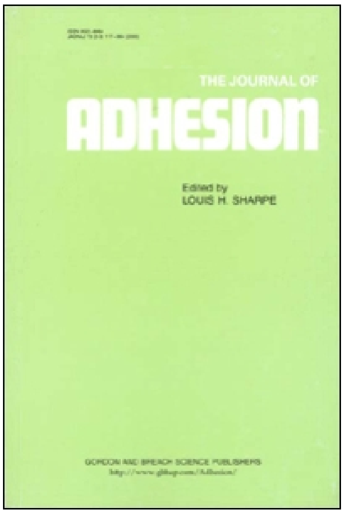

The Journal of Adhesion

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

Synthesis of Cobalt Adhesion Promoters and Their Evaluation in a Passenger Radial-Belt Skim Compound

N. Mandal[a]; P. Sajith[a]; S. L. Agrawal[a]; S. Bandyopadhyay[a]; R. Mukhopadhyay[a]; B. D'Cruz[b]; A. S. Deuri[b]
[a] Hari Shankar Singhania Elastomer and Tyre Research Institute (HASETRI), Rajsamand, Rajasthan, India [b] R&D Centre, J.K. Tyre, Rajsamand, Rajasthan, India

To cite this Article Mandal, N. , Sajith, P. , Agrawal, S. L. , Bandyopadhyay, S. , Mukhopadhyay, R. , D'Cruz, B. and Deuri, A. S.(2005) 'Synthesis of Cobalt Adhesion Promoters and Their Evaluation in a Passenger Radial-Belt Skim Compound', The Journal of Adhesion, 81: 9, 911 — 923

To link to this Article: DOI: 10.1080/00218460500222843

URL: http://dx.doi.org/10.1080/00218460500222843

The Journal of Adhesion, 81:911–923, 2005
Copyright © Taylor & Francis Inc.
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460500222843

Synthesis of Cobalt Adhesion Promoters and Their Evaluation in a Passenger Radial-Belt Skim Compound

N. Mandal
P. Sajith
S. L. Agrawal
S. Bandyopadhyay
R. Mukhopadhyay
Hari Shankar Singhania Elastomer and Tyre Research Institute (HASETRI), Jaykaygram, Rajsamand, Rajasthan, India

B. D'Cruz
A. S. Deuri
R&D Centre, J.K. Tyre, Jaykaygram, Rajsamand, Rajasthan, India

Cobalt adhesion promoters have gained considerable acceptance in the rubber industry during the past two decades and are considered the most important tool for the promotion of adhesion between the rubber compound and the brass-plated steel cord in the manufacture of steel-cord-reinforced radial tires. Most of the commercially available cobalt compounds are either higher fatty acid salts or cobalt–chelate complexes, e.g., cobalt octanoate, napthenate, stearate, and cobalt–boron complexes. Of the various cobalt salts and chelate complexes, cobalt–boron complexes are the most popular, and they form good bonding. Considering the availability, economics, and performance of this material, an attempt has been made in this study to synthesize different cobalt–chelate complexes, make a comparative evaluation of rubber compounds, and simulate field performance with laboratory tests.

Keywords: Brass-plated steel tire cord; Cobalt adhesion promoter; Cobalt–chelate complex; Copper sulfide; Dezincification; Direct bonding; Perthiomercaptides; Pull-out force

Received 10 December 2004; in final form 15 March 2005.

Address correspondence to S. Bandyopadhyay, HASETRI, Jaykaygram, P. O. Tyre Factory, Rajsamand, 313 342, Rajasthan, India. E-mail: sbanerjee@ktp.jkmail.com

INTRODUCTION

Polymers generally do not adsorb on a metal surface for entropic reasons. However, if polymers contain specific (*e.g.*, polar) groups that can interact with the metal surface, adsorption can be enhanced [1]. Because most of the rubbers used for adhesion purposes are nonpolar in nature, poor adhesion properties are observed. Better direct bonding can be achieved by either modifying the rubber or the bonding additives in the rubber compound. Sulfur vulcanizing rubbers are able to form a direct bond to brass [2], zinc [3, 4], palladium [5], nickel [6], and nickel/zinc- or zinc/cobalt-plated steel [7] during curing.

