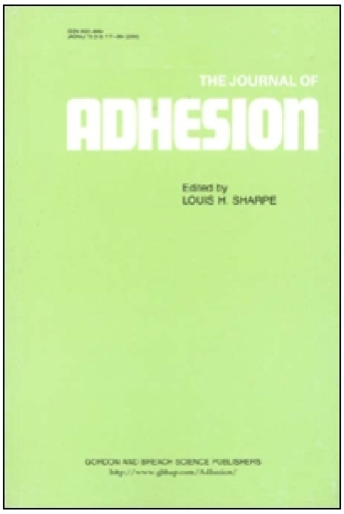

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Adhesion Between Rubber Compound and Copper-Film-Plated Steel Cord

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Four copper-film-plated steel cords (abbreviated hereafter as copper-plated cord) with different thickness of copper film from 32 to 90 nm were prepared and their adhesion properties with rubber compound were investigated. Adhesion properties improved with the decrease in the thickness of the copper film. Unaged pull-out force and rubber coverage of copper-plated cords were inferior to those of brass-plated cord, but adhesion degradation was significantly slower on copper-plated cords resulting in better adhesion after humidity aging of 15 days and salt solution aging of 5 days. The excellent adhesion stability of copper-plated cords can be explained by the suppression of the excessive growth of copper sulfide and the inhibition of dezincification due to the small amount of copper plating and the lack of metallic zinc at the outer surface.

Keywords: Adhesion; rubber compound; copper-film-plated steel cord; adhesion stability

1. INTRODUCTION

Steel cords, the surfaces of which have been plated with brass for adhesion with rubber compound, are inserted into the rubber compounds of the belt and carcass of a tire in order to enhance its mechanical stability. The adhesion between the rubber compound and the

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brass-plated steel cord is obtained by the reaction of copper in the brass and sulfur in the rubber compound during vulcanization, forming copper sulfide in the adhesion interphase [1,2]. Besides copper sulfide, oxides and hydroxides of copper and zinc are formed as well in the adhesion interphase due to the reaction of brass with residual water and air in the rubber compound. Therefore, the adhesion properties between the rubber compound and brass-plated cord are strongly dependent on the composition and status of the adhesion interphase. Thus, elaborate controls of the composition and plating weight of the brass, as well as the composition and cure condition of the rubber compound, are required for a strong and stable adhesion interphase [3,4].

Brass has been used as a plating material for steel cord for a long time because of its excellent processability and adhesion properties. But the additional growths of copper sulfide and zinc oxide, which cause adhesion degradation [1,5], is inevitable due to the heat generated from a tire during service and the contact with moisture and oxygen in air. The excessive growths of sulfides and oxides result in the cohesive rupture of the adhesion interphase, so a continuous search has been made for substitutes which maintain adhesion interphase integrity under severe service conditions for a long period. Lowering the plating amount of brass enhances the stability of the adhesion interphase [6], but excessive lowering induces exposure of bare iron resulting in failure in adhesion. Ternary alloy plating containing cobalt or nickel with copper and zinc instead of brass, and changes in plating order have been studied in order to improve adhesion stability [2,7,8].

With steel cords plated with only copper, copper sulfide grows so rapidly that its excessive growth brings about a cohesive failure, resulting in no adhesion formation [1,2,9-13]. But excellent adhesion was reported for ultra thin copper film (< 50 nm) with rubber compound [14]. Superior adhesion stability can be expected if copper plating thickness is sufficiently large to form a stable copper sulfide layer, but small enough not to induce cohesive failure in the copper sulfide layer. Thin copper film as a plating material has significant advantages because there is no excessive growth of copper sulfide and no dezincification. However, copper-film-plated steel cords are not yet commercially available because of difficulty in manufacturing them. The advantages of copper-film-plated cords can be diminished with uneven thicknesses of copper film due to the roughness of the steel rod; *i.e.*, in parts where the copper is plated too thick, the adhesion will be poor because of the overgrowth of copper sulfide, and in parts where the copper is plated too thin, the exposed steel surface will lead to an easy rupture in the adhesion layer. An effective method to overcome this problem is to coat copper uniformly on the surface of an almost-perfect circle of steel cord, which is made by drawing after plating it with a soft metal such as zinc. Contact plating by the substitution of zinc by copper cation [15] may be helpful in causing the copper to exist only on the outer surface of the steel cord.

In this research, four copper-film-plated steel cords with different thicknesses of copper film were prepared by plating thin copper film by a substitution (displacement) plating method on zinc-plated steel filament. The adhesion property between the rubber compound and the copper-plated cord was investigated, and adhesion stability was also studied under thermal, humidity and salt solution aging treatments.

