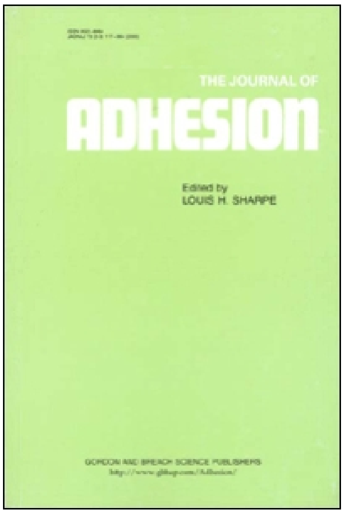

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Effect of Anion in Cobalt Promoters on the Adhesion between Steel Cord and Rubber Compound

Arup K. Chandra[a]; Arabinda Biswas[a]; R. Mukhopadhyay[a]; Anil K. Bhowmick[b]
[a] R & D Centre, J. K. Industries Limited, Kankroli, Rajasthan, India [b] Rubber Technology Centre, Indian Institute of Technology, Kharagpur, India

To cite this Article Chandra, Arup K. , Biswas, Arabinda , Mukhopadhyay, R. and Bhowmick, Anil K.(1994) 'Effect of Anion in Cobalt Promoters on the Adhesion between Steel Cord and Rubber Compound', The Journal of Adhesion, 44: 3, 177 — 196

To link to this Article: DOI: 10.1080/00218469408027076

URL: http://dx.doi.org/10.1080/00218469408027076

J. Adhesion, 1994, Vol. 44, pp. 177–196
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B. V. Published under license by
Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Effect of Anion in Cobalt Promoters on the Adhesion between Steel Cord and Rubber Compound

ARUP K. CHANDRA, ARABINDA BISWAS, R. MUKHOPADHYAY

R & D Centre, J. K. Industries Limited, Kankroli 313 342, Rajasthan, India

and

ANIL K. BHOWMICK*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India

(Received November 8, 1993; in final form March 7, 1994)

There is widespread use of two main groups of adhesion promoters, the SRH-system and an organic cobalt salt. They are used either jointly or individually in the rubber compound for promotion and maintenance of good adhesion of rubber to brass-coated steel cord in radial tyres.

This paper describes the influence of anions associated with cobalt promoters on the adhesion energy and the pull-out force between brass-coated steel cord and rubber and their relationship to other relevant physical properties, under the influence of various environments which simulate tyre service conditions.

It is observed that incorporation of a cobalt promoter greatly enhances the adhesion energy and influences the Young's modulus and crosslink density of the rubber compound in a similar fashion. The study establishes the supremacy of boroacylate among the anions considering its overall good performance and the protection offered against various hostile environments. However, the benefits of the cobalt promoter is not realised with stearate ion. The results are explained on the basis of chemical stability of the promoter and the properties of the interfacial film and the compounds.

KEY WORDS steel cord; brass coating; adhesion; adhesion energy; pull-out force; ageing.

INTRODUCTION

The tyre industry has witnessed a dramatic move towards radialisation of car and truck tyres in which multifilament brassed steel cords (brass plated from a Cu/Zn plating solution) remain the dominant strength member, offering the best compromise for strength, stiffness, modulus, durability, dimensional stability, elasticity, uniformity and economy. With increased customer demand for longer service life coupled with a larger number of retreadings for steel radial tyres, the need for achievement and maintenance of excellent adhesion and compound properties has been felt, as the performance and

---

* Corresponding author.

durability of a tyre composite depend mainly on the integrity of the bond between rubber and reinforcing cords. For promotion of adhesion between rubber and brass-coated steel cord, it is a normal practice to incorporate two main groups of adhesion promoters: a resin former (SRH-system-silica, resorcinol and hexamethyl melamine system) and an organic cobalt salt, either individually or jointly.[1-5] Addition of both the systems leads to better bonding and durability.[6]

Several authors[7-11] studied the effect of these systems on the static adhesion between rubber and brass-coated steel cord mainly using the ASTM D 2229 pull through test.[12] In such cases no part of the rubber block is subjected to simple extension; rather the rubber is largely sheared between the central cord and an external clamp or holder. 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.[13] The literature survey reveals that there is no systematic study of the effect of the anion associated with cobalt promoters on static adhesion between steel cord and rubber compound. This paper describes these effects on adhesion energy between brass-coated steel cord and rubber compound 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 adhesion energy of a given cord-rubber system.[14-16]

THEORETICAL CONSIDERATIONS

While working with the TCAT test specimen, Gent *et al.*,[15] and Fielding-Russell *et al.*,[16] observed that the cord pullout force (F) is directly proportional to the Young's modulus (E) of the rubber, the specimen's cross-sectional area (A), the cord radius (r) and the adhesion energy (G_a), *i.e.*, the energy required to fracture unit area of the rubber cord interface which is governed by the following equations;

$$F = (4\pi rEAG_a)^{1/2} \tag{1}$$

or

$$G_a = \frac{F^2}{4\pi rEA} \tag{2}$$

The above equation 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. Hamed and Donatelli[17] also used this equation for rubber-to-cord adhesion.

We have considered the interfacial debonding energy in this paper since it is independent of test piece parameters.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

Materials used for these experiments are given in Table I.

Other chemicals, not shown in the table, were received from the standard Indian suppliers.

Mixing and Cure Characteristics

The various rubber compositions used in the investigation, along with their Mooney viscosity, cure characteristics and physical properties are shown in Table II.

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		-do-
N-phenyl-N'(1,3-dimethyl butyl)-p-phenylene diamine	Vulkanox-4020 (Antioxidant-6PPD)		-do-
N,N-dicyclohexyl-2-benzothiazole sulphenamide	Vulkacit-DZ (Accelerator DCBS)		-do-
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		Kali Chemical, Germany
Cobalt Adhesion Promoters*			
	Cobalt content (%)	Grade	Suppliers
Cobalt Naphthenate	10.6	LP-839	Manchem Ltd., UK
Cobalt Stearate	9.5	CS-95	-do-
Cobalt Neodecanoate	20.5	740-C	-do-
Cobalt boroacylate	23.0	680-C	-do-
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			

* The organic cobalt complexes with different anions used in this work are proprietory additives, claimed to be better than simple cobalt soaps and to provide better consistancy in bonding.[18]

** 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 a micrometer, assuming close packing as shown in Figure 1.

TABLE II
Formulations and characterisation of mixes

Ingredients (parts of metal ion per hundred parts of rubber)	Mix Number							
	A	B	C	D	E	E_1	E_3	E_4
Cobalt naphthenate	—	0.25	—	—	—	—	—	—
Cobalt stearate	—	—	0.25	—	—	—	—	—
Cobalt neodecanoate	—	—	—	0.25	—	—	—	—
Cobalt boroacylate	—	—	—	—	0.25	0.15	0.35	0.45
Properties								
Mooney viscosity (ML_{1+4} at 100°C)	85.3	77.5	69.8	87.4	89.3	89.3	88.1	87.6
Scorch time (t_2), min	5.5	5.2	5.0	5.2	5.2	5.3	5.2	5.1
Optimum cure time (t_{90}), min	38.6	30.2	29.2	30.3	28.7	32.4	26.9	25.6
Reversion (t_{98}) (after crossing maximum), min	No reversion up to 90 min.	71.5	71.0	70.0	75.0	89.0	63.0	64.0
V_r	0.286	0.298	0.310	0.298	0.299	0.30	0.307	0.307
Young's modulus (MPa)	7.0	7.1	7.8	7.1	7.4	7.4	7.8	7.8
Energy to break (kJ/m^2)	22.4	18.5	16.1	18.4	14.1	17.5	15.9	15.4

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.