As far as the tire industry is concerned, brass coating on steel wire is preferred for natural rubber (NR) to steel-wire adhesion [8]. This is because of the resulting better strength, durability, dimensional stability, elasticity, and uniformity. During curing of steel-belted radial tires, a tight mechanical interlocking of polymer with the porous copper sulfide (Cu_xS) film of the brass is formed [9–12]. The desired chemical reaction that takes place at the rubber/brass-plated steel-cord interface, during the tire vulcanization, may be considered as a mixed ionic-covalent chemical reaction, whereas the rubber–carbon–sulfur linkage is considered a relatively slow covalent reaction and the sulfur–copper linkage a fast ionic reaction [13]. Several authors gave extended reviews on the direct bonding of sulfur-vulcanized rubbers to brass [14–17]. The influence of metal organic promoters on the properties of steel-cord skim compounds with special reference to adhesion was extensively studied [18–26].

The retention of adhesion after aging is taken care of by the cobalt–boron complexes that act as adhesion promoters. Moreover, the cobalt sulfide formed at the rubber–metal interface has good bonding properties. The cobalt salt will undergo a displacement reaction to form Co^{+2} ions that will be incorporated in the zinc oxide (ZnO) layer of brass as Co^{+3}. This retards the formation of zinc sulfide (ZnS) that, in turn, stimulates the formation of Cu_xS. Cobalt sulfide can also be formed and can be incorporated in the Cu_xS film because both are P type semiconductors [9, 10].

In an overcure or heat aging, the Cu_xS film will eventually be overtaken by either ZnS or $ZnO/Zn(OH)_2$, degrading adhesion. This is because once the copper inclusions are depleted, the Zn^{+2} ions will diffuse through the interfacial layer. ZnS forms as a result of an overcure or heat aging in a dry environment. Formation of $ZnO/Zn(OH)_2$ is a result of a moist or humid environment. The formation of $Zn(OH)_2$ from the precipitation of Zn^{+2} ions destroys the integrity of the Cu_xS layer and, therefore, the adhesion. These reactions are part of what is known as "dezincification." Similarly, there are no fundamental differences between humidity and steam aging. Both lead to an interfacial film containing relatively large quantities of $ZnO/Zn(OH)_2$ and copper sulfide and practically no zinc sulfide. Salt-water aging is an acceleration of dezincification [9, 27]. Compounding with zinc oxide discourages dezincification at the brass surface. Because, there is an elevated level of ZnO in the compound, removal or diffusion of Zn^{+2} to the cord surface is decreased. The Cu_xS layer is also not overtaken [28, 29].

The corrosion-inhibiting properties of cobalt and its effect on rubber properties are, in fact, totally independent of each other. Adhesion protection through corrosion control is the result of interaction between cobalt ions and interfacial sulfide film. Interference of cobalt with rubber compounds consists of a series of homogeneous reactions under the formation of soluble perthiomercaptides [11]. It was also reported that if the promoters that would be completely insoluble in the rubber compound would slowly release the cobalt ions, the corrosion protection afforded by cobalt would be retained [11]. The rate of rust formation in the tire cord would also be reduced [30].

The present study was aimed at developing new cobalt adhesion promoters with better adhesion properties for natural rubber to steel-wire bonding. A study was made to judge the effect of the developed system on the cure characteristics, stress–strain properties, and adhesion properties of the natural rubber-based compound. The performance of the complex was also studied after aging to get an idea of how the product would perform in service. The nature of the failure was also studied from the rubber coverage factor.

EXPERIMENTAL

Materials

The suppliers of all the materials used in this study are given in Table 1.

Chemical Synthesis of the Cobalt Complexes

The cobalt complexes were prepared with the use of boric acid, cobalt hydroxide, and fatty acids (stearic acid and oleic acid) at a molar ratio of 1:3:3. Initially, the methanolic solution of each of cobalt hydroxide, boric acid, stearic acid, and oleic acid was prepared at the 20% concentration level. The stearic acid was warmed at 50°C for 10 min to

