

## EFFECT OF ZnO CONTENTS AT THE SURFACE OF BRASS-PLATED STEEL CORD ON THE ADHESION PROPERTY TO RUBBER COMPOUND

Gyung Soo Jeon<sup>†</sup>, Min Hyeon Han<sup>\*</sup> and Gon Seo<sup>\*\*</sup>

Department of Chemical Technology, Provincial College of Damyang, Damyang, Chonnam 517-800, South Korea

<sup>\*</sup>R & D Center, Kumho Tire Co and Inc., Ltd., Kwangju 506-040, South Korea

<sup>\*\*</sup>Department of Chemical Technology, Chonnam National University, Kwangju 500-757, South Korea

(Received 18 September 1998 • accepted 6 January 1999)

**Abstract**—An effect of ZnO concentration at the surface of brass-plated steel cord on the adhesion property between a rubber compound and a brass-plated steel cord was investigated. Cord composition was determined by an Auger microscope with Ar ion sputtering. Two different steel cords were prepared; one (cord A) had higher ZnO concentration at the cord surface compared to the other (cord B). Pull-out force of unaged adhesion sample of cord A was lower than that of cord B. But the adhesion durability of the humidity-aged adhesion sample of cord A was better than the latter. Rubber coverage of the pull out cord for the unaged adhesion samples of cord A was poor, indicating insufficient formation of an adhesion layer. Pull-out force of the thermal-aged adhesion samples decreased with increasing aging time and that of cord A was lower than that of cord B. The enhancement of rubber coverage during initial aging period could be explained by an additional formation of copper sulfide at the adhesion interphase and an increase of modulus of rubber compound adjacent to the adhesion layer. With further increases of aging time, adhesion interphase grew excessively and the physical property of rubber compound deteriorated significantly, such that rubber coverage of adhesion samples decreased markedly with increasing aging time.

Key words : Adhesion, Rubber Compound, Brass-Plated Steel Cord, ZnO Concentration at Surface, Auger Electron Spectroscopy

### INTRODUCTION

A common reinforcement material in modern radial tires is a brass-plated steel tire cord. Brass on steel cords reacts with the sulfur in the rubber compound during the curing process of tire manufacturing, forming an adhesion interface between the steel cord and the rubber compound. Copper sulfide is a key material for the adhesion formation, but zinc sulfide usually coexists. Oxides and hydroxides of copper and zinc are also formed at the adhesion interface by the reaction of brass with oxygen and water in the rubber compound [van Ooij, 1977, 1984; van Ooij and Kleinhesselink, 1980]. It is well established that too large a content of any component in the adhesion interface causes a cohesive failure, so it is very important to control the surface composition of the steel cord and the composition of rubber compound so as not to induce excessive growth of copper sulfide or zinc oxide.

Many studies have thus already been carried out regarding the optimal copper content and plating thickness of brass [Haemers and Mollet, 1978], as well as the optimal for rubber composition and curing condition [Ishikawa, 1984; van Ooij, 1978] to obtain a strong and stable adhesion interface.  $\alpha$ -Brass with high content of copper is used as a plating material to form a sufficient amount of copper sulfide, and a zinc oxide layer is formed on the outer surface due to high affinity of zinc to

oxygen. A thick zinc oxide layer leads to poor adhesion because of slow formation of copper sulfide. Otherwise, the zinc oxide, with proper thickness, has a positive contribution to the stability of the adhesion interface by suppression of the excessive growth of copper sulfide. The zinc oxide layer may also become thicker through humidity aging, so the adhesion interface can be easily broken because of its excessive growth and lack of metallic zinc [Jeon et al., 1998a, b, 1999a, b]. However, optimum thickness of the zinc oxide layer in the adhesion interface improves the adhesion stability, especially in prompting the stability which in turn results in the suppression of the additional reaction of copper and zinc when a tire is exposed to heat, water and oxygen. Therefore, the content of zinc oxide in the outer surface of brass-plated steel cord is carefully controlled by the cord manufacturer to sustain the optimal reactivity of brass and the high stability of adhesion.