Mixing was carried out in three stages using a laboratory Banbury (Stewart Bolling, USA) of capacity 1.2 kg (batch wt.), having a 2-wing rotor (model No. #00). All ingredients except the cobalt adhesion promoter, the methylene donor and the vulcanising agents were mixed in the masterbatch stage. These batches were remilled in the Banbury in the second stage. In the final stage, the remaining ingredients were

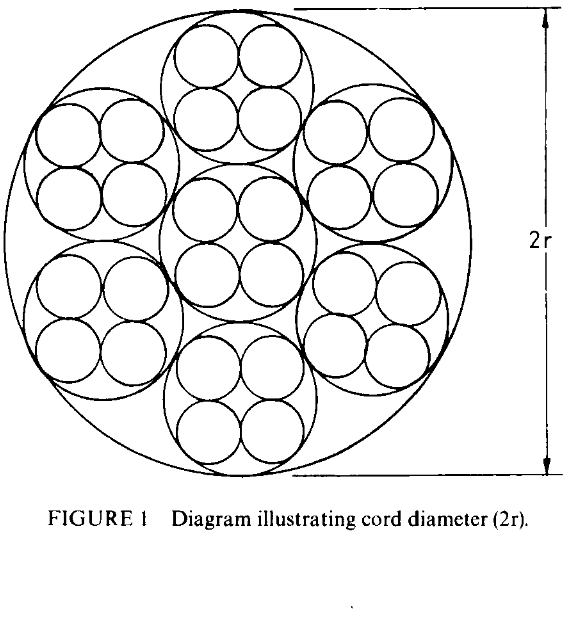

FIGURE 1 Diagram illustrating cord diameter (2r).

added. Cure characteristics of the specimens were studied at 141°C using a rheometer (Monsanto MDR-2000). Mooney viscosity was determined using a Monsanto Mooney viscometer (MV-2000) as per ASTM D 1646.

Moulding of TCAT Specimen

TCATtest pieces having dimensions 10.0 mm × 12.0 mm × 50.0 mm (Fig. 2) were prepared by a compression moulding technique in a specially-designed, six-cavity mould. Rubber pieces of 5.1 mm × 12.0 mm × 50.0 mm were placed in each of the six mould cavities. Brass cord was cut to the required length carefully, to avoid any ragged edges and fray cords, with the help of a chopper of our own design.

Freshly cut brass cords were put symmetrically on top of each rubber layer with the embedment depth as per the requirement. Another piece of the rubber was placed on the top half of the mould and then the top mould was positioned over the bottom half. The outer portion of two sides of the cords was clamped by a steel bar to resist shifting (if any) of the cords during moulding.

TCAT samples were cured at four different cure times, 2, 4, 8 and 16 hours at 141°C to simulate exactly the ageing of steel cord in a tyre under anaerobic conditions (*e.g.*, the belt and carcass skim formulations were subjected to thermal ageing during service).

Testing

Young's Modulus: Young's modulus for the rubber compounds cured to different extents was determined from the slope of the initial linear portion of the stress-strain curves

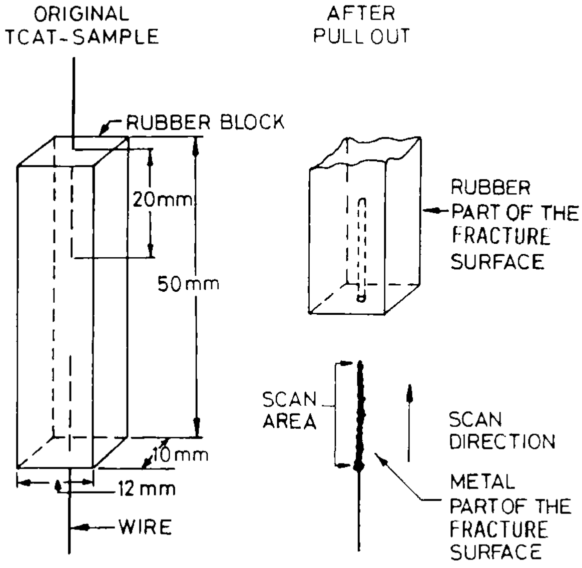

FIGURE 2 TCAT pull out test specimen and scan area of fracture surface.

obtained using a Zwick Universal Testing machine (model 1445) at a cross-head speed of 50 mm/min at 25 ± 2°C.

Adhesion Testing: To measure the pull-out force, the two opposite axial free cord ends 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.

To see the effect of different ageing environments on rubber-to-steel-cord adhesion, TCATsamples were aged under different conditions (Table III). The parameters involved in tyre ageing simulation testing are temperature, time, and presence of aggresive media.

Crosslink Density: V_r (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.[19] The swelling measurement was carried out in toluene at 25°C for 72 hrs., when equilibrium was attained.

Mechanical Properties: Rupture energy or energy to break was determined from the area under the stress-strain curve at a cross-head speed of 50 mm/min at 25 ± 2°C using the Zwick Universal Testing machine.

Scanning Electron Microscopy: For studying the nature of the adhesion failure, failed metal surfaces after the TCAT pull-out test were sputter-coated with gold within 24 hrs. of testing and studied by a Cam Scan Series-II Scanning Electron Microscope. The mode of testing and the portion of the failed specimen used for SEM studies are shown in Figure 2. All the photographs were taken in the same direction and under the same conditions.

TABLE III
Different ageing conditions and their simulated effects

Parameter Combination	Test	Test conditions	Simulation
Time and temperature	Thermal ageing (*i.e.*, anaerobic ageing)	Curing TCAT samples at 141°C for 2, 4, 8 and 16 hrs.	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 hrs in an autoclave	Humid conditions during tyre service
Time, humidity and aggresive medium	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 hrs were considered.

RESULTS AND DISCUSSION

Characterisation of the Compounds

The properties of the rubber compounds are presented in Table II. It is evident that the systems containing different cobalt adhesion promoters exhibited both a higher rate and state of cure, with a corresponding reduction in scorch safety as compared with those of the control compound. Cobalt stearate showed the lowest Mooney viscosity. However, Mooney viscosity was not very sensitive to the variation of dosage of cobalt ion. The mechanical properties were also affected to various extents. These data will be discussed later to explain the adhesion results.