TABLE 1 Material Used in the Study

Material	Supplier
Natural rubber, RMA #4	MARDEC International, Kualalumpur, Malayasia
PCTP-based peptiser, PEPTIZOL-7	Acmechem Limited, Ankeleshwar, India
Low-structure high-abrasion furnace black (HAF-LS, N326)	Cabot India Ltd., Mumbai, India
Aromatic oil, RPO 701	Sah Petroleum Limited, Daman, India
Precipitated silica, MFIL 200	Madhu Silica Pvt. Ltd., Bhabhnagar, Gujarat, India
Rubber seal zinc oxide	Zinc–O–India, Ltd., Alwar, Rajasthan, India
Stearic acid	Godrej Soaps Ltd., Vikhroli, Mumbai, India
Antiozonant 6PPD, PILFLEX 13	NOCIL, Thane, India
Antioxidant TMQ, PILNOX TDQ	NOCIL, Thane, India
Tackifying phenol formaldehyde resin	CECA, France
Hexa methoxy methyl melamine, 72% HMMM resin	Techno Wax Chem Pvt. Ltd., Kolkata, India
Cobalt–boron 2 ethyl hexanoate, Manobond 680C	OMG Ltd., Manchester, U.K.
Oil-treated insoluble sulfur, OT 20	Oriental Carbon and Chemical Ltd., Dharuheda, India
Accelerator, di-cyclo hexyl benzo thiazyl sulfenamide (DCBS), PILCURE DCBS	NOCIL, Thane, India
Boric acid	Ranbaxy India Ltd., New Delhi, India
Oleic acid	Godrej Soaps Ltd, Vikhroli, Mumbai, India
Resorcinol formaldehyde resin, penacolite resin, B19 S	Indspec Ltd., USA
Scorch inhibitor, N-cyclo hexyl thio pthalimide, CTP (prevulcanizing inhibitor), PVI 100, ACCITARD RE	ICI, Rishra, India
Steel cord of construction $2+2\times 0.25$ with brass plating: 3.5 gm/kg and copper content: 63.5%	Bekaert Ltd., Belgium

complete its dissolution. The cobalt hydroxide solution was treated with the boric acid solution, and the fatty acid solutions were added separately to this mixture. The mixture was refluxed for 2 h. Excess of methanol was evaporated and the precipitated cobalt salt was removed. The percentage cobalt content was calculated and reported in a subsequent section. The two cobalt complexes—cobalt complex A, cobalt–boron oleic acid complex, and cobalt complex B, cobalt–boron stearic acid complex—obtained were found to be insoluble or partially soluble in the rubber compound.

Characterization of Cobalt Complexes

The cobalt content of the complexes was determined by following a complexometric titration with a di-sodium salt of ethylene diamine tetra acetic acid (EDTA). The specific gravity of the samples was determined in accordance with ASTM D1817. The melting point of the samples was measured in accordance with ASTM D1519. The free-fatty-acid content was determined by titrating the methanolic solution of the cobalt complexes with sodium hydroxide using the Orion 960 autotritor from M/s Orion, USA.

Compound Mixing and Characterization

Mixing of the rubber compound was carried out using a two-wing rotor laboratory Banbury mixer of 1.5 L capacity (M/s Stewart Bolling, USA) in four stages (Master 1, Master 2, Remill, and Final) and the formulation used in the study is given in Table 2. The adhesion promoters used in the study were added at the Master 2 stage.

Master 1 compound mixing was done keeping the temperature control unit (TCU) at 90°C and rotor speed at 30 rpm. Batch dumping was done at a power integrator (PI) reading of 0.32 kWh. The dump temperature of the Master 1 stage mixed batches were found to be within 145–150°C. The Master 2 stage mixed batches were dumped at approximately 140°C, keeping the TCU at 80°C and rotor speed at 30 rpm at a PI reading of 0.24 kWh. The remilling stage was done at a TCU setting of 60°C and a rotor speed of 30 rpm. The batch dumping

TABLE 2 Compound Formulation

Ingredients (parts of metal ions per 100 g of rubber)	Mix identifier A	B	C	D	E	F
Cobalt boron 2-ethyl hexanoate, Manobond 680C	—	0.12	—	—	—	—
Cobalt acetate	—	—	0.12	0.12	—	—
Boric acid	—	—	—	1.0	—	—
Cobalt complex A	—	—	—	—	0.12	—
Cobalt complex B	—	—	—	—	—	0.12