2. EXPERIMENTAL

2.1. The Preparation of Copper-film-plated Steel Cords

Zinc was plated on the surface of a steel filament (high tensile, carbon content: 0.82%) of 1.0 mm diameter by using electroplating and then the zinc-plated steel filament was drawn to 0.25 mm. Zinc plating on the steel filament worked as a solid lubricant. The other role of zinc was that of a coating material to reduce surface roughness. Since the surface of the steel filament was very rough, the direct plating of copper could not completely cover the iron surface, resulting in severely weak points initiating a rupture in adhesion. The surface of the filament was cleaned by a 5% NaOH solution to remove greese and other contaminants. After rinsing the filament with clean water, copper was plated onto it by contacting a copper sulfate solution of $17 \sim 20\,\mathrm{g \cdot L^{-1}}$ at 20°C. Since copper has a higher reduction preference than zinc, copper cation is substituted with the surface zinc metal. The thickness of the copper film was controlled by changing the contact time of the copper sulfate solution with the zinc-plated steel filament.

The copper-plated filament was washed with water at 85°C and dried in hot air at 90°C. Copper-plated filaments were twisted together to make a copper-plated cord of $2+2\times0.25$ construction.

The average thicknesses of zinc and copper plating were measured by the XRF (X-ray fluorescence) method, and confirmed by quantitative analysis of dissolved plating material[16]. The thickness of zinc was 0.15 μm for the zinc-plated filament, and those of copper for the copper-plated cords were 32, 45, 70 and 90 nm. Copper-plated cords were named as Cu( ) cord, with the thickness in nm being the number in the parentheses. A brass-plated steel cord of $2+2\times0.25$ construction was used for comparison; its plating weight and composition were 4.2 g/kg (brass thickness: 150 nm) and Cu/Zn = 64/36 (as wt.%), respectively. Copper-plated and brass-plated cords used in this study were manufactured by Hyosung T & C Co., Korea.

2.2. The Preparation and Evaluation of the Rubber Compound

A simplified rubber compound was prepared to clarify the difference in adhesion properties of the copper-plated cords. Therefore, resinous bonding agents (resorcinol formaldehyde resin and methylene donor) and silica were not added, and carbon black and antidegradant were kept at minimum levels. Masterbatch components were as follows; natural rubber (Lee Rubber Co., Malaysia, SMR-20), 100 phr; carbon black N351 (Lucky Co., Korea), 30 phr; aromatic processing oil (Michang Co., Korea, A#2), 5 phr; zinc oxide (Hanil Co., Korea), 10 phr; antioxidant (Monsanto Co., USA, Kumanox-RD, 2,2,4-trimethyl-1,2-dihydroquinone), 1 phr; and cobalt salt (Rhone Pouluenc Co., France, Manobond 680C), 2.0 phr. Final rubber compound components were as follows: masticated rubber masterbatch, 100 phr; stearic acid (Pyungwha Co., Korea), 1.5 phr; accelerator (Monsanto Co., USA, Santocure MOR, 2-(morpholinothio)-benzothiazole sulfenamide), 0.7 phr; and insoluble sulfur (Akzo Co., The Netherlands, Crystex HS OT 20), 5.0 phr. The effect of rubber composition, especially the cobalt salt and resinous bonding agents, on the adhesion property of the copper-plated cord will be reported [17].

The rubber compound components were mixed following the procedures described in ASTM D-3184-91, using an internal mixer (Farrel

Co., USA, Banbury Mixer model 82). The masterbatch components were mixed for 5 min at a rotor speed of 40 rpm and dumped at 150°C. After the masterbatch compound was cooled to room temperature, the final mixing components were added and mixed for 5 min at a rotor speed of 30 rpm. After dumping at 90°C, the rubber compound was sheeted out using a two-roll mill (Farrel Co., model MKIII, USA).

The rheocurve was recorded using a Monsanto Rheometer 100 at 160°C. The t_{90} time, defined as the time achieving 90% of maximum torque was obtained from this rheocurve. Mooney viscosity was also measured on a Monsanto MV-2000 instrument according to ASTM D-1646-91. A tensile sample of rubber compound was cured at 160°C for 5 min using a Cure Press (Osaka Jack Co. Ltd., Japan). Hardness of the vulcanizate was measured using a Shore A durometer according to ASTM D-2240-91, and the tensile properties were determined by a tensile tester at a crosshead speed of 500 mm $\cdot$ min^{-1} (Instron model 6021, USA) as described in ASTM D-412-91.