Effect of Cord Embedment Length

In order to optimise the embedment length, pull-out forces were measured after random variation of cord embedment length using the control compound. The results indicate that the pull-out force (F) and the adhesion energy (G_a) were almost independent of the embedment length (l) at lengths above about 20 mm. Below 20 mm, however, the pull-out force increased with the increase in the embedment length due possibly to higher volume of the rubber deformed and, hence, larger dissipation of energy. Our observations are in line with those demonstrated in the original TCAT publications.[15,16] To overcome the problem of dependence of pull-out force and the adhesion energy on cord embedment length, the latter was kept at 21.0 mm throughout the experiment.

Adhesion Energy

Adhesion Energy of Various Joints and the Effect of Aerobic Ageing: The adhesion energy of the compounds without and with different cobalt promoters, as a function of ageing time, is shown in Figure 3a.

The adhesion energy of the control compound increased substantially with the incorporation of cobalt promoters containing different anions except for the stearate ion which was comparable with the reference compound. The extent of increase in adhesion energy for the unaged sample was comparable.

The observed effects of adhesion promoters depend on three major factors:[20]

(i) the changes in properties of the rubber compounds;
(ii) the modifications of the interfacial film of reaction products; and
(iii) the chemical stability of the promoters.

The improvement in the adhesion of sulphenamide-accelerated systems to brass by cobalt promoters may be explained by assuming that the accelerator-sulphur complex reacts with the cobalt and forms a complex:

$$\text{Acc—Sx—Acc} + \text{CoX}_2 \longrightarrow \text{Co—Sy—X}_2 + \text{Acc—S}_{x-y}\text{—Acc}$$

This cobalt complex is assumed to promote the Cu_xS formation needed for bonding.

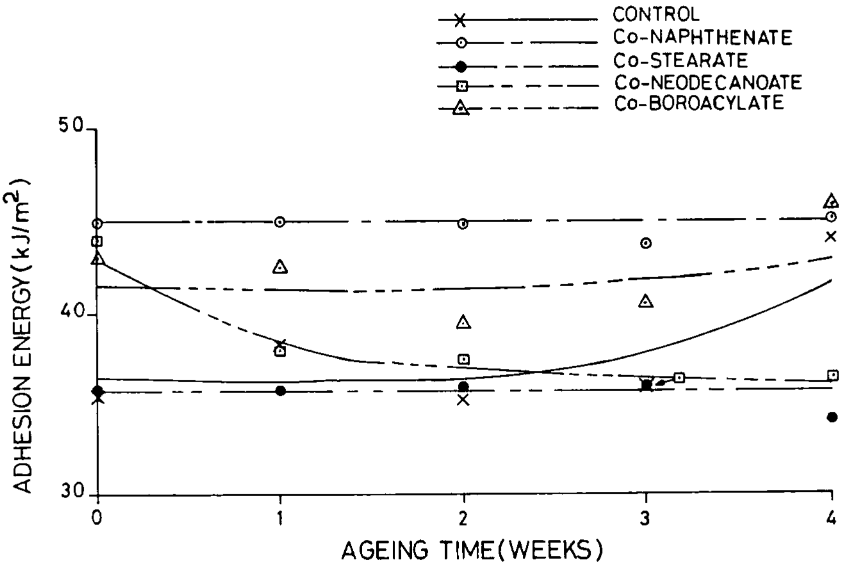

FIGURE 3a

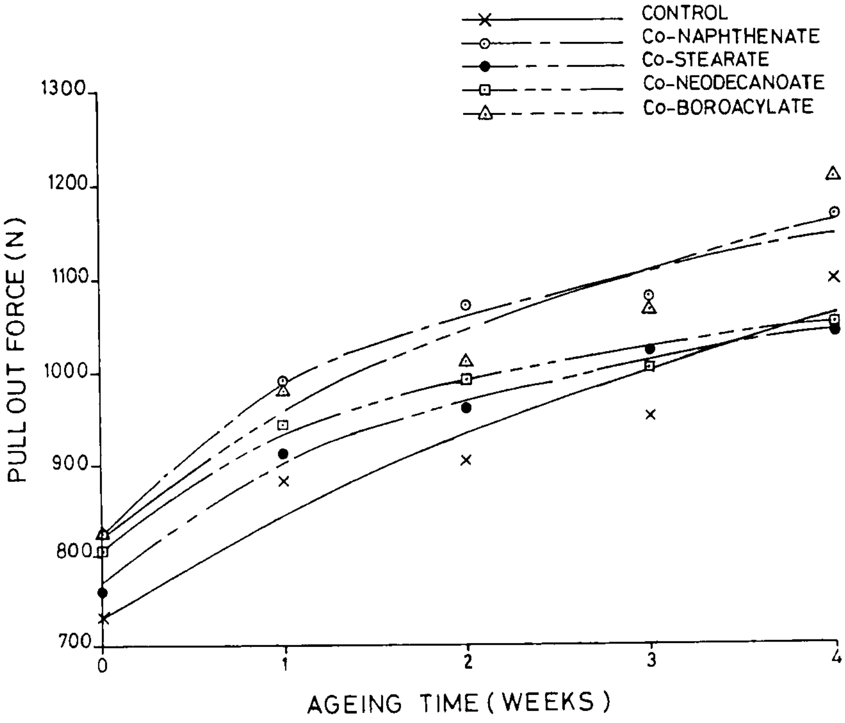

FIGURE 3b

The observed negative effect of cobalt stearate is in line with the result reported by Hick and Lyon.[21] Perhaps the poorest performance with stearate ion may be due to the fact that the bond between cobalt and stearate ion is weak and, therefore, cobalt dissociates from the molecule very rapidly. Because of the accelerator-activating effect of stearate ion, the sulphur and promoter are possibly used more efficiently for modificiation of rubber rather than for the interfacial film on brass. This is evident also from cure characteristics, crosslink density and Young's modulus data (Table II). Comparable adhesion energy was noticed with all other anions, because cobalt would not dissociate so rapidly and participate so much in the cure of rubber. That was also evident, as the physical properties of the promoter containing other anions were quite similar.

With ageing time, the adhesion energy of the cobalt-containing compounds remained practically unchanged except in the case of neodecanoate. The initial adhesion energy was comparable with those of boroacylate and naphthenate but it decreased very rapidly within one week of ageing to the value of adhesion between the cord and stearate-ion-containing promoter. That was because of disproportionate changes of pull-out force with Young's modulus (Figs. 3b and 3c). Both these values increased with ageing time. But the changes in pull-out force were lower as compared with those in