Other ingredients used in the formulation kept constant are (phr) RMA # 4-100, N326 black—55.0, PCTP—0.10, aromatic oil—12.0, ppt. silica—10.0, zinc oxide—8.0, stearic acid—1.0, 6PPD—2.0, TMQ—1.0, PF resin—2.5, HMMM 72%—3.5, insoluble sulfur—6.0, DCBS—0.80, Penacolite resin—2.0 and PVI 100—0.10.

was done at a PI reading of 0.18 kWh at a dump temperature around 120°C. In the case of the final stage mixing, the TCU was kept at 60°C and the rotor speed at 30 rpm. The batch was dumped at a PI reading of 0.12 kWh. The dump temperature of the batches was found to be within 90–100°C. In between each stage of mixing, a maturation period of 4–8 h was maintained for all the compounds. The dumped batches from the Banbury mixer were sheeted out in a laboratory two-roll mill from M/s Santosh Industries, New Delhi, India.

Rheometric Properties

Rheometric properties of the green compounds were determined at 160°C for 1 h using 0.5° arc in a moving die rheometer, MDR 2000E, in accordance with ASTM D5289. The Mooney viscosity, ML $(1+4)$ at 100°C, was determined in a Mooney viscometer, MV 2000E, in accordance with ASTM D1646. Both pieces of equipment were from M/s Alpha Technologies, USA.

Physical Properties

Sample Preparation

The green rubber compounds were cured in accordance with ASTM D3182 in an electrically heated hydraulic curing press from M/s Hind Hydraulics, New Delhi, India, using compression moulding. The moulding conditions followed to cure the compounds were 141°C for 1 h at a molding pressure of 15 MPa. The T-pull adhesion samples were also cured at 141°C for 1 h.

Aging of Samples

To simulate the service conditions of a tire, the cured tensile samples were subjected to aerobic aging and adhesion test samples were subjected to anaerobic aging, humid aging, steam aging and salt aging. The aerobic aging of tensile samples was carried out at 70°C for 2 weeks in a multicell aging oven from M/s Tempo Industries, New Delhi, India. For adhesion samples, the anaerobic aging was carried out in the adhesion mold itself for an extended curing time period of 8 h and 16 h at 141°C. The humid aging was carried out at 90% relative humidity at 55°C for 2 weeks and 4 weeks in a humid aging oven from M/s Tempo Industries, New Delhi, India. The salt aging was carried out using 10% sodium chloride solution for 3 days and 7 days, and the steam aging was done at 120°C for 3 days and 7 days.

Testing

The tensile properties (including tear strength) were measured using a universal testing machine, Zwick UTM 1445 from M/s Zwick, Germany, in accordance with ASTM D412 and ASTM D624. The hardness was measured with a dead-load IRHD hardness tester, M/s H. W. Wallance and Company Ltd., U.K., in accordance with ASTM D1415. The T-pull adhesion samples were tested in accordance with ASTM D2229 using the Zwick UTM 1445. The coverage of the initial T-pull adhesion samples was studied. The relative extent of rubber coverage on the pulled-out steel cord by the naked eye was expressed by bare steel cord as 0% and fully rubber-covered cord as 100%.

RESULTS AND DISCUSSION

Chemical Characterization of Cobalt Complexes

The chemical characterization of the cobalt complexes is reported in Table 3. It was found that the cobalt–boron oleate complex had the lowest cobalt content, whereas cobalt acetate showed the highest melting point. The free fatty acid was found to be the least for cobalt–boron 2-ethyl hexanoate.

Rheometric Properties

The rheometric properties are given in Table 4. All the experimental compounds showed similar maximum torque, scorch time (ts2), and optimum cure time (tc90), whereas the compound having no adhesion promoter showed low ts2, tc90, and cure rate. Usually the lower tc90 indicates that the adhesion promoters accelerated the cure reaction. It has been reported that the adhesion promoters influence the rate-determining step and thereby reduce the activation energy and lead to an early onset of curing and higher cure rate [25].