We obtained two sample cords with different amounts of zinc oxide at the outer surface, with other characteristics of brass-plated steel cord such as plating amount, bulk copper/zinc ratio, and cord construction being the same. These cords are adequate to investigating the effect of zinc oxide content on its adhesion properties to rubber compound. In this study, scanning Auger electron spectroscopy was used to characterize the surface composition of these cords. Adhesion properties before and after humidity aging, as well as thermal aging treatments, were subsequently examined and the mechanism on how zinc oxide affects the adhesion properties was discussed.

<sup>†</sup>To whom correspondence should be addressed.

E-mail : gjeon@damyang.ac.kr

**Table 1. Rubber compound recipe**

| Material         | Trade name                  | Manufacturer                | Contents (phr) |
|------------------|-----------------------------|-----------------------------|----------------|
| Masterbatch      |                             |                             |                |
| Natural rubber   | SMR-10                      | Lee Rubber Co., Malaysia    | 80             |
| Butadiene rubber | BR-01                       | Kumho Petrochem. Co., Korea | 20             |
| Carbon black     | N351                        | Lucky Co., Korea            | 40             |
| Processing oil   | A#2                         | Michang Co., Korea          | 5              |
| Activator        | ZnO                         | Hanil Co., Korea            | 10             |
| Antioxidant      | Kumanox-RD <sup>1)</sup>    | Monsanto Co., U.S.A.        | 1              |
| Final mixing     |                             |                             |                |
| Activator        | Stearic acid                | Pyungwha Co., Korea         | 1.5            |
| Accelerator      | Santocure MOR <sup>2)</sup> | Monsanto Co., U.S.A.        | 0.7            |
| Sulfur           | Crystex HS OT 20            | Akzo Co., The Netherlands   | 5              |

<sup>1)</sup>2,2,4-trimethyl-1,2-dihydroquinone.<sup>2)</sup>2-(Morpholiniothio)-thiobenzothiazole sulfenamide.

## EXPERIMENTAL

A rubber compound was prepared and the formulation for the master batch and final mixed compound is given in Table 1. All the components were mixed as described in ASTM D3184-80 using an internal mixer (Banbury Mixer model 82, Farrel Co., U.S.A.). Details of the mixing procedure for the rubber compound are similar to those explained in our previous monographs [Seo, 1997; Jeon et al., 1998a, b, 1999a, b].

A rheocurve for the prepared rubber compound was recorded on a oscillating disk-type rheometer (model 100, Monsanto Instrument, U.S.A.) at 160 °C. The  $t_{90}$  time and maximum torque were obtained from the rheocurve. Mooney viscosity and scorch time were measured according to ASTM D1646-95 using a Monsanto MV-2000 viscometer.

The hardness of vulcanizates was measured using a Shore A durometer according to ASTM D2240-91 and tensile properties using a tensile tester (Instron model 6021, U.S.A.) according to ASTM D412-92.

T-test adhesion samples were prepared in accordance with ASTM D2229-93 by curing at 160 °C for the time of  $t_{90}$  plus 5 min using a cure press (Osaka Jack Co. Ltd., Japan). The brass-plated steel cords used were supplied by Bekaert Co. (Belgium), and they have the same construction of 4×0.28 in, of which 4 steel filaments having the same diameter of 0.28 mm were twisted together. All specifications of those cords are identical except the surface concentration of Cu and ZnO. Cord A has higher ZnO content at the surface than cord B. The plating weight of brass on the steel cords was 3.6 g/kg and the copper content was 63.6 %. For humidity aging, the adhesion samples were placed in a humidity chamber for 15 days at 85 °C and 85 % relative humidity. Also, the adhesion samples were aged thermally for 15 days at 90 °C. Pull-out force was determined as the maximum force exerted by the tensile tester (Instron model 6021, U.S.A.) on the T-test sample during the pull-out test, with 10 mm/min of crosshead speed. Rubber coverages were also noted. Each value reported was an average of the results obtained from six specimens.

