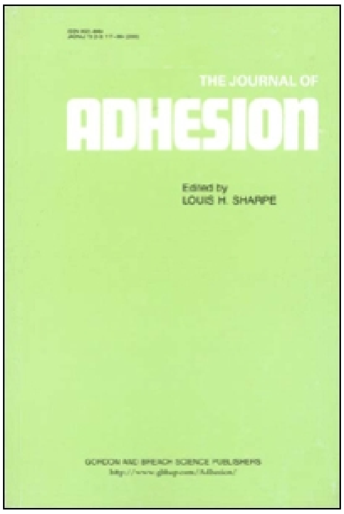

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A Study of Brass/Squalene Interfacial Compositions Using Surface Analytical Technique

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A model system using squalene has been reacted with sulphur, accelerators *etc.* against a cleaned brass surface without and in the presence of adhesion promoters based on cobalt. The interfacial layer found to exist between the purely organic material and the metal substrate has been examined by XPS/ESCA and SIMS after successive periods of ion etching. The interfacial interlayer proceeds from being almost entirely organic through a mixed organic/metal sulphide layer to copper sulphide with some zinc sulphide, then zinc oxide and finally to the bulk metal of the substrate. Cobalt compounds are carried into the copper sulphide there forming cobalt sulphide. There are subtle differences of behaviour between cobalt-MBT, cobalt neodecanoate and cobalt boroacylate. The latter seems to be more closely associated with the copper sulphide than other materials investigated. The effect of steam ageing is briefly considered.

KEY WORDS Rubber-metal bonding; surface analysis; XPS; ESCA; SIMS; interface; organo-cobalt; squalene.

INTRODUCTION

The chemistry of rubber-brass interfaces and the mechanism of their formation have been reviewed by Van Ooij[1,2] and surface analytical techniques such as X-ray photoelectron spectroscopy (XPS/ESCA), Auger electron spectroscopy (AES), energy-dispersive X-rays (EDX) and secondary ion mass spectroscopy (SIMS) have allowed the changes in chemical composition at interfaces to be characterised. The use of these techniques is well documented.[3,4,5]

Practical problems of examining the interface in commercial brass coated steel tire cord systems have been overcome either by using model systems, based on squalene, or by the separation of the rubber-brass interface in liquid nitrogen. Although much information can be obtained from the surface analysis, reconstruction of the complete interface is difficult. Coppens *et al.*,[6] overcame the problems by vulcanising vacuum-deposited brass films to rubber, access to the interface being obtained by etching through the brass towards the rubber followed by analysis with AES and XPS.

TABLE I
Rubber/Metal adhesion (N/12.7 mm) in presence of adhesion promoters

	Control	Cobalt neodecanoate	Cobalt boroacylate	Cobalt MBT
Initial	500 (6)	710 (9)	760 (9)	650 (8)
Heat aged, 7d; 85°C	380 (4)	660 (9)	640 (9)	580 (7)
Humidity aged 7d; 70°C, 95% R.H.	400 (4)	450 (7)	550 (8)	550 (6)
Steam aged, 16 h; 121°C	410 (2)	450 (4)	470 (5)	400 (3)
Salt aged, 14d; R.T. 10% soltn.	450 (5)	500 (7)	500 (7)	500 (6)

Bracketed figures indicate observed interface from 0 (at the brass) to 10 (in the rubber).

Previous work has studied the effect on the interface of varying both the rubber compound and the composition of the brass surface. The role of cobalt as an adhesion promoter has been examined and its beneficial effect on adhesion, particularly after natural or accelerated ageing, explained in term of its regulation of copper sulphide growth and its reduction of dezincification. Such work has placed little emphasis on the organic portion of the adhesion promoter, the importance of which is illustrated in this paper. The organic portion has to solubilise the cobalt in the rubber compound, ensure release of cobalt ions during vulcanisation and not affect the corrosion resistance of the system. The importance of these qualities is illustrated by comparing a range of adhesion promoters (Table I). These are not trivial qualities and have a great effect on retained adhesion performance.

In this paper a study of the interface obtained using a squalene/brass model system with a number of cobalt bonding promoters is presented. The promoters included cobalt carboxylate, cobalt boroacylate and a cobalt accelerator complex. The interface composition will be correlated to the organic portion of the promoter and the retained adhesion performance of the system.