TABLE 3 Chemical Characterization of Cobalt Complexes

Cobalt complexes	Specific gravity	Melting point (°C)	Free fatty acid content (%)	Cobalt content (%)
Cobalt–boron 2-ethyl hexanoate, Manobond 680C	1.40	99	0.5	23.5
Cobalt acetate	1.36	128	4.0	23.7
Cobalt complex A—cobalt–boron oleic acid complex	1.00	81	6.0	5.4
Cobalt complex B—cobalt–boron stearic acid complex	1.10	84	5.0	11.5

TABLE 4 Rheometric Properties

Sample id.	Test parameter Maximum torque (dN-m)	ts2 (min)	tc90 (min)	Cure rate (dN-m/min)	Mooney viscosity (MU)
A	24.11	2.66	17.56	1.37	60
B	25.06	2.21	11.94	2.28	60
C	25.24	2.10	10.50	2.68	62
D	24.11	2.10	11.20	2.68	62
E	23.75	2.01	10.16	2.67	56
F	25.20	2.19	12.00	2.32	60

Note: The rheometric properties reported are the averages derived from three test specimens.

During curing, the accelerator sulfur complex reacts with cobalt to form a new complex. This cobalt complex assumed to promote the cure reaction as

$$\text{Acc-S}_x + \text{CoX}_2 \longrightarrow \text{Co-S}_y\text{-X}_2 + \text{Acc-S}_{(X\text{-}Y)} \tag{1}$$

The Mooney viscosity of all the compounds was found to be comparable.

Physical Properties

The stress–strain properties, including hardness, are given in Table 5. A schematic representation of the tensile properties (300%

TABLE 5 Physical Properties

Sample id.	Test parameter M300% (MPa)	TS (MPa)	EB (%)	Hardness (IRHD)	Tear (N/mm)
A	14.6 (–)	19.8 (51)	402 (21)	84 (+6)	67 (33)
B	14.3 (–)	19.6 (54)	403 (24)	83 (+7)	59 (38)
C	15.3 (–)	20.2 (47)	398 (21)	84 (+7)	66 (28)
D	14.8 (–)	20.0 (45)	397 (22)	84 (+8)	64 (34)
E	13.6 (–)	19.6 (46)	419 (21)	83 (+8)	61 (31)
F	15.1 (–)	18.8 (53)	370 (23)	86 (+4)	55 (33)

Note: The physical properties reported are the medians derived from five test specimens. Results in the parentheses () are the percent retention of physical properties after air aging at 70°C for two weeks. In case of hardness, the + values indicate increase in hardness after aging.

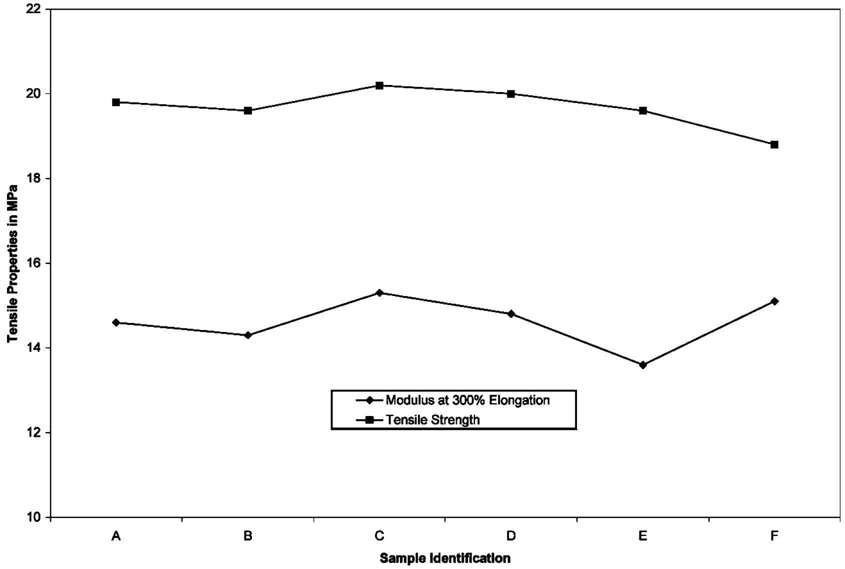

FIGURE 1 Effect of cobalt adhesion promoters on tensile properties.