Depth profiles from the outer brass surface to the bulk brass

were recorded on an Auger electron spectrometer (Phi 670, Perkin-Elmer Co., U.S.A.) [Seo, 1997; Jeon et al., 1998a, b, 1999a, b]. Sputtering rate for the sample cords was determined to be 25 nm/min. Generally, it is difficult to determine the sputtering rate for the adhesion interface precisely because it includes various chemical components with variable concentrations. Therefore, a sputtering time instead of an absolute depth was used as a measure of the adhesion interface depth in this paper.

Scanning electron microscopy (SEM, model 840A, JEOL Co., Japan) was used to investigate the fracture mode of adhesion. Also, the concentration of Cu, Zn and S on pulled out cord surface after an adhesion test was determined employing energy dispersive X-ray analysis (EDX, model JXA-840, England).

## RESULTS AND DISCUSSION

### 1. Surface Compositions of Sample Cord by AES

Surface compositions of each cord were measured by AES with Ar sputtering depth profile. As shown in Fig. 1, the surface compositions of these cords were markedly different. The carbon detected at the outer surface was a result of partial contamination. With increased sputtering time, the carbon concentration decreased drastically. Copper content increased up to 2 min and remained nearly constant at about 3 min of sputter-

**Table 2. Cure characteristics of the rubber compound by an oscillating disk (OD) type rheometer and Mooney viscometer**

| OD rheometer <sup>1)</sup> |          |                      |      |            | Mooney viscometer <sup>2)</sup> |                         |      |
|----------------------------|----------|----------------------|------|------------|---------------------------------|-------------------------|------|
| Time (min)                 |          | CRI <sup>3)</sup>    |      | Torque (J) | Time (min)                      | Viscosity <sup>4)</sup> |      |
| $t_2$                      | $t_{90}$ | (min <sup>-1</sup> ) | min  | max        | $t_5$                           | $t_{35}$                | (J)  |
| 2.7                        | 6.4      | 27.0                 | 1.30 | 5.85       | 20.6                            | 27.6                    | 3.95 |

<sup>1)</sup>The rubber compounds were sheared to  $\pm 1^\circ$  and 1.67 Hz at 160 °C.<sup>2)</sup>The rubber compounds were sheared to 2 rpm at 125 °C.<sup>3)</sup>CRI = 100 / ( $t_{90} - t_2$ ).<sup>4)</sup>ML<sub>1+4</sub>, 125 °C