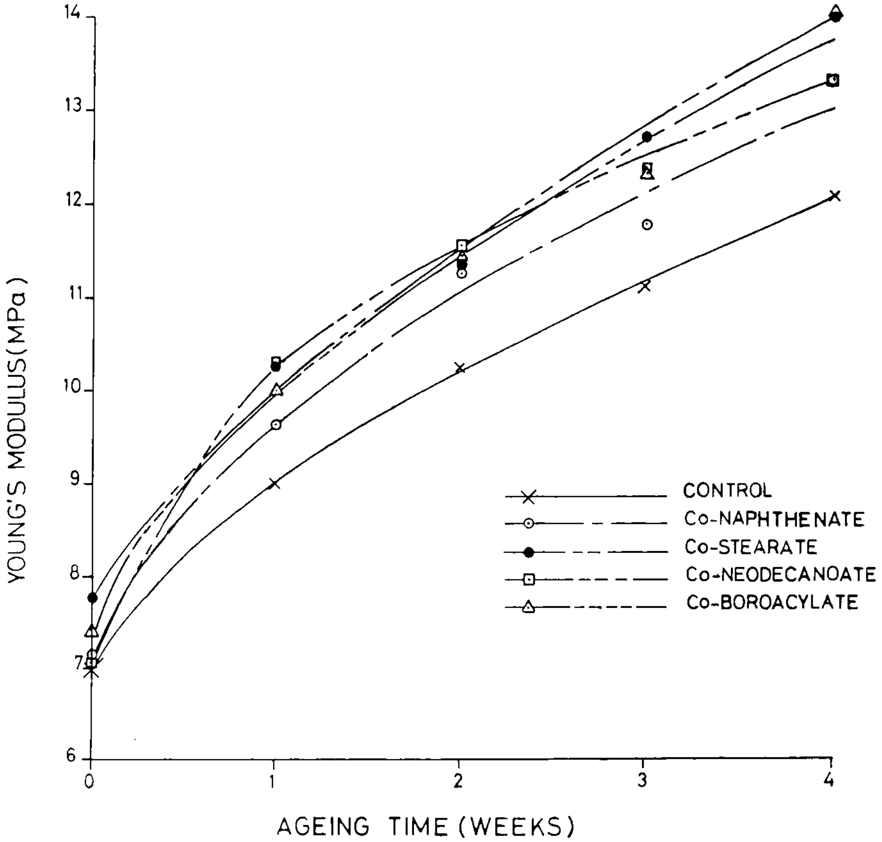

FIGURE 3c

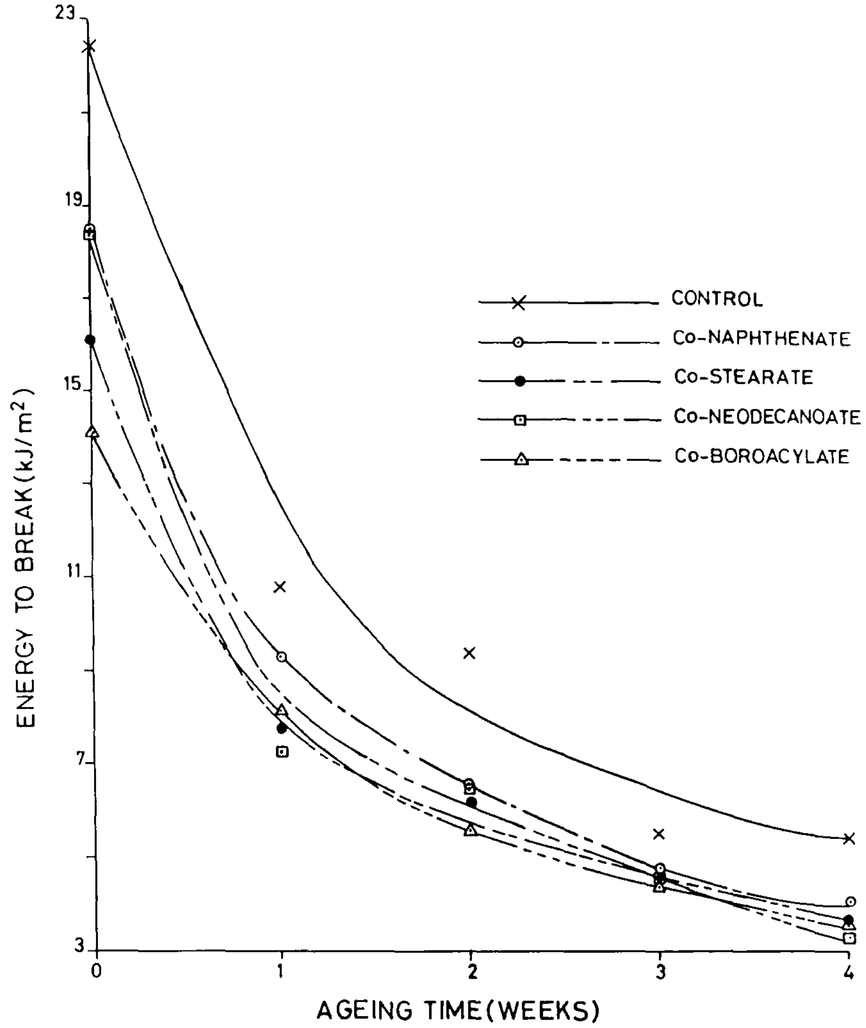

FIGURE 3d

Young's modulus at the initial stage (Equation 2). The increase in adhesion energy of the control compound at the later stage of ageing time can also be explained in the same way.

Since the adhesion energy of all the compounds ($34\,kJ/m^2$ to $46\,kJ/m^2$) was much higher than their corresponding compound rupture energy ($3\,kJ/m^2$ to $23\,kJ/m^2$) (*i.e.*, energy to break, Fig. 3d), cohesive failure of the rubber occurred during cord pull out and a good correlation was observed between cord pull-out force and rubber properties such as V_r (Figs. 3b and 3e), Young's modulus and all other properties dependent on V_r, within the limit of experimental error. A plot of the cord pull-out force against the Young's modulus showed almost a linear relationship as reported before. The relationship between cord pull-out force and Young's modulus of a representative compound (mix No. E) is presented in Figure 4. The pull-out force, the Young's modulus and V_r

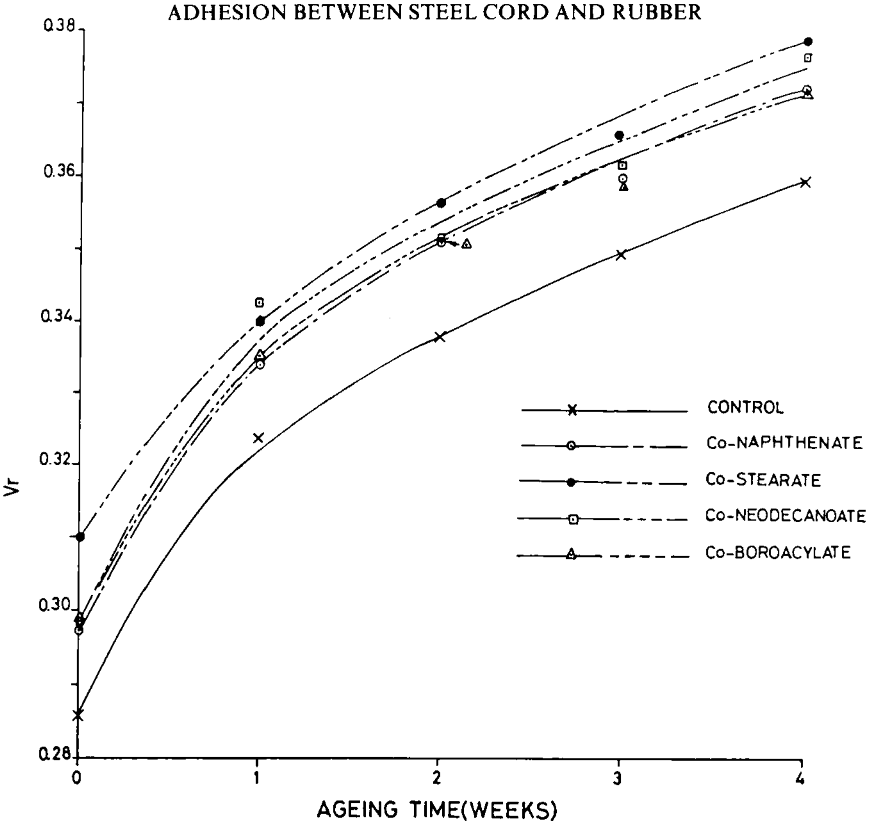

FIGURE 3a–e Influence of aerobic ageing on (a) Adhesion energy; (b) Pull-out force; (c) Young's modulus; (d) Energy to break and (e) degree of crosslink.