TABLE 6 T-Pull Adhesion Properties

	Test parameter						
Sample id.	Unaged adhesion (N)	Anaerobic aged adhesion[a] (N)	Anaerobic aged adhesion[b] (N)	Steam aged adhesion[c] (N)	Steam aged adhesion[d] (N)	Salt aged adhesion[e] (N)	Salt aged adhesion[f] (N)
A	384 (85)	385	278	288	220	294	229
B	445 (95)	396	322	376	342	373	319
C	420 (90)	390	290	321	278	310	277
D	418 (90)	388	315	355	322	325	290
E	423 (95)	390	344	369	337	357	290
F	426 (95)	389	337	371	334	330	287

[a] Anaerobic aging at 141°C for 8 h.

[b] Anaerobic aging at 141°C for 16 h.

[c] Steam aging at 120°C for 3 days.

[d] Steam aging at 120°C for 7 days.

[e] Salt aging in 10% NaCl solution for 3 days.

[f] Salt aging in 10% NaCl solution for 7 days.

The T-pull adhesion results are averages of seven test specimens.

The values within the parentheses () indicate the percent coverage as observed through naked eye.

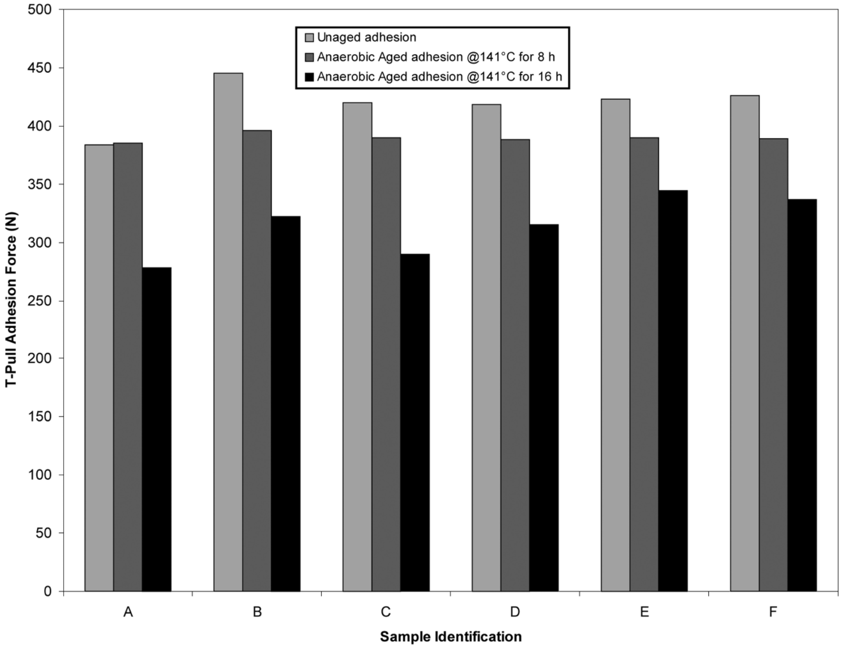

FIGURE 2 Effect of cobalt adhesion promoters on anaerobic aged T-pull adhesion.

Modulus and tensile strength) is also shown in Figure 1. The compounds made with the synthesized cobalt salts as well as the cobalt acetate–boric acid combination showed comparable physical properties with that of the batch that had Manobond 680C®. The retention of properties after air aging was also found to be comparable.

T-Pull Adhesion

The unaged and aged T-pull adhesion results are given in Table 6. The schematic representation of the unaged, aerobic aged, salt aged, and steam aged T-pull adhesion are also shown in Figures 2–4.

The initial pull-out force values obtained for compounds containing cobalt acetate, cobalt acetate–boric acid combination, and the synthesized cobalt complexes were found to be comparable with that of the compounds with Manobond 680C. The retention of pull-out force for the cobalt acetate–boric acid combination and the synthesized cobalt complexes after anaerobic and steam aging was also found to be