EXPERIMENTAL

Model system formulation

The three formulations used in this study are detailed in Table II. They are minimum formulations without the addition of fillers. The adhesion promoters studied were cobalt neodecanoate, cobalt boroacylate and a cobalt accelerator complex (cobalt mercaptobenthiazole). Cobalt neodecanoate and cobalt boroacylate were both commercial products (Manobond 740C and Manobond 680C, Manchem Ltd). Cobalt mercaptobenzthiazole (Cobalt MBT) was prepared by standard synthetic routes.

Sample preparation

In the initial stages of this work the brass surface was prepared by being lightly abraded before reaction. The XPS, and in particular the SIMS results, revealed

TABLE II
Model system formulations

	Compound		
	1 phr*	2 phr	3 phr
Squalene	100	100	100
Zinc Oxide	5.0	5.0	—
Magnesium oxide	—	—	5.0
Stearic acid	0.5	0.5	0.5
6PPD[a]	2.0	2.0	2.0
Promoter (metal content)	0.3	0.3	0.3
DCBS[b]	0.7	—	0.7
Insoluble sulphur	5.0	5.0	5.0

* Parts per hundred of "rubber."

[a] N(1,3 dimethyl butyl) N^1 phenyl-p-phenylene diamine.

[b] N,N-dicyclohexyl benzothiazole sulphenamide.

that this method caused considerable contamination of the surface and it was clear that an improved method of sample preparation was needed.

Electropolishing gave a smooth surface but with very high copper enrichment at the surface. Lapping with diamond or alumina compounds also gave a good surface but the diamond compound introduced a hydrocarbon contamination. The alumina-based compound introduced no such contamination and was adopted for the remainder of the work, lapping to a mirror finish followed by washing with distilled water then treated ultrasonically a) in water, b) in propan-2-ol before being stored in propan-2-ol.

The test formulations were sandwiched between two brass strips and heated for up to 32 minutes at 150°C in a forced air oven. The strips were then washed, ultrasonically cleaned for one minute and then stored under propan-2-ol until required.

Surface analysis

XPS analysis was carried out using a VG ESCALAB 5 with an aluminium target giving an X-ray energy of 1486.6 eV. The area of sample analysed was 8 mm × 8 mm. After a spectrum of the original surface had been obtained, the specimen was sputtered with Ar^+ ions of 5 keV energy (current 20 μA) for up to 40 minutes in order to obtain a depth profile of the interface. It will be noted that in all the XPS results etching time is referred to rather than depth. The rate of ion etching is taken from established data for metals but, as the surface is a complex mixture which varies with depth, etching will not be uniform. Caution needs to be exercised in relating etch time to depth but, in general, 40 minutes etching will result in profiling to a depth of about 70 nm.

The SIMS analysis was carried out using a Comeca IMS 3f instrument with a beam of O_2^+ ions (beam current 20 μA) to sputter material from a square of side 250 μm. Positive ions (B^+, S^+ or O_2^+, Ni^+, Co^+, Cu^+, Zn^+) from a spot (diameter 50 μm) were monitored.

For each system being studied, the depth profile of the interface formed by vulcanising for 32 minutes at 150°C was examined by both XPS and dynamic SIMS. The XPS results were used to provide a quantitative measure of the variation in atomic concentration through the interface. However, since XPS is rather insensitive to small concentrations of boron, SIMS was used to provide qualitative information on the boron distribution in the interface in addition to more information on the other elements.

As well as obtaining the depth profile of the fully-formed interface, a study was undertaken into the composition of the interface as it was being built up. Samples were taken after 4, 8, 16 and 32 minutes curing at 150°C and examined by XPS. Etching was carried out for three minutes to remove surface contamination, then measurements were taken to provide a picture of the surface composition of the growing interface.

RESULTS AND DISCUSSION

Untreated brass

The XPS depth profile of the lapped and cleaned brass showed that any organic contamination remaining is removed during the first five minutes of etching to give a surface containing copper, zinc and oxygen.