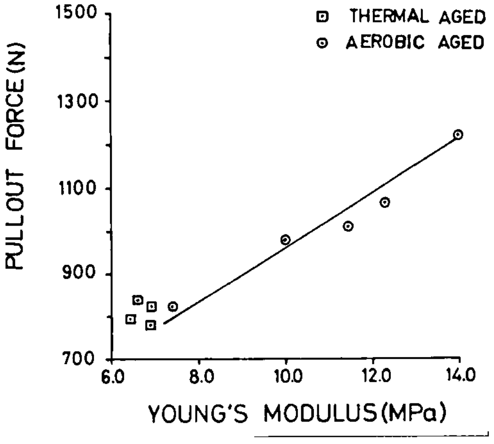

FIGURE 4 Relationship between cord pull-out force and Young's modulus of aerobic and thermally aged compounds containing boroacylate.

gradually increased with ageing time (Figs. 3b, 3c and 3e) for all the compounds including the control. These values were comparatively higher for cobalt-containing compounds owing to the influence of cobalt ion on crosslink density as well as on the interfacial film, which is under investigation in our laboratory.

The failure, mainly cohesive in nature, is further supported by the SEM study. Cobalt boroacylate (compound No. E) was selected as being representative of other promoters and the fracture features are compared with the reference compound in Figure 5. The nature of the failure was found to be similar and the fracture surface contained short, fine, curved tear lines and vaccuoles due to dewetting phenomena which were characteristics of the presence of silica filler in the compound. These photographs clearly indicate that the failure was mainly cohesive and random in nature.

Effect of Thermal Ageing: Figure 6a illustrates the effect of overcuring on the adhesion energy, which decreased continuously with overcuring. The effect was more pronounced in the case of the reference compound and the compound containing stearate ion. However, the compounds containing naphthenate and neodecanoate, followed by boroacylate, were least susceptible to such effects of overcuring. The above observation can be explained on the basis of the following factors as discussed earlier:

- influence of cobalt promoters on compound properties, especially on crosslink density
- formation of CoS which has good bonding properties (similar to Cu_xS) at the rubber-metal interface
- chemical stability of the cobalt complex.

It appeared quite reasonable that CoS formed at the rubber-metal interface (which was absent in the reference compound) and protected the CoS and Cu_xS layer from further degradation due to thermal ageing. The adhesion energy followed a trend similar to the pull-out force and the Young's modulus (Figs. 6b and 6c). The pull-out

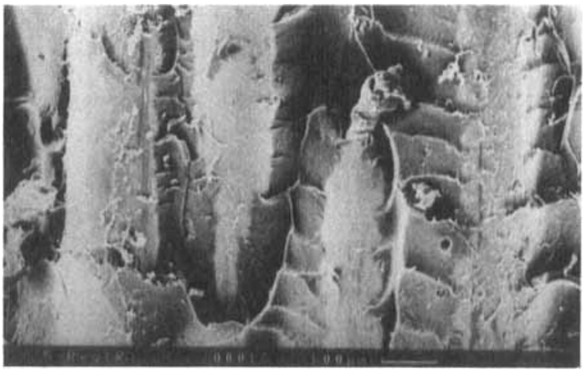

FIGURE 5 SEM photograph of brass-palated steel cord and the failed rubber surface containing cobalt boroacylate after TCAT pull-out test.