2.3. The Preparation and Evaluation of Adhesion Samples

Using the procedure described in ASTM D-2229-91, T-test specimens were cured at 160°C on a cure press. Curing was maintained for 7 min longer than the t_{90} time to compensate for heat transfer. For humidity aging, rubber samples and adhesion samples were placed in a humidity chamber (Weiss Technik, model 305B) for 5, 10 and 15 days under conditions of 85°C and 85% relative humidity. Thermal aging was performed at 95°C for 5, 10 and 15 days. For salt solution aging, the rubber block of T-test specimens were immersed completely in a 20 wt% NaCl solution at 25°C for 5 days.

Pull-out force was determined as the maximum force exerted by the tensile tester (Instron model 6021, USA) on a T-test adhesion sample during the pull-out test at 100 mm $\cdot$ min^{-1} of crosshead speed. Rubber coverage was also noted. The rubber coverage which denoted the relative extent of rubber covered on the pulled out cord was determined by the naked eye with a 5% interval; bare steel cord as 0% to fully-covered rubber as 100%. Each value reported was the average derived from six specimens.

2.4. The Surface Analysis of Copper-plated Cords

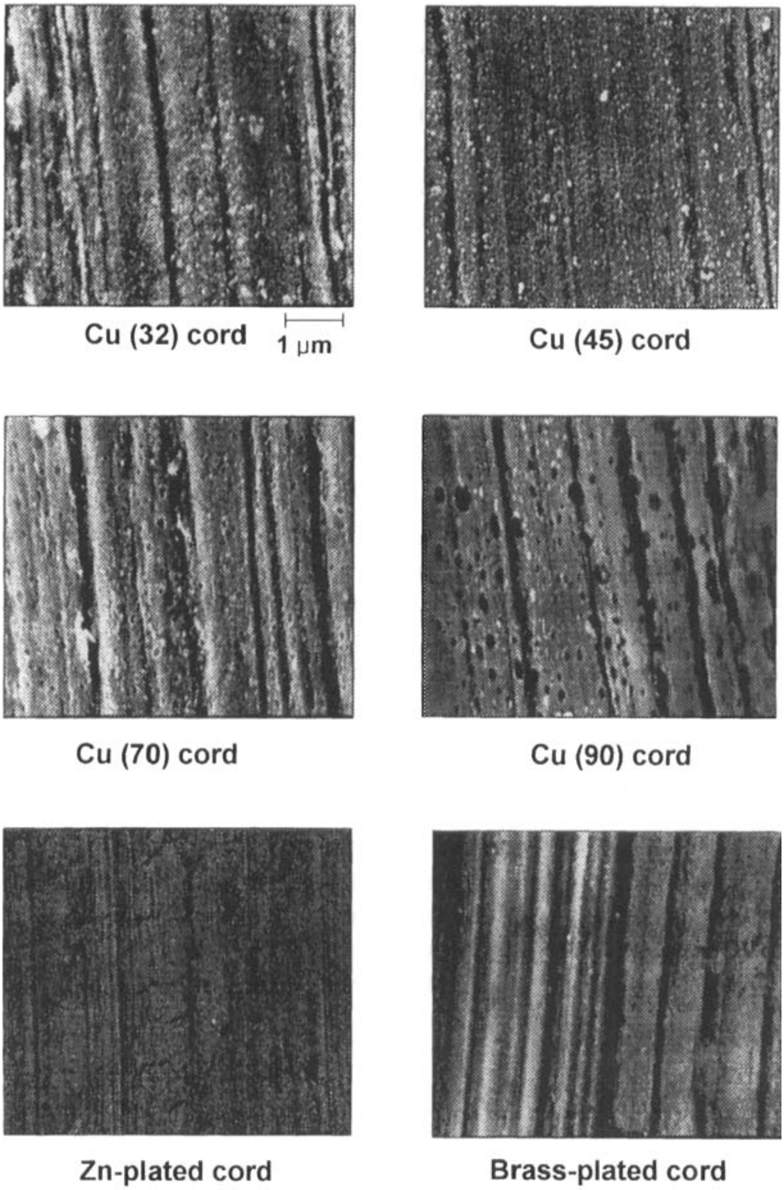
The surfaces of the copper-plated cords were investigated with a SEM (JEOL Co., model 840A). The depth profiles from the outer cord surface to the inner cord were recorded on a Perkin-Elmer Auger spectrometer (Phi 670). A surface area of $10 \times 10\,\mu m^2$ was examined at a potential of 5.0 keV, a current of 0.03 μA, and an incident angle of 60° to the specimen as in previously published papers [18–20]. Surface concentrations were determined at every 0.5 min from the Auger peaks of detected elements with compensation for their sensitivities. A sputter gun with an argon ion beam rastered on a $2 \times 2\,mm^2$ area was used for the depth profiling. The sputtering rate for the brass film was determined to be $25\,nm \cdot min^{-1}$.