If it is assumed that all the oxygen is in the form of zinc oxide then the zinc oxide concentration of the surface is 13.6% after two minutes, 7.8% after five minutes and 2.6% after 10 minutes. These etch periods correspond to depths of about 4 nm, 9 nm and 18 nm below the surface. Further etching reveals a uniform layer containing only copper and zinc in the ratio 85:15 to depth of at least 70 nm from the surface. This ratio is in conflict with the 70:30 ratio established by chemical analysis of the bulk sample and EDX analysis at about 100 nm below the surface. It is usually accepted that zinc is removed by sputtering at a faster rate than copper, by ratio of 1.41 thus leaving a surface enriched in copper. Alternatively, it could be the result of the original zinc oxide surface layer, removed by lapping, which, by its formation, had left a copper-enriched substrate.

Compound with bonding promoter absent

Figure 1 shows the depth profile from XPS analysis of a brass strip cured for 32 minutes at 150°C in formulation 1 but without the addition of a cobalt bonding promoter. This shows that the sulphur and carbon quickly decrease on moving through the interface towards the metal whilst the copper content increases. As zinc is present both in the brass and in the compound it is difficult to determine the source of the zinc seen in the interface. Replacement, as in formation 3, of zinc oxide with magnesium oxide, an activator with good adhesion properties but which gives a slightly slower cure rate, allows clear interpretation of results. As only the zinc profile is altered appreciably by this change, this profile is also

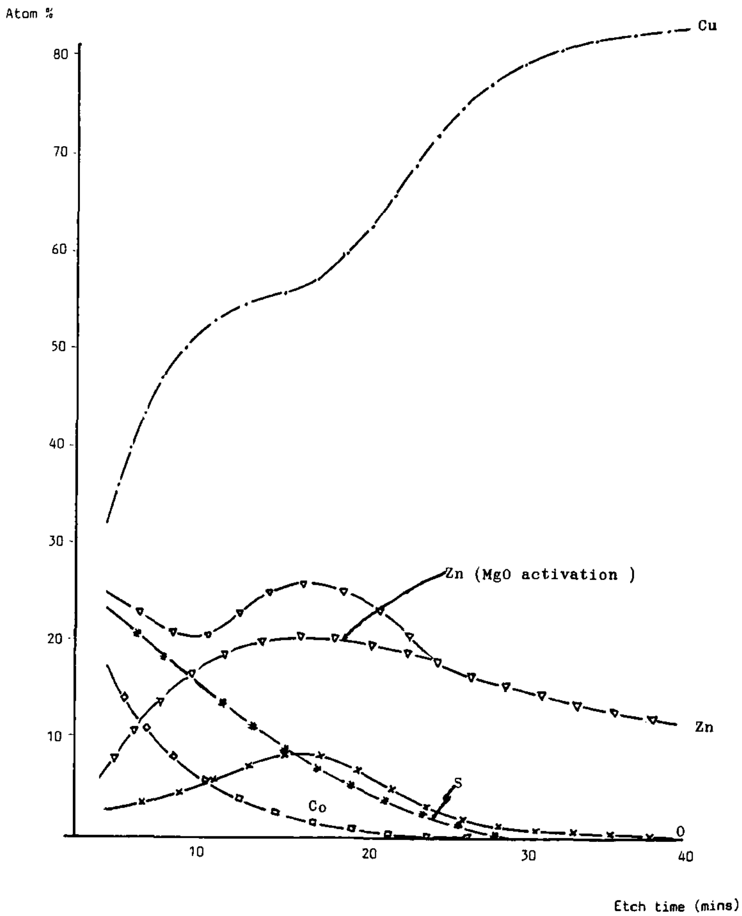

FIGURE 1 XPS, No promoter, ZnO activation.

shown in Figure 1. The use of a magnesium oxide leads to a reduction in the zinc content which is not replaced by magnesium.

This could imply a change of mechanism but is more likely to be a physical effect associated with the solubility or diffusion characteristics of the corresponding magnesium compounds.

The SIMS results, illustrated for the magnesium oxide activated samples, confirm the general trends of the XPS results. Figure 2 shows the concentration of the elements in arbitrary units plotted against sputtering time. The concentrations are not absolute and so different elements cannot be compared directly. However, for a given element, concentrations in different figures can be directly compared. As with XPS, the change in composition as sputtering proceeds will cause the etch rate to vary. However, 50 cycles is equivalent to about 100 nm etch depth.