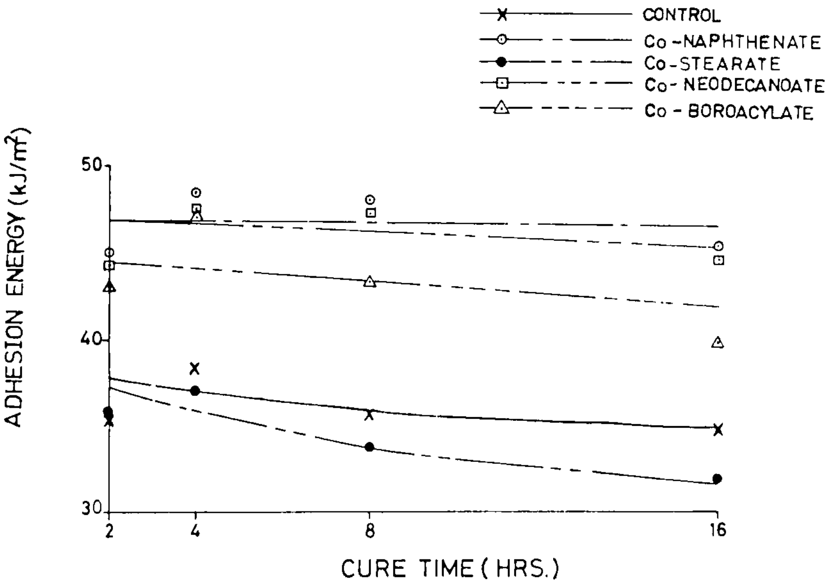

FIGURE 6a

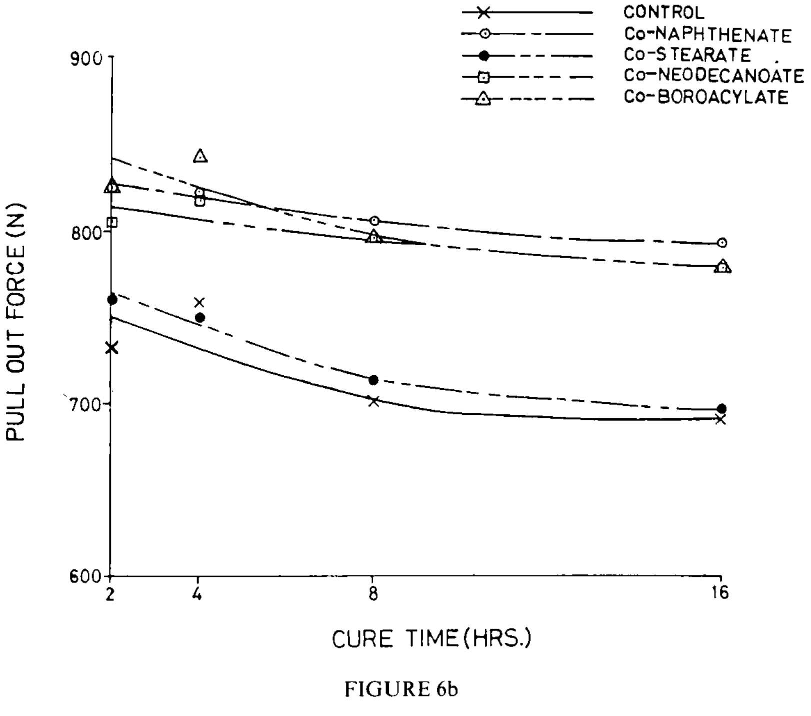

FIGURE 6b

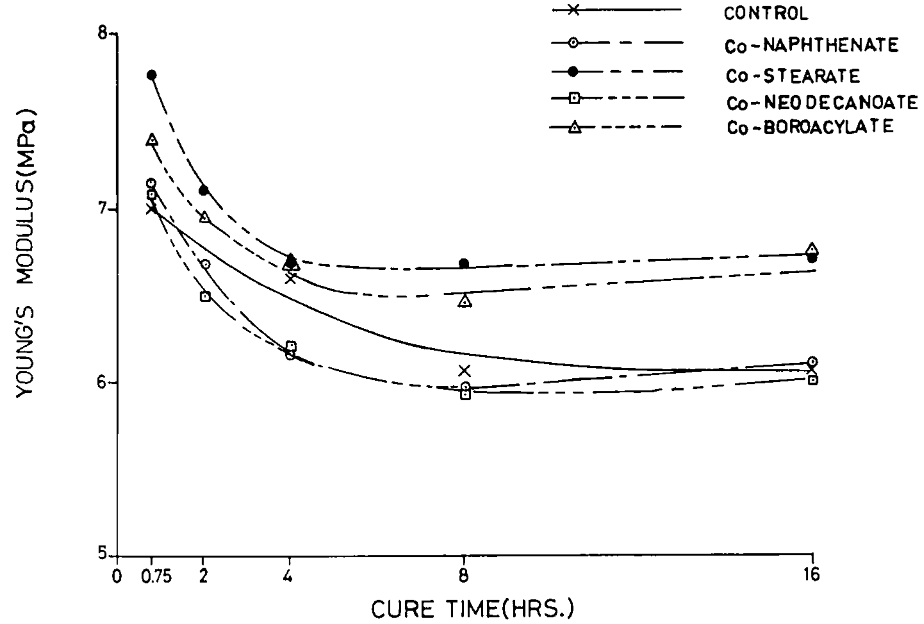

FIGURE 6a–c Influence of thermal ageing on (a) Adhesion energy; (b) Pull-out force and (c) Young's modulus.

force of the reference and the stearate-ion-containing compound reduced drastically during the initial stage of the overcuring (up to 8 hrs) and later on remained practically constant. The pull-out forces of the compounds B, D and E were found to be comparable and they reduced very slowly with cure time. The Young's modulus of the compounds also were reduced rapidly with cure time in the initial stage. These changes in Young's modulus with cure time were found to be relatively high when compared with their corresponding reductions in pull-out force on overcuring. As a result, the pull-out force did not maintain a linear relationship with Young's modulus as observed earlier in Figure 4. However, such a relationship would only be expected in the case of 100% cohesive failure of the rubber. As highlighted by Van Ooij *et al.*,[8] there are at least five possible modes of failure:

—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

From the data for the adhesion energy and the compound rupture energy (Table IV), it was evident that the adhesion energy was appreciably higher than the compound rupture energy under similar conditions which, in turn, should have led to cohesive failure of the compound during pull out. But, unlike aerobic ageing, the corresponding compound rupture energies were always much higher in the case of thermal ageing. This apparently shifted 100% cohesive failure of rubber to other modes of failure.

TABLE IV
Physical properties of the mixes after ageing

Compound number	Physical properties	Aerobic aged (week)				Thermal aged (hrs)				Salt aged	Steam aged
		1	2	3	4	2	4	8	16		
A	V_r	0.323	0.338	0.349	0.360	0.285	0.288	0.288	0.290	0.286	0.322
	Young's modulus (MPa)	9.00	10.23	11.11	12.08	6.67	6.6	6.06	6.06	6.58	7.54
	Energy to break (kJ/m^2)	10.8	9.4	5.5	5.4	14.1	13.9	12.4	12.8	18.4	8.4
B	V_r	0.334	0.351	0.357	0.372	0.288	0.286	0.292	0.295	0.298	0.318
	Young's modulus (MPa)	9.63	11.25	11.76	13.33	6.67	6.15	5.96	6.1	7.41	7.5
	Energy to break (kJ/m^2)	9.3	6.6	4.8	4.1	16.1	14.2	13.9	12.9	15.2	8.2
C	V_r	0.340	0.356	0.363	0.379	0.297	0.295	0.298	0.303	0.310	0.323
	Young's modulus (MPa)	10.27	11.36	12.72	14.00	7.11	6.67	6.67	6.70	8.33	7.92
	Energy to break (kJ/m^2)	7.8	6.2	4.6	3.7	13.3	11.7	11.0	10.2	12.7	7.5
D	V_r	0.342	0.351	0.362	0.376	0.288	0.288	0.287	0.296	0.298	0.310
	Young's modulus (MPa)	10.30	11.58	12.38	13.33	6.48	6.2	5.93	6.0	7.33	7.64
	Energy to break (kJ/m^2)	7.3	6.5	4.6	3.3	15.1	12.9	12.3	13.3	16.5	7.4
E	V_r	0.335	0.351	0.356	0.371	0.292	0.287	0.293	0.304	0.299	0.316
	Young's modulus (MPa)	10.00	11.43	12.31	14.03	6.95	6.67	6.45	6.75	7.72	7.74
	Energy to break (kJ/m^2)	8.2	5.7	4.4	3.6	12.5	11.7	11.2	9.7	14.1	8.1

Salt and Steam Ageing: Incorporation of cobalt promoter containing different anions (except stearate ion) improved the initial adhesion energy markedly, but this did not prevent completely the degradation due to salt and steam ageing. After ageing, the adhesion energy was substantially reduced (Fig. 7). Moreover, the salt ageing had a more deterimental effect than steam ageing, since the former medium was a combination of humidity and corrosive environment. In the case of salt ageing, boroacylate offered the highest protection, followed by neodecanoate and naphthenate. The poorest performance was exhibited by stearate promoter. Boroacylate was very effective against steam ageing and the deterioration of adhesion energy was less in this case. Naphthenate could be ranked second in this regard (considering % retention of adhesion). The performance of stearate and neodecanoate was even poorer than that of the control compound.