The surface composition and chemical states of copper and zinc on the outer surface of copper-plated cord were investigated on a XPS (X-ray Photoelectron Spectroscopy, Shimadzu-750) with the Mg source at 8.0 kv and 30 mA. With a very short sputtering time, the substitution of zinc by copper on the top surface was investigated. The sputtering rate for brass was examined as $5\,nm \cdot min^{-1}$.

3. RESULTS AND DISCUSSION

3.1. The Preparation of Copper-plated Cords

The surface appearances of the copper-plated cords were different from those of both brass-plated and zinc-plated cords, as shown in Figure 1. The surface of the zinc-plated cord was generally smooth, and that of the brass-plated cord was relatively smooth except for scratches obtained during drawing. Though the general features of copper-plated cords were similar to those of the brass-plated cord, there were some holes and fine particles on the surface of the copper-plated cords. Since the substitution plating was carried out using an acidic copper sulfate solution, a part of the zinc reacted with a proton, generating hydrogen gas. Small holes, which seemed to be produced by the emission of hydrogen, were observed on the surface of Cu(70) and Cu(90) cords with a relatively large plating thickness of copper. Long exposure of the zinc-plated cord to the copper sulfate solution induced



Cu (32) cord

Cu (45) cord

Cu (70) cord

Cu (90) cord

Zn-plated cord

Brass-plated cord

FIGURE 1 Scanning electron micrographs of the copper-plated cords.

the dissolution of a lot of zinc into the acidic solution, thus, producing a lot of hydrogen gas as well as substitution of surface zinc to copper. In contrast, small copper particles of around 0.05 μm were observed on the surface of the Cu(32) and Cu(45) cords with a relatively small plating thickness of copper. A short exposure to the copper sulfate solution was not enough to form a planar copper film, because the plating thickness to copper was too small to make an even growth of the copper layer.

The compositions of copper and zinc in the cords analyzed by an EDX are tabulated in Table I. The detected contents of copper and zinc were almost the same in the Cu(32) cord which had the lowest amount of copper plating. However, with an increasing amount of copper plating, the detected content of zinc decreased, indicating that the copper was plated thicker from the Cu(32) cord to the Cu(90) cord. The fact that a part of the zinc was dissolved in the plating solution during the substitution plating was due to the low content of zinc on the Cu(90) cord, because a long exposure to the acidic solution should be required for a large amount of copper plating. The standard deviations of both copper and zinc contents became smaller as the copper plating increased, representing an improvement in the uniformity of the copper film.

The substitution of zinc by copper on the copper-plated cord was proven by the XPS spectra shown in Figure 2. At the outer surface of the initial cord, both signals of copper and zinc were not observed for the Cu(70) cord due to surface contamination. After a sputtering of 0.03 min, only a copper signal was observed, while a zinc signal was not observed. Even for a sputtering of 0.12 min, corresponding to about 0.5 nm, the intensity of the zinc signal did not exceed the noise level indicating that the copper metal, not an alloy of copper and zinc,

TABLE I Relative compositions[a] of copper and zinc on the surface of the copper-plated cords

Species (*atomic* %)	*Cord*	*Cu*(32)	*Cu*(45)	*Cu*(70)	*Cu*(90)	*Br*[b]
Cu		51 ± 8	71 ± 4	85 ± 8	97 ± 1	64.3 ± 0.8
Zn		49 ± 8	29 ± 4	15 ± 8	3 ± 1	35.7 ± 0.8

[a] Measured by EDX.
[b] Brass-plated cord.

