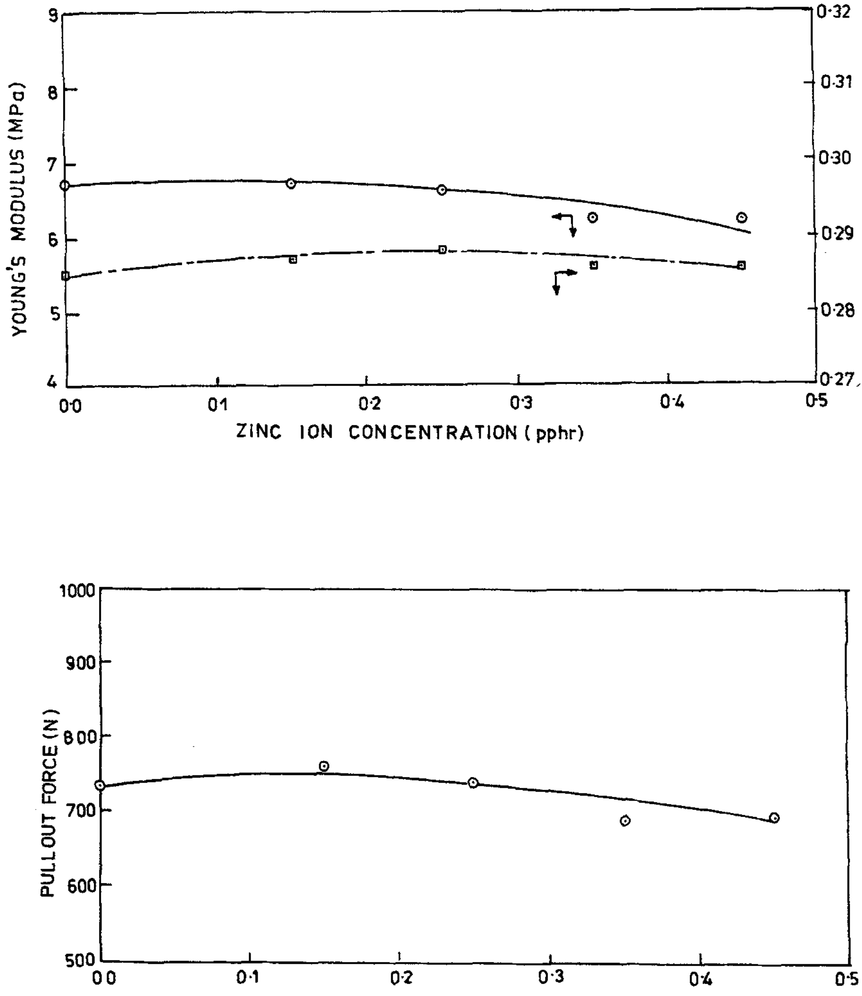
ness of the weak boundary layer of $ZnO/Zn(OH)_2$, the system becomes gradually non-bonding owing to the cohesive failure of this layer. Retention of good bond strength depends on the formation of the initial Cu_xS/ZnS layer and suppresion of the formation of the $ZnO/Zn(OH)_2$ layer during salt and steam ageing. Probably cobalt is successful in achieving the optimum Cu_xS/ZnS layer thickness and effective in inhibiting dezincification reaction. In turn, this leads to enhancement and maintenance of good bond strength during salt and steam ageing in the presence of cobalt boroacylate.

Effect of zinc concentration We reported the influence of the variation of the concentration of the Co ion in our earlier publication, while studying the effect of the anion in the Co adhesion promoter on steel cord skim formulations.[10] In the present study, we have varied the concentration of zinc promoter only, since the nickel salts are highly toxic in nature.[19,32] The influence of the zinc ion concentration variation on adhesion energy is not pronounced (Fig. 8a). A slight increase in adhesion energy is noticed with the incorporation of 0.15 pphr of zinc ion in the reference compound with the SRH-system. The adhesion energy reduces slowly with further addition of the zinc boroacylate.

The Young's modulus is constant up to 0.15 pphr of zinc ion concentration and then reduces slowly. Vr follows an almost similar trend (Fig. 8b). The rupture energy of the compound shows (Fig. 8a) a maximum at 0.25 pphr of metal ion concentration.



(8a)



(8b)

(8c)

FIGURE 8 Influence of zinc ion concentration on (a) Adhesion energy and energy to break; (b) Young's modulus and crosslink density; (c) Pull out force.

It varies from 14 kJ/m^2 to 18.5 kJ/m^2 and is far below the adhesion energy (34 kJ/m^2 to 38 kJ/m^2) of the compound; this leads mostly to cohesive failure of the rubber during cord pullout. As a result, pullout force (Fig. 8c) follows a trend similar to that of Young's modulus, resulting in the behaviour of the compounds as shown in Figure 8a.

Actually, the increase in Zn ion accelerates the formation of new corosslinks and at the same time enhances the chances of reversion, as observed from cure characteristics data (Table II). Moreover, the large amount of Zn ion already present in the matrix dilutes the effect of minor variation of Zn ion concentration of Zn boroacylate.

CONCLUSIONS

The pullout force and ageing resistance of a steel cord-rubber skim compound system are enhanced by the incorporation of a resin former containing silica, resorcinol and hexamethylene melamine (the SRH-system) and organometallic boroacylate salts individually or jointly. However, addition of both the organometallic adhesion promoters and the SRH-system leads to best results for the pullout force. The poorest performance is exhibited by the control without any adhesion promoters.

Adhesion energy is not much influenced by the incorporation of different adhesion promoters except for cobalt boroacylate. Incorporation of cobalt promoters enhances the adhesion energy significantly. The performance of the promoter is influenced by the ease of dissociation of the transition metal ion from the promoter, its participation in the rubber curing and the modification of the interfacial film responsible for adhesion.

The adhesion energy is much higher than the compound rupture energy. This leads to mainly cohesive rubber failure during pullout (especially in the case of aerobic ageing) or a mixture of cohesive and adhesive failure. As a result of cohesive failure, the pullout force changes with the changes in rubber properties.

Cobalt followed by nickel is found to be effective during aerobic ageing, whereas cobalt and, partially, zinc salts offer certain resistance in the case of thermal ageing (*i.e.* anaerobic ageing). Among all the organometallic adhesion promoters, cobalt boroacylate is very effective against steam and salt ageing followed by the zinc salt. The supremacy of cobalt among all the cations considered is established, considering its overall performance and the resistance it offers against various ageing conditions.

The adhesion energy and pullout force of the compound containing zinc boroacylate both show a maximum at 0.15 parts of metal ion per 100 parts of rubber. Beyond the maximum both properties decrease slowly with increasing beyond zinc ion concentration.

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