In interpreting the results of the elemental analysis, it is assumed that oxygen is

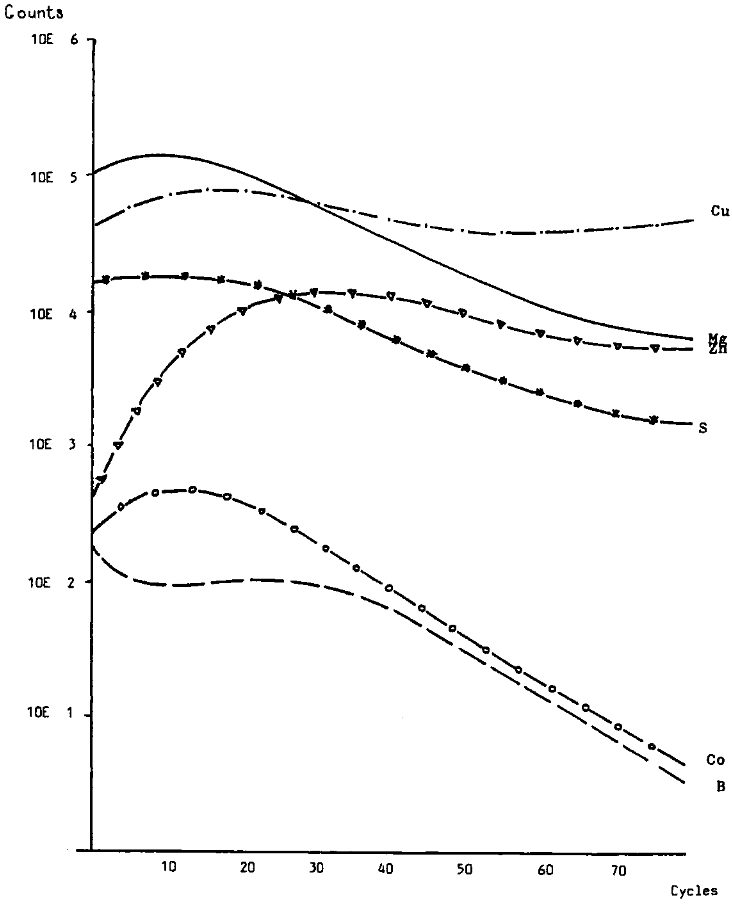

FIGURE 2 SIMS, No promoter, MgO activation.

present as zinc or magnesium oxide and copper is present as copper sulphide or a copper-S-squalene complex to the extent that sulphur is available. Thus the data can be used to calculate the distribution of copper sulphide and zinc oxide shown in Table III. From these results the following picture of the interface emerges. Once the surface contamination has been removed by etching, a copper sulphide layer containing a substantial amount of free copper, some zinc oxide and organic material is exposed. Nearer the bulk metal the copper sulphide and organic concentrations decrease while the zinc oxide concentration increases slightly and then remains constant. The copper sulphide/organic layer extends to an etch time of about 25 minutes (*ca.* 45 nm) below the surface. Beyond that the copper:zinc ratio is that of the bulk metal substrate, indicating complete erosion of the interface. It is interesting to note that a fairly constant proportion of zinc oxide is present in both the copper sulphide/organic layer and the brass.

TABLE III
XPS depth profile—no cobalt bonding promoter magnesium oxide as activator

Etch time (minutes)	CuS %	ZnO %	Maximum Remaining free Cu %	Zn %	Ratio Cu/Zn
3	44.0	3.0	2.5	2.1	15.5:1
8	36.4	10.8	36.8	9.3	34.0:1
15	21.4	8.8	50.4	11.1	4.5:1
25	5.6	9.4	69.7	13.4	5.2:1
40	0	7.6	80.3	11.7	6.9:1

Note: Cu/Zn ratio in untreated brass = 5.7:1.

Compound containing cobalt-accelerator complex

In order to differentiate between the effect of cobalt on the interface and that of the carboxylic acid groups normally found in cobalt bonding promoters, the cobalt salt of the accelerator mercaptobenthoazole (MBT) was used in formulation 2. The XPS and SIMS measurements on brass coupons vulcanised for 32 minutes at 150°C are shown in Figures 3 and 4. The XPS results are very similar to those shown in Figure 1 for the system without bonding promoter although the carbon content is somewhat higher towards the surface of the interface and the copper content is lower. The obvious difference is that cobalt is now detected during the first 15 minutes of etching (*ca.* 25 nm depth). The SIMS results confirm these trends.