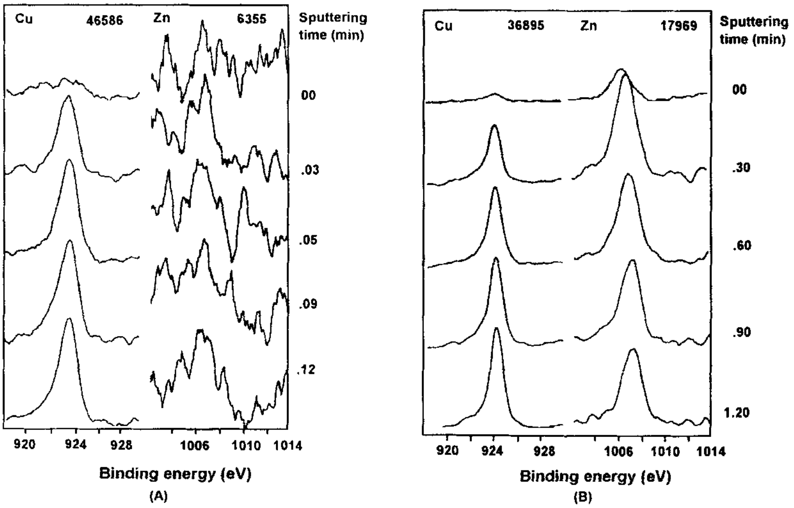


FIGURE 2 XPS spectra of the Cu(70) cord (A) and the brass-plated cord (B). The numbers in the upper part of the figures denote the counts scale, so a small number means a low content of copper or zinc.

was the main component of the top surface of the copper-plated cord. The binding energies of copper on copper-and brass-plated cords were in the same range of $932.0 \sim 932.4$ eV, showing the metallic state of copper.

The plating state of the copper-plated cords was investigated by AES. Since the surfaces of the copper-plated cord were not homogeneous, as shown in Figure 1, the depth profiles were quite different along the position. Several runs of AES investigations revealed only a qualitative trend, but a quantitative trend was not observed, as shown in Figure 3. Carbon content on the outer surface was high due to surface contamination; the carbon signal was diminished remarkably after sputtering for 30 s indicating that carbon was concentrated only on the outer surface. So the carbon signals were omitted in order to show clear profiles.

Around the outer surface of the Cu(32) cord, copper, zinc and oxygen were detected, then iron, which means that some copper and zinc are mixed together at the outer surface. Even though the outer surface of the copper-plated cord was composed of copper metal, copper mixed zinc beneath the outer surface. The similar shape of the

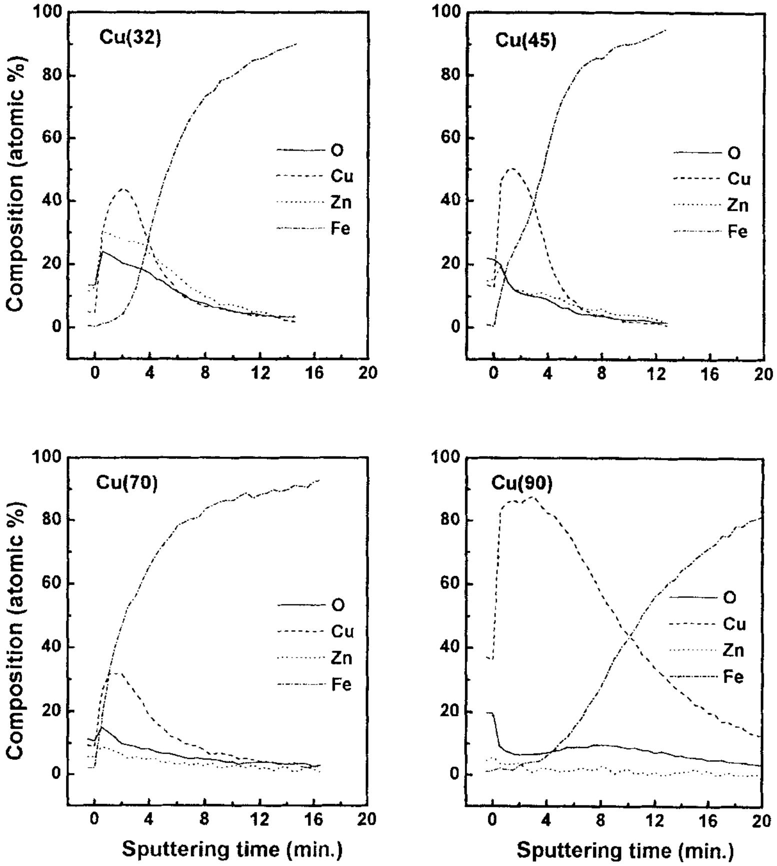


FIGURE 3 AES depth profiles of copper-plated cords.

zinc and oxygen profiles suggests that some of the zinc exists in oxidized form at the outer surface due to its high affinity to oxygen. The plating thickness of zinc was larger than that of copper-plated cord, even on the Cu(90) cord, but the detected zinc content from AES profiles was very small for all copper-plated cords. This small amount of retained zinc means that a lot of zinc is spent by being dissolved in the acidic solution during the substitution plating.