Steam ageing leads to the formation of $ZnO/Zn(OH)_2$ and Cu_xS at the metal-rubber interface without any ZnS (Fig. 8).[20] With the increase in the thickness of the weak boundary layer of $ZnO/Zn(OH)_2$, the system becomes gradually non-bonding due to bond failure within this film. To achieve a bond of high strength, this reaction must be supressed. Probably cobalt is effective in inhibiting this dezincification reaction and leads to an enhancement of bond strength.[20]

However, all cobalt complexes are not equally effective in preventing dezincification. This may be due to the different chemical stabilities of the Co—X bond in the cobalt promoter CoX_2 complexes (X = anion) as well as their involvement in the modification

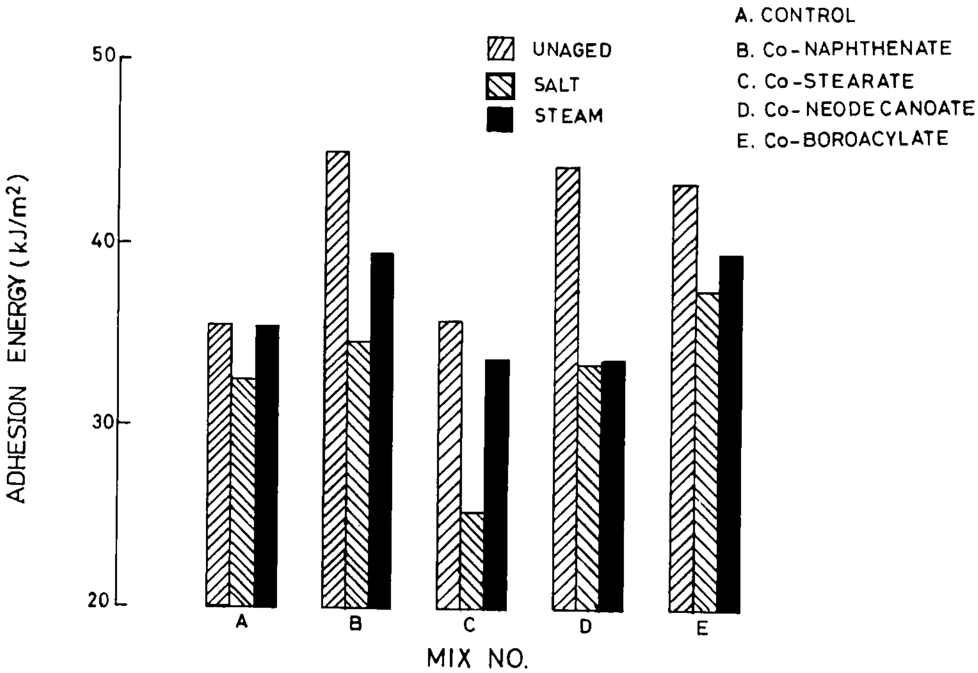

FIGURE 7 Influence of salt and steam ageing on adhesion energy.

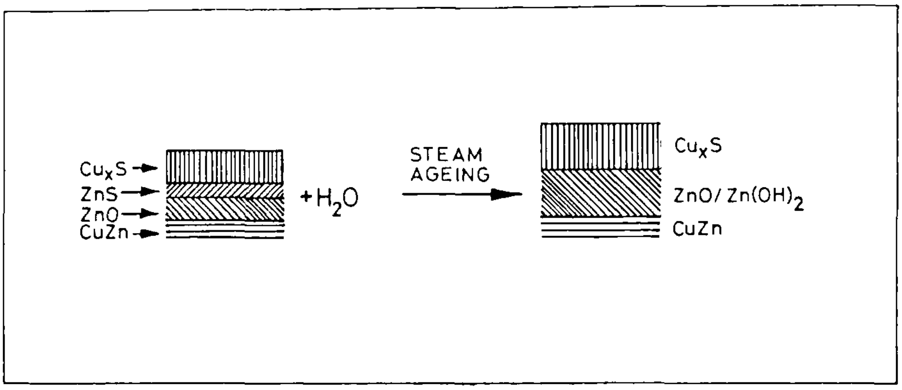

FIGURE 8 Schematic presentation of interfacial film formed between rubber and brass due to steam ageing.

of rubber properties. As a consequence, different rates of cobalt incorporation into the ZnS film can be expected.[20]

Here, the pull-out force followed a similar trend of adhesion energy, since the effect of ageing on Young's modulus was not very dominant (Tables II and IV).

However, no direct correlation was noticed between the pull-out force and various physical properties basically due to mixed mode of failure as a consequence of the dezincification reaction.

A SEM photograph of the failed surface of a steam aged sample of the boroacylate-containing compound is presented in Fig. 9. The effect of an agressive environment was evident from a more random, thick tear line with frequent vaccuoles.

Effect of Cobalt Concentration: Owing to its all-around better performance and its commercial importance, boroacylate was selected, among the different anions, for studying the effect of cobalt ion concentration.

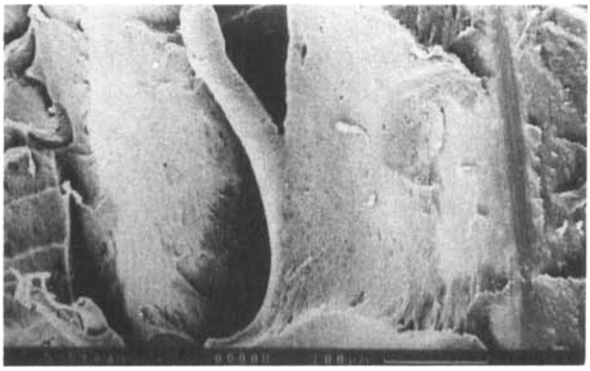

FIGURE 9 SEM photograph of the failed TCAT joint of brass-plated steel cord and rubber vulcanizate containing cobalt boroacylate after steam ageing for 8 hrs.