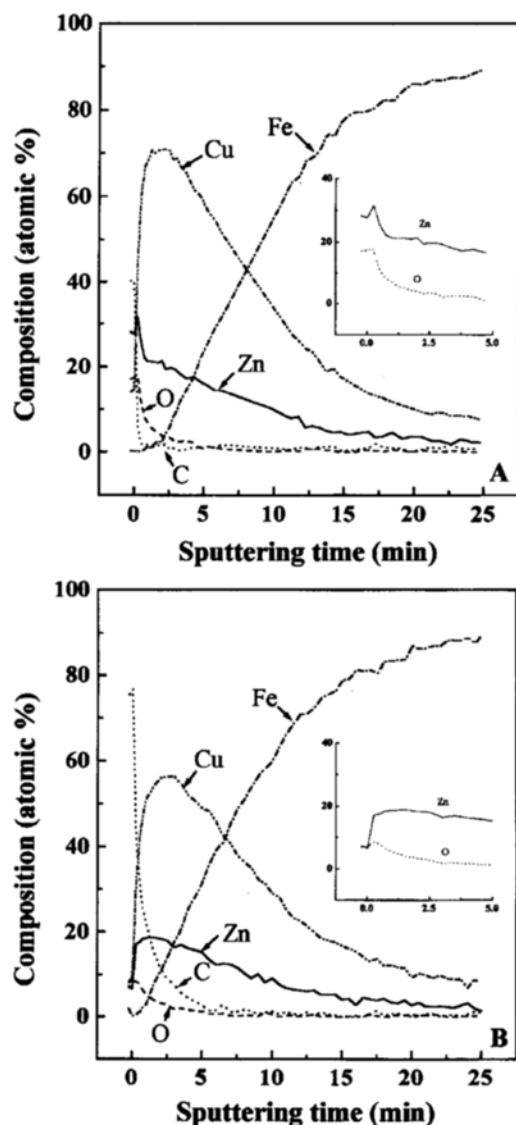


Fig. 1. AES depth profiles of brass-plated steel cords.  
(a) cord A, (b) cord B

Table 3. Tensile properties of vulcanizate

|                           | Hardness<br>(Shore A) | Modulus (MPa) |       |       |       | T.S. <sup>2)</sup><br>(MPa) | E.B. <sup>3)</sup><br>(%) |
|---------------------------|-----------------------|---------------|-------|-------|-------|-----------------------------|---------------------------|
|                           |                       | 5 %           | 100 % | 200 % | 300 % |                             |                           |
| Before aging              | 65                    | 0.43          | 3.65  | 9.11  | 15.3  | 23.7                        | 439                       |
| After aging <sup>1)</sup> | 77                    | 0.71          | -     | -     | -     | 6.8                         | 77                        |

<sup>1)</sup>The tensile specimens were thermally aged for 15 days at 95 °C.

<sup>2)</sup>Tensile strength.

<sup>3)</sup>Elongation-at-break.

ing. Over this region of sputtering time, the copper concentration decreased continuously. At the outer surface, zinc and oxygen contents were high due to the high affinity of zinc to oxygen on both cords. Though the zinc content was higher than the oxygen content, their similar concentration profiles showed that zinc at the outer surface was oxidized. At the surface of steel cord, little iron was detected. After sputtering of 1 min, iron began to emerge in the depth profile. With in-

creasing sputtering time, iron concentration increased steadily. At the sputtering time of 20 min, iron became a dominant element and showed a constant concentration. After sputtering of 20 min, most copper, zinc, oxygen and carbon disappeared and iron was dominant, indicating an iron substrate. The fact that zinc oxide developed at the cord surface followed by a subsequent brass layer agrees well with the depth profile of steel cords reported previously [van Ooij, 1978; Kurbatov et al., 1991a, b; Seo, 1997].

At the outer surface, ZnO was predominant and underneath it brass alloy was present. After 1 min of sputtering, copper was observed in its metallic state. None of the zinc was present as a metallic state until after 5 min of sputtering. Oxygen concentration first increased sharply and then dropped, and it seemed to be related to the zinc concentration at the outer surface.

The conspicuous difference between the cord A and cord B in the depth profile was the content of ZnO at the outer surface; compared to cord B, cord A had a larger amount of ZnO at the cord surface. Though the difference of ZnO concentration at the outer surface may stem from either the manufacturing process of steel cords or the storage condition, the adhesion properties should be considered in conjunction with the difference of ZnO content.