Copper makes a layer at the outer surfaces of the Cu(45) and Cu(70) cords, but the mixed region of zinc and oxygen with copper observed at the outer surface. Since the copper film disappeared after sputtering for 4 min, the copper film thickness of the Cu(90) cord was estimated to be 100 nm, assuming that the sputtering rate of copper was almost the same as that of brass. Such a thickness was in agreement with the 90 nm estimated from the plating amount measured by XRF. Although the plating amount of copper in the Cu(70) cord was larger than that in the Cu(45) cord, the detected copper content from AES profiles was much lower in the Cu(70) cord. But, on the other hand, the copper layer of Cu(70) cord was too high compared with the Cu(32) and Cu(45) cords. This difference may be caused by the heterogeneity of the cord surface and the uneven thickness of the copper film. The Cu(90) cord, which had the largest amount of copper plating among the copper-plated cords prepared in this study, showed a complete copper layer in the AES depth profile, indicating that a perfect and extremely thin copper plating is not an easy goal in the manufacture of copper-plated cord.

3.2. The Physical Properties of the Rubber Compound

Cure characteristics derived from rheocurve and viscosity measurement on a Mooney viscometer are listed at Table II. The curing rate of the simple rubber compound prepared was faster than that of the commercially-used tire compound because of the exclusion of a cure retarder [19]. Torque and viscosity of the simple rubber compound were also low because reinforcing materials such as silica and resinous bonding agents were not added to it. The t_5 time, denoting scorch time and the viscosity were moderate, so there was no difficulty in processing this simple rubber compound.

The physical properties of the simple rubber compound before and after thermal aging are tabulated in Table III. The unaged hardness and modulus of the simple rubber compound were low compared with

TABLE II Cure and viscoelastic properties of the rubber compound determined by a oscillating disc type rheometer and Mooney viscometer

OD rheometer[a]					*Mooney viscometer*[b]			
Time (min)		*CRI*	*Torque (J)*		*Time (min)*		*Torque (J)*	
t_2	t_{90}	(min^{-1})	*min*	*max*	t_5	t_{35}	*initial*	*min*
2.0	4.3	43.5	1.7	4.7	14.6	18.0	5.78	4.65

[a] Sheared to ± 1° and 1.67 Hz at 160°C.

[b] Sheared to 2 rpm at 125°C.

TABLE III Physical properties of the rubber compound before and after thermal aging

	Period	*Hardness*	*Modulus (MPa)*		*T.S.*[a]	*E.B.*[b]
	(day)	*(Shore A)*	100%	200%	*(MPa)*	(%)
Unaged		49	1.48	3.24	20.6	575
Thermally	5	59	2.75	6.62	11.2	295
Aged	10	60	3.45	–	3.8	111
	15	64	–	–	2.5	50

[a] Tensile strength.
[b] Elongation-at-break.

those of the compound commercially used for tire belts [19], but tensile strength and elongation-at-break of both compounds were high enough to test the adhesion property. The low hardness and modulus at the unaged state can be ascribed to the small loading of carbon black and no addition of resinous bonding agents. Tensile strength after thermal aging for 10 days was reduced to one fifth of the unaged value. Elongation-at-break decreased concomitantly, but its degradation rate was slow compared with tensile strength. The degradation with thermal aging seemed to be somewhat severe compared with commercial belt rubber compound due to exclusion of heat-stabilizing reagents from the simple rubber compound. However, though the physical properties of the simple rubber compound are slightly lower than those of the commercial one [19], the physical properties, especially tensile strength and modulus, are high enough to permit examination of the adhesion properties of the copper-plated cord [21]. Though the adhesion properties depend on not only the structure, thickness and composition of the adhesion interface but also the physical properties of the rubber compound, the simplified rubber compound showed adequate physical properties for the evaluation of the adhesion properties of the copper-plated cords.

3.3. The Adhesion Properties of Copper-plated Cord

The adhesion properties of copper-plated cords were different from those of the brass-plated cords, as shown in Table IV. The unaged and thermally-aged adhesion properties of copper-plated cords were inferior to those of the brass-plated cord. However, the adhesion properties of copper-plated cords were high when the copper film was thin. The unaged pull-out force of the Cu(32) cord, which had the

TABLE IV Adhesion properties of the copper-plated cords with the rubber compound after thermal aging[a]

Cord	*Pullout force (N)*[b]				*Rubber coverage (%)*			
Aging period (day)	0	5	10	15	0	5	10	15
Cu(32)	332	282	279	273	45	45	50	55
Cu(45)	185	167	149	167	10	25	25	30
Cu(70)	161	153	159	144	5	15	15	10
Cu(90)	140	158	145	124	0	10	5	10
Br[c]	589	425	375	335	100	100	100	95