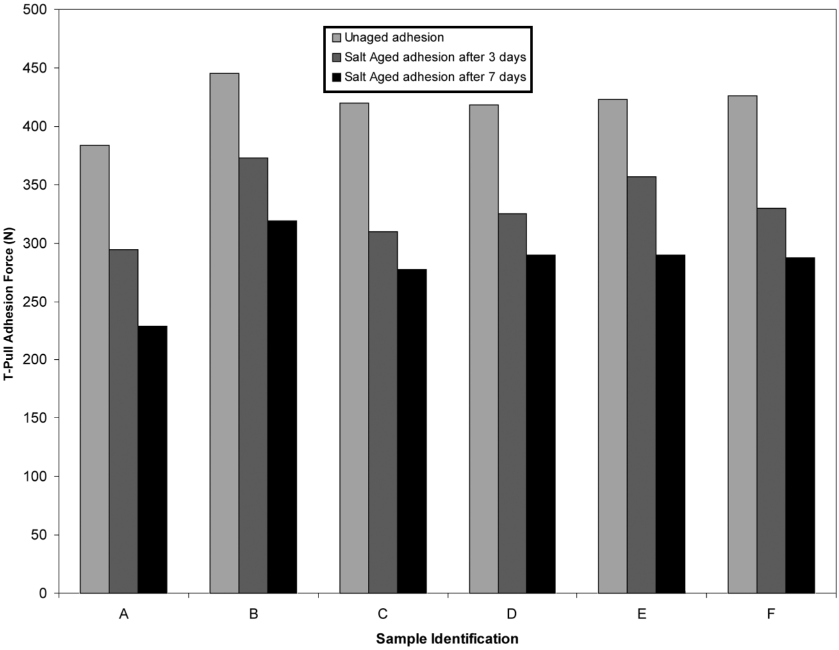

FIGURE 3 Effect of cobalt adhesion promoters on salt aged T-pull adhesion.

comparable with that of Manobond 680C. The retention of the pull-out force of the compound with cobalt acetate (compound C) was found to be lower in the case of an extended period of steam and salt aging. The batch with Manobond 680C showed slightly better retention of pull-out force after salt aging. Because the cobalt complexes were partially soluble in the rubber compounds, the rate of formation of inactive sulfides during the cure reaction might be also slow. Therefore, corrosion protection, which is demanded for longer tire life, can be expected with the developed system. The analysis of the failed adhesion samples before aging indicated that the coverage of the compound with developed complexes was comparable with that of Manobond 680C.

CONCLUSION

Addition of cobalt complexes to the system increased the retention of pull-out force including the rubber coverage. Simple cobalt salts such as the cobalt acetate and cobalt acetate–boric acid combination can also act as adhesion promoters. The synthesized cobalt complexes that

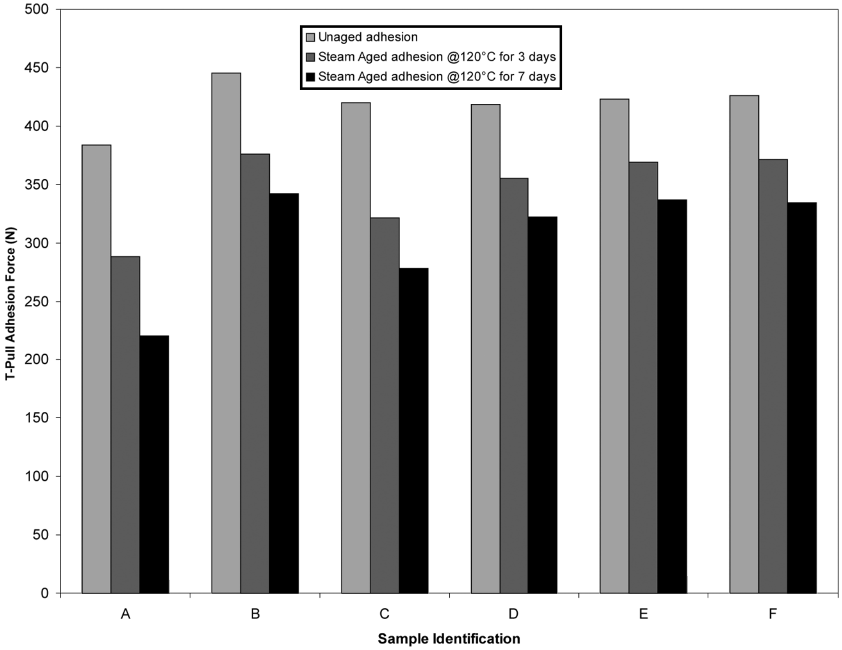

FIGURE 4 Effect of cobalt adhesion promoters on steam aged T-pull adhesion.

contained boron as part of the ligand showed comparable properties with that of Manobond 680C, and they can also be used as a substitute for Manobond 680C.

ACKNOWLEDGMENT

The authors thank HASETRI and J.K. Tyre management for kind permission to publish this work.