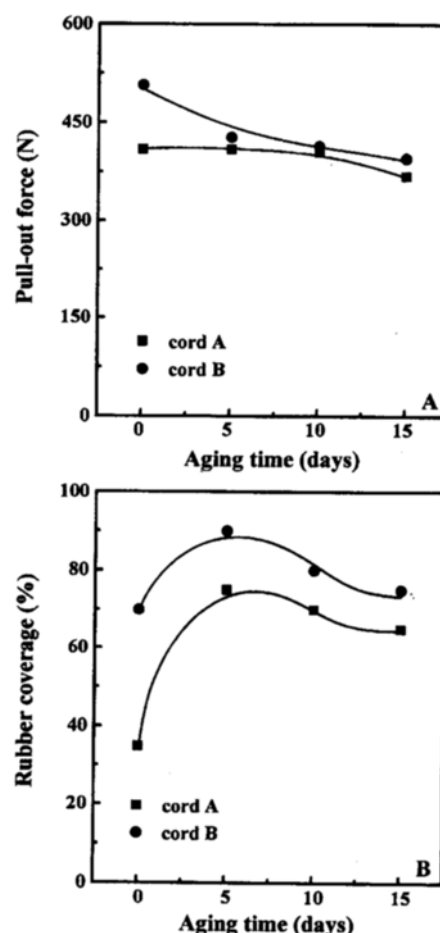


Fig. 2. The adhesion force of the humidity-aged sample and the rubber coverage on the surface of the pulled out steel cord for the cord having different surface concentrations of Cu and ZnO.

## 2. Adhesion Properties

Pull-out force and rubber coverage of adhesion samples prepared using cord A and cord B are shown in Fig. 2. Unaged pull-out force of cord A was poorer than that of cord B. Rubber coverage of cord A before aging was very low as only one half of cord B was attained. The unaged adhesion properties of cord A, higher ZnO content, were by far poorer than those of cord B.

The magnitude of change in the adhesion property under humidity aging also varied depending on the cord type used for either cord A or cord B. The pull-out force for cord A was nearly constant irrespective of the humidity aging time, whereas that for cord B decreased slightly with increasing humidity aging time. On the other hand, rubber coverage increased significantly after humidity aging of 5 days for both cord A and cord B. Further increase of humidity aging time diminished the rubber coverage. The tendency of rubber coverage for cord A with respect to humidity aging time was similar to that for cord B.

Though pull-out force of thermal-aged samples decreased with increasing aging time on both cords (Fig. 3), the pull-out force of cord A was always lower than that of cord B. Rub-

ber coverage of these cords increased with thermal aging time, whereas that of cord A decreased with prolonged aging treatment about 10 days.

Surface compositions of pulled out cord for unaged adhesion samples were measured by SEM/EDX analysis (Table 4). Sulfur concentration of cord A, a measure of the formation of adhesion layer, was by far lower than that in cord B, indicating insufficient formation of copper sulfide.

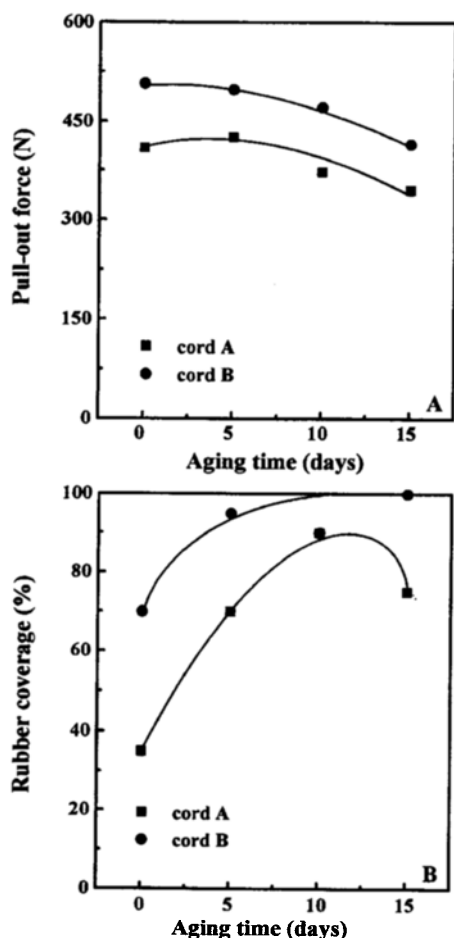
## 3. Effect of Zinc Oxide on the Adhesion

Zinc oxide concentration at the outer most surface of steel cord has a large effect on the adhesion property. Cord A, which has high zinc oxide content, showed poor initial adhesion property compared to that of cord B with low zinc oxide. The surface composition, obtained through an EDX investigation of the pull-out surface of a cured adhesion sample, indicated that the sulfur concentration at cord A surface is relatively lower than cord B, as shown in Table 4. The diminished adhesion property of cord A can be attributed to an insuffi-