[a] Thermal aging: 95°C.
[b] Force per cord.
[c] Brass-plated cord.

thinnest copper film, was 332 N, while that of the Cu(90) cord was 140 N. Rubber coverage also became higher as the thickness of copper film decreased. Rubber coverage was found to be zero on the Cu(90) cord, but on the Cu(32) cord it was 45%, almost half of that of the brass-plated cord. The pull-out force and rubber coverage are better on copper-plated cords with a small amount of copper plating; therefore, the Cu(32) cord having the thinnest copper film shows the best adhesion properties among the copper-plated cords prepared in this study. However, the unaged adhesion properties of copper-plated cords, even the Cu(32) cord, are as low as one-half of those of the brass-plated cord.

The adhesion stability of copper-plated cords against thermal aging was considerably higher than that of the brass-plated cord. Although the unaged adhesion properties of copper-plated cords were inferior to those of the brass-plated cord, the degradation rate was considerably lower for the copper-plated cord; *i.e.*, the pull-out force of the Cu(32) cord with the thinnest copper film after thermal aging of 15 days was recorded as 273 N, 82% of the unaged force, and the rubber coverage was noted as 55%, which was much higher than the unaged rubber coverage of 45%. On the other hand, the unaged pull-out force of the brass-plated cord was as high as 589 N, but after thermal aging of 15 days it was reduced to 335 N, which was 57% of the unaged force. It is worth noting that for the unaged state the pull-out force of the Cu(32) cord was just one-half that of the brass-plated cord, but that after thermal aging of 15 days, it was almost the same as that of the brass-plated cord. The rubber coverage of the brass-plated cord was slightly lowered with thermal aging, while that of the Cu(32) cord improved.

The important point relating to adhesion for tire manufacturing is a stability in resisting heat, air, salt and humidity as well as good initial adhesion. The brass-plated cord showed a large degradation of adhesion properties. For the copper-plated cord, the adhesion properties after thermal aging became better with decreasing thickness of copper. Excellent adhesion retention after thermal aging was exhibited by the Cu(32) cord.

The adhesion stability of copper-plated cords against humidity aging was more exceptional than that of the brass-plated cord, as shown in Table V. Although the unaged adhesion properties of copper-plated cords was inferior to those of the brass-plated cord, pull-out force and rubber coverage of the Cu(32) cord after humidity aging of 15 days were both superior to those of the brass-plated cord. With humidity aging, the pull-out forces of both cords decreased regardless of whether they were copper-plated or brass-plated, but the degradation rate was extremely slow on the Cu(32) cord. The rubber coverage of the brass-plated cord after pullout was significantly decreased with humidity aging, while that of the Cu(32) cord was rather improved. The rubber coverages of the Cu(45), Cu(70), and Cu(90) cords for the unaged state were poor; however, after humidity aging, they were slightly enhanced. This result shows the exceptional adhesion stability of the copper-plated cord compared with the adhesion degradation of the brass-plated cord. The pull-out force of the brass-plated steel cord was reduced to 33% of the unaged force after humidity aging of 15 days, and the rubber coverage abruptly decreased to 25%.

TABLE V Adhesion properties of the copper-plated cords with the rubber compound after humidity aging[a]

Cord		*Pullout force* (*N*)[b]				*Rubber coverage* (%)			
	Aging period (*day*)	0	5	10	15	0	5	10	15
Cu(32)		332	282	279	273	45	45	50	55
Cu(32)		332	242	253	245	45	50	55	35
Cu(45)		185	204	190	173	10	20	25	25
Cu(70)		161	172	171	178	5	5	10	20
Cu(90)		140	125	149	138	0	10	5	10
Br[c]		589	240	202	193	100	40	60	25

[a] Humidity aging: 85°C and 85% relative humidity.
[b] Force per cord.
[c] Brass-plated cord.

The adhesion properties between the rubber compound and the copper-plated cords were also stable during salt solution aging. The adhesion properties after salt solution aging of 5 days are listed in Table VI. Longer aging was impossible due to tremendous corrosion. The adhesion properties after salt solution aging were greatly dependent on the copper film thickness, as were those after humidity and thermal aging. The pull-out force of the Cu(32) cord with the thinnest copper film after salt solution aging of 5 days was low, at 246 N compared with the unaged force of 332 N; however, the rubber coverage of 45% was retained even after salt solution aging. On the other hand, the pull-out force of the brass-plated cord dropped from 589 to 163 N with salt solution aging, and the rubber coverage was reduced from 100% to 20%. Although the unaged adhesion properties of the brass-plated cord were better than any of the copper-plated cords, those after salt solution aging of 5 days were considerably superior on the Cu(32) cord with a thin copper film.