REFERENCES

[1] van der Aar, C. P. J., van der Does, L., Noordermeer, J. W. M., Bantjes, A., and Albers, A., *Prog. Rubber Plastics Technol.* **16**(2), 87–116 (2000).

[2] Sanderson, C., British Patent 3288 (1862).

[3] Ashida, M., Nakatani, M., Takemoto, Y., and Goto, M., *International Polym. Sci. Technol.* **12**, T41–48 (1985).

[4] Davies, J. R., *Kautschuk Gummi Kunststoffe* **37**, 493 (1984).

[5] Ikeda, Y. and Yamaguchi, K., *Nippon Gomu Kyoukaishi* **63**, 372 (1990).

[6] Mori, K., Hirhara, H., and Oishi, Y., *Rubber Chem. Technol.* **70**(2), 211–221 (1997).

[7] van Ooij, W. J., *Rubber World* 26 (November 1996).

[8] Skeist, I., "*Handbook of Adhesive,*" 3rd ed. (Van Nostrand Reinhold, New York, 1990), Chap. 35, pp. 593–596.

[9] van Ooij, W. J., *Rubber Chem. Technol.* **52**(3), 605–675 (1979).

[10] van Ooij, W. J., *Rubber Chem. Technol.* **57**(3), 421–456 (1984).

[11] Van Ooij, W. J. and Biemond, M. E. F., *Rubber Chem. Technol.* **57**(4), 686–702 (1984).

[12] van Ooij, W. J. Giridhar, J., and Ahn, J. H., *Kautschuk Gummi Kunststoffe* **44**(4), 348–359 (1991).

[13] Swarts, J. M., *Rubber World* 26–27 (February 2002).

[14] Buchan, S., *Rubber to Metal Bonding*, 2nd ed. (Crosby Lockwood and Son Ltd., London, England, 1959).

[15] Haemers, G., *Rubber World* 26 (September 1980).

[16] Ashida, M., *International Poly. Sci.* **11**, 83 (1984).

[17] Ishikawa, Y., *International Polym. Sci. Technol.* **19**, T89–97 (1992).

[18] Hassan, M., Chandra, A. K., Mukhopadhyay, R., and Bhowmick, A. K., *Rubber World* **207**, 25–28 (January 1992).

[19] Chandra, A. K., Biswas, A., Mukhopadhyay, R., and Bhowmick, A. K., *Plast. Rubber Compos. Process. Appl.* **22**(4), 249–258 (1994).

[20] Chandra, A. K., Biswas, A., Mukhopadhyay, R., and Bhowmick, A. K., *J. Adhes.*, **44**, 177–196 (1994).

[21] Chandra, A. K., Kumar, N. R., Mukhopadhyay, R., Bhattacharya, A. K., and Bhowmick, A. K., *Kautschuk Gummi Kunststoffe* **49**(2), 125–130 (1996).

[22] Chandra, A. K., Mukhopadhyay, R., and Bhowmick, A. K., *J. Adhes.* **63**, 71–93 (1996).

[23] Chandra, A. K., Mukhopadhyay, R., Konar, J., Ghosh, T. B., and Bhowmick, A. K., *J. Mat. Sci.* **31**, 2667–2676 (1996).

[24] Chandra, A. K., Biswas, A., Mukhopadhyay, R., and Bhowmick, A. K., *J. Adhes. Sci. Technol.* **10**(5), 431–460 (1996).

[25] Chandra, A. K., Deuri, A. S., Mukhopadhyay, R., and Bhowmick, A. K., *Kautschuk Gummi Kunststoffe* **50**(2), 106–111, (1997).

[26] Chandra, A. K., Ph.D. thesis, Indian Institute of Technology (IIT), Kharagpur, India (July 1996).

[27] Ishikawa, Y. and Kawakami, S., *Rubber Chem. Technol.* **59**(1), 1–15 (1986).

[28] Seibert, R. F., Paper No. 52, presented at the 144th meeting of the Rubber Division, American Chemical Society, Orlando, Florida (October, 25–29, 1993).

[29] Carpenter, G. T., *Rubber Chem. Technol.* **51**(4), 788–798 (1978).

[30] Barker, L. R., *NR Technology* **12**(4), 77–84 (1981).