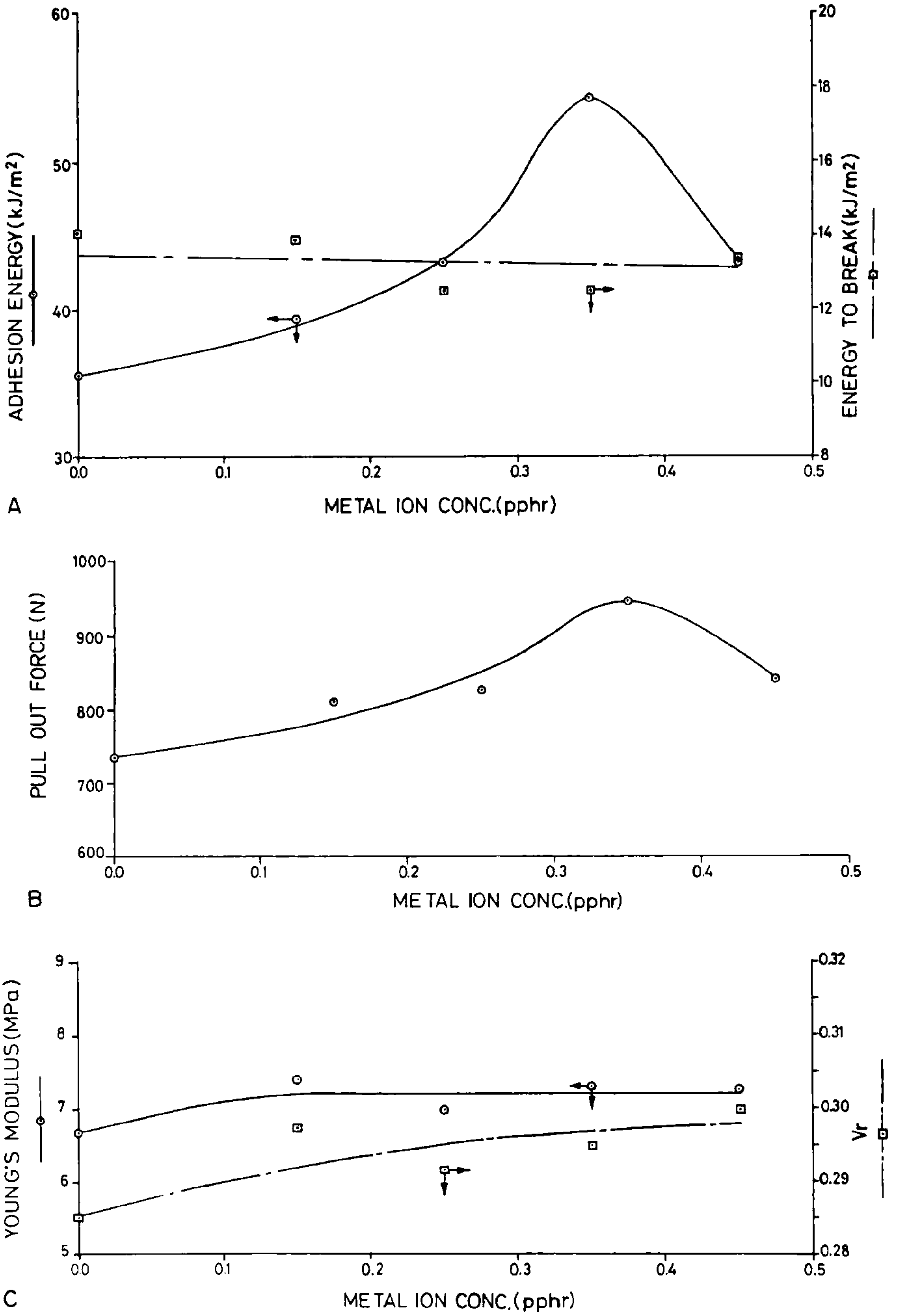

FIGURE 10 Influence of cobalt ion concentration on (a) Adhesion energy and energy to break; (b) Pull-out force and (c) Young's modulus and crosslink density.

The adhesion energy increased with an increase in cobalt ion concentration and attained a maximum at 0.35 pphr metal ion concentration (Fig. 10a). This may be related to the formation of an optimum thickness of the Cu_xS and CoS layers at the brass-rubber interface (a subject which we are now studying).

The pull-out force behaved in a similar fashion, as Young's modulus was not much affected by the changes in cobalt ion concentration (Fig. 10b and 10c). With the addition of cobalt promoter, V_r and the Young's modulus marginally increased initially at 0.15 pphr of metal ion and were practically unaltered with further increase in cobalt ion concentration. The compound energy to break was not affected by changes in the metal ion concentration.

CONCLUSIONS

Incorporation of cobalt promoters (except for the stearate promoter) increased the adhesion energy significantly. It is believed that the performance of the promoter was influenced by the ease of dissociation of cobalt from the promoter, its participation in the rubber curing and the modification of the interfacial film responsible for adhesion.

The adhesion energy was much higher compared with the rupture energy of the rubber compound. As a result, failure was mainly cohesive during pull-out (especially in the case of aerobic ageing) or a mixture of cohesive and adhesive in nature. This was further supported by an SEM study.

Naphthenate and boroacylate were found to be effective in the case of heat ageing in the presence of air. Boroacylate provided the highest resistance to salt ageing followed by neodecanoate and naphthenate. Boroacylate was also very effective against steam ageing. The supremacy of the boroacylate among all the anions was established, considering its overall performance and the resistance which it offered against various ageing conditions. However, the beneficial effect of the cobalt promoter was not realised in the case of stearate ion.

The adhesion energy and the pull-out force showed a maximum at 0.35 parts of metal ion per 100 parts of rubber and, hence, the metal ion should not be used at concentrations exceeding 0.35 pphr.

Acknowledgement

The authors wish to thank J. K. Industries Limited for permission to undertake and publish this work. Thanks are due also to Manchem Limited, UK, for providing samples of the cobalt promoters.

References

1. E. J. Weaver, *Rubber and Plastic News*, July 10, 1978, p. 22.
2. W. J. Van Ooij, *Rubber Chem. Technol.* **51**, 52 (1978).
3. W. E. Weening, paper presented at *Eur. Rubb. Conf., IRI*, Brussels, April, 1975.
4. R. R. Barnhardt and P. H. McKinstry, *J. Elast. Plast.* **10**, 216 (1978).
5. P. P. Langevin, R. J. Payne and C. S. Shepard, *Rubber Chem. Technol.* **47**, 171 (1974).
6. G. R. Hamed and J. Huang, *Rubber Chem. Technol.* **64**, 285 (1991).
7. L. R. Barker, *NR-Technol.* **12**, 77 (1981).
8. W. J. Van Ooij, W. E. Weening and P. F. Murray, *Rubber Chem. Technol.* **54**, 227 (1981).

9. M. Hassan, A. K. Chandra, R. Mukhopadhyay and A. K. Bhowmick, *Rubber World* **207**(1), 25 (1992).
10. A. Peterson and M. I. Dietrick, *Rubber World* **190**(5), 24 (1984).
11. P. E. R. Tate, *Rubber World* **192**(1), 37 (1985).
12. D2229/85, "Standard test method for rubber property-adhesion to steel cord", *Annual Book of ASTM-Standards* **09.01**, 415–420 (1990).
13. K. Kendall, *J. Mater. Sci.* **10**, 1011 (1975).
14. D. W. Nicholson, D. I. Livingston and G. S. Fielding-Russell, *Tire Science and Technol.* **6**, 114 (1978).
15. A. N. Gent, G. S. Fielding-Russell, D. I. Livingston and D. W. Nicholson, *J. Mater. Sci.* **16**, 949 (1981).
16. G. S. Fielding-Russell, D. I. Livingston and D. W. Nicholson, *Rubber Chem. Technol.* **53**, 950 (1980).
17. G. R. Hamed and T. Donatelli, *Rubber Chem. Technol.* **56**, 450 (1983).
18. *Monobond Cobalt Adhesion Promoters*, Product Data, Rhone-Poulenc Chemicals, Manchem Ltd., 1991.
19. B. Ellis and G. N. Welding, *Techniques of Polymer Science* (Society of Chemical Industries, London, 1964), p. 46.
20. W. J. Van Ooij, *Rubber Chem. Technol.* **52**, 605 (1979).
21. A. E. Hicks and F. Lyon, Presented at a meeting of the Rubber Division, American Chemical Society, Montreal, May 2–5, 1967. Abstract in *Rubber Chem. Technol.* **40**, 1607 (1967).