3.4. The Specificity of the Adhesion Between Rubber Compound and Copper-plated Cord

The adhesion properties of the copper-plated cords are somewhat different from those of the brass-plated cord. The copper-plated cords exhibited a strong dependence on the amount of copper plated, and excellent stability in the humidity and salt solution aging treatments. First, the pull-out force and rubber coverage of the copper-plated

TABLE VI Adhesion properties of the copper-plated steel cords with the rubber compound after salt solution aging[a]

Cord	*Aging period (day)*	*Pullout force (N)*[b] 0	5	*Rubber coverage (%)* 0	5
Cu(32)		332	246	45	45
Cu(45)		185	145	10	5
Cu(70)		161	96	5	0
Cu(90)		140	85	0	0
Br[c]		589	163	100	20

[a] Salt solution aging: 25°C and 20% NaCl solution.

[b] Force per cord.

[c] Brass-plated cord.

cords were improved with the decrease in the amount of plated copper, from the Cu(90) to the Cu(32) cords. Second, the adhesion properties of the Cu(32) cord which had the lowest amount of copper plating was superior to the brass-plated cord after humidity or salt solution aging, while the unaged adhesion properties were inferior.

Since the rubber coverage for most of the copper-plated cords pulled out of the simple rubber compound were below 50%, it is reasonable to consider that the rupture occurred in the adhesion interphase instead of in the rubber layer. Therefore, the adhesion properties of copper-plated cords are strongly related to the structure and stability of the adhesion interphase, and the specificity of copper-plated cord is due to the difference in the adhesion interphase from that of the brass-plated cord.

The adhesion between the copper-plated cord and rubber compound is achieved by the formation of copper sulfide, as in the brass-plated cord. However, the excessive formation of copper sulfide, which induces its own cohesive failure leading to the deterioration of the adhesion layer, is limited by the amount of copper plated on the copper-plated cord. The primary reason for better adhesion on copper-plated cord with a small thickness of copper is the suppression of excessive growth of copper sulfide [17]. The average thickness of the copper-plated cord is 32 nm, so the amount of copper plating is small enough to form copper sulfide as a separate layer resulting in cohesive failure.

The suppression of copper sulfide formation on the Cu(32) cord also contributes to excellent adhesion stability during humidity aging. Dezincification of brass is accelerated in humid conditions since zinc is easily dissolved in the presence of water [1]. The copper atom in brass becomes active due to the loss of the zinc atom, and results in the excessive growth of copper sulfide during humidity aging [11, 22, 23]. In contrast, there is a negligible amount of non-reacted copper on the Cu(32) cord so the possibility of the excessive growth of the copper sulfide layer is also negligible, resulting in exceptional stability during humidity aging.

The excellent adhesion stability of the copper-plated cord during salt solution aging is due to the lack of zinc at the outer surface. Although zinc was plated on the steel cord prior to the copper plating, the remaining fraction of metallic zinc at the surface of the copper-plated cord is very low. Generally, the degradation of the adhesion interphase by salt solution aging is related to the severe loss of zinc [1, 2]. So the adhesion on copper-plated cord ought to be stable. Since zinc oxide is inert to salt solution, the fact that most of the surface zinc on the Cu(32) cord existed as zinc oxide may be a possible cause for excellent stability during salt solution aging.

In this research, after copper plating, there was no additional drawing of the copper-plated cords to remove copper particles. Also, a simple rubber compound without a thermal stabilizer and bonding enhancing reagents was used. Even with these conditions, the adhesion properties of the copper-plated cords are competitive with those of the brass-plated cord, and are better after aging, especially during the humidity and salt solution aging treatments. If the homogeneity in the thickness of the copper plating is improved, copper-plated cords may be suitable to manufacture a highly durable tire.

4. CONCLUSION

Copper-plated cords with an extremely thin copper film of about 30 nm shows good adhesion with a rubber compound. The adhesion properties between copper-plated cords and the rubber compound improved with the decrease in the thickness of the copper film. In the unaged state, the adhesion properties of copper-plated cords were inferior to those of brass-plated cord, but after humidity and salt solution aging treatments those properties were superior. The exceptional adhesion properties of the Cu(32) cord with a thin copper film of 32 nm is due to the suppression of the excessive growth of the copper sulfide layer which induces adhesion failure. The excellent stability against humidity or salt solution aging is explained by the suppression of the additional formation of copper sulfide, and dezincification due to the lack of metallic copper and zinc on the outer surface of the copper-plated cord.

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