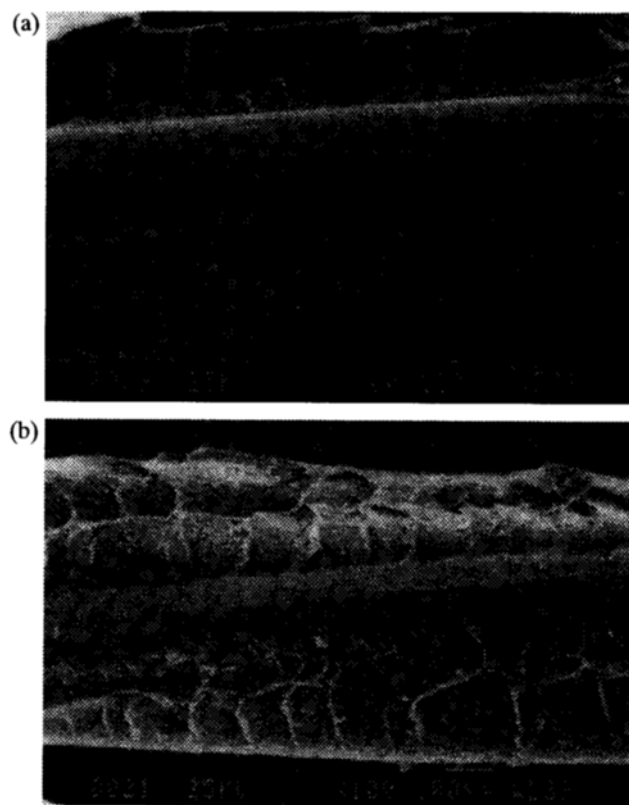
**Table 4. The relative surface composition<sup>b)</sup> of pulled out cord from unaged T-test samples determined by EDX analysis**

|        | Relative composition (wt%) |      |     |
|--------|----------------------------|------|-----|
|        | Cu                         | Zn   | S   |
| Cord A | 60.4                       | 39.1 | 0.5 |
| Cord B | 62.0                       | 34.3 | 3.7 |

<sup>b)</sup>The exposed metal planes of pulled out cord were randomly chosen.



**Fig. 3. The adhesion force of the thermal-aged sample and the rubber coverage on the surface of the pulled out steel cord for the cords having different surface concentrations of Cu and ZnO.**



**Fig. 4. The SEM micrographs of pulled out cord surface for unaged adhesion samples.**

(a) cord A, (b) cord B

cient growth of adhesion layer by hindered copper sulfide formation because the zinc oxide layer at the surface of cord A leads to a lowered activity and suppressed diffusion of copper.

After humidity or thermal aging, the pull-out force decreased while rubber coverage increased for both cords. Since adhesion specimens were cured on  $t_{90}$  basis with rubber vulcanization of about 90 %, a less desirable adhesion property was achieved immediately after curing as a consequence of the lack of growth of the adhesion layer which consists of copper sulfide and so on. On the contrary, rubber coverage improves because an elevated temperature causes a relatively higher probability of fracture propagating through the rubber matrix.

After thermal aging, cord A with high zinc oxide content also exhibited poor adhesion property. Despite some differences depending on the cord or treatment, better adhesion property was attained for cord B with low zinc oxide concentration. As zinc oxide has weak mechanical strength, the higher the zinc oxide content, the lower the stability of the adhesion layer.

Zinc oxide is necessarily formed at the cord surface during the drawing process of the cord after zinc plating. Some researchers argued that zinc oxide improves adhesion because it suppresses an excessive growth of copper sulfide, which causes an eventual adhesion failure, by hindering the copper diffusion. However, when zinc oxide is as much as observed as a layer at the outermost surface, adhesion property becomes diminished because of the deficiency in copper sulfide formation or accelerated growth of zinc oxide during thermal aging. Although zinc oxide content is not the only decisive factor for determining the adhesion property, excessive formation of zinc oxide at the brass-plated cord surface can result in poor adhesion.