In the presence of cobalt, different assumptions must be made concerning the composition of the phases at the interface. It is assumed that all cobalt will be present as cobalt sulphide or a Co—S-organic complex. Any remaining sulphur will then react to form copper sulphide. From the XPS results shown in Figure 3, the interface composition given in Table IV can be obtained. The picture that emerges is of an interface whose surface initially contains a substantial amount of zinc and organic material together with a smaller amount of copper sulphide, zinc oxide and cobalt, but no free copper. Nearer the bulk metal the copper sulphide, organic and cobalt concentrations decrease, the concentration of zinc oxide reaches a maximum as the copper sulphide declines, then remains constant and free copper concentration increases. The copper sulphide/organic layer extends to an etch time of about 20 minutes (*ca.* 35 nm). There is no sign of cobalt below the copper sulphide layer.

Compound containing cobalt neodecanoate

Cobalt neodecanoate has been of commercial interest in recent years as a replacement for cobalt naphthenate. As available, it is not a pure compound but contains a proportion of propionic acid. Figures 5 and 6 show the XPS and SIMS results, respectively, on coupons vulcanised for 32 minutes at 150°C using formulation 1. The XPS depth profile shows that the interface has a very different composition from the two previous examples. The level of all the elements, with

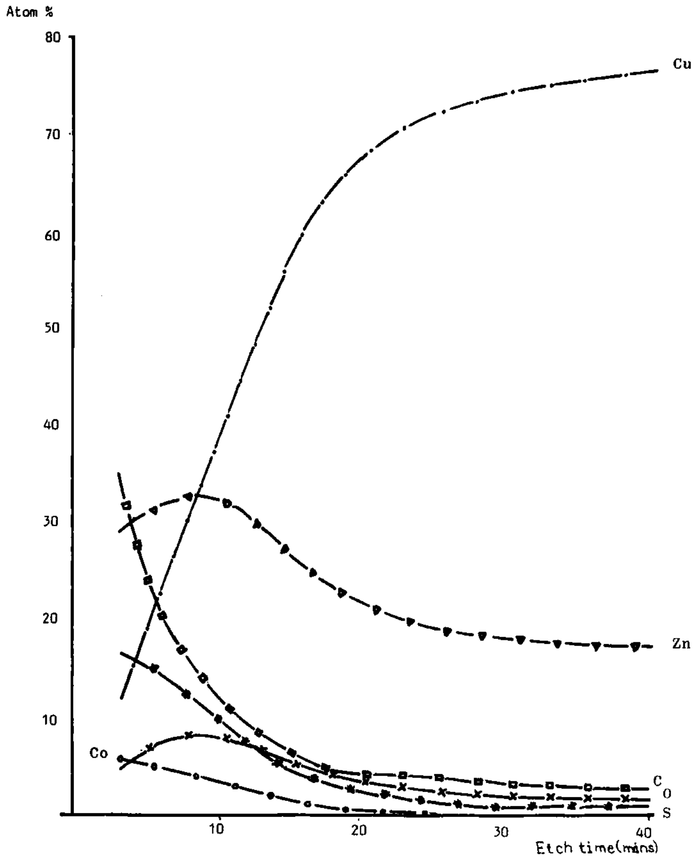

FIGURE 3 XPS, Promoter, Cobalt MBT.

the exception of copper, is very much higher than previously and these levels are fairly constant throughout the interface, showing little tendency to decline after 40 minutes etching. The SIMS data again supports the XPS results and, in particular, show high levels of cobalt and sulphur at depths of up to 200 nm in the film. The SIMS results do show a significant decline in the zinc concentration in the region beyond the sampling depth of XPS.

Using the previous assumptions regarding the fate of the elements, the information from Figure 5 yields the results given in Table V. It is clear from these results that even 40 minutes etching is not sufficient to erode the interfacial layer down to the bulk metal. Thus the interfacial layer formed using cobalt neodecanoate is very much thicker or more dense, and hence slower to etch, than those formed using no promoter or the cobalt accelerator complex. The level of zinc in the interface is higher than seen in the previous system. This may arise from the zinc oxide used as an activator being solubilised by the neodecanoic and propionic acids.