## CONCLUSION

1. Poor adhesion was obtained both before and after thermal aging for cord A which had high zinc oxide contents.

2. Initial adhesion property became poor because of insufficient formation of the adhesion layer due to suppressed copper sulfide formation by zinc oxide.

3. Optimization of zinc oxide content should be taken into account for the improvement of pull-out force, and aging stability should also be considered in relation to such a viewpoint.

## ACKNOWLEDGMENTS

Thanks are due to Dr. Y. M. Kim, Dr. S. H. Han and Mrs. J. H. Lee in Korea Institute of Science and Technology (KIST)

for their assistance in performing the AES with ion sputtering analyses.

## REFERENCES

- Haemers, G. and Mollet, J., "The Role of the Brass Surface Composition with Regard to Steel Cord Rubber Adhesion," *J. Elast. Plast.*, **10**, 241 (1978).
- Ishikawa, Y., "Effects of Compound Formulation on the Adhesion of Rubber to Brass-Plated Steel Cord," *Rubber Chem. Technol.*, **57**, 855 (1984).
- Jeon, G. S., Han, M. H. and Seo, G., "Improving Adhesion Properties between Rubber Compound and Brass-Plated Steel Cord by the Addition of Epoxidized Natural Rubber to Rubber Compound," *Korean J. Chem. Eng.*, **15**, 317 (1998a).
- Jeon, G. S., Kim, Y. M. and Seo, G., "Adhesion Properties between Cobalt Salt-Containing Rubber Compound and Brass-Plated Steel Cord," *HWAHAK KONGHAK*, **36**, 179 (1998b).
- Jeon, G. S., Han, M. H. and Seo, G., "Effect of Tetrachlorobenzoquinone on the Adhesion between Rubber Compound and Brass-Plated Steel Cord," *J. Adhesion*, **69**, 39 (1999a).
- Jeon, G. S., Han, M. H. and Seo, G., "Enhancing Adhesion Properties between Rubber Compound and Brass-Plated Steel Cord by Incorporating Silica into Rubber," *J. Adhesion Sci. Technol.*, **13**, 153 (1999b).
- Kurbatov, G. G., Beshenkov, V. G. and Zaporozhenko, V. I., "AES and Factor Analysis Study of Cord-Oxidized Brass Layers and Rubber-to-Brass Interface Chemical Composition," *Surf. Interface Anal.*, **17**, 779 (1991a).
- Kurbatov, G. G., Zaporozhenko, V. I., Gorayev, V. M., Gofman, A. M., Kukharensko, Y. A. and Goryaev, V. M., "Quantitative AES with High Spatial Resolution for Determination of Oxidized Brass Layers of Cords and Rubber-to-Brass Interface Chemical Composition," *Mittwoch Sektion B*, **26**, 161 (1991b).
- Seo, G., "Stabilizing the Adhesion Interphase between Rubber Compound and Brass Film by the Addition of Resorcinol Formaldehyde Resin to the Rubber," *J. Adhesion Sci. Technol.*, **11**, 1433 (1997).
- van Ooij, W. J., "Mechanism of Rubber-to-Brass Adhesion. Part 1: X-Ray Photoelectron Spectroscopy Study of the Rubber-to-Brass Interface," *Kautsch. Gummi, Kunst.*, **30**, 739 (1977).
- van Ooij, W. J., "Mechanism of Rubber-to-Brass Adhesion: Effect of Rubber Composition on the Adhesion," *Rubber Chem. Technol.*, **51**, 52 (1978).
- van Ooij, W. J. and Biemond, M. E. F., "A Novel Class of Rubber to Steel Tire Cord Adhesion Promoters," *Rubber Chem. Technol.*, **57**, 686 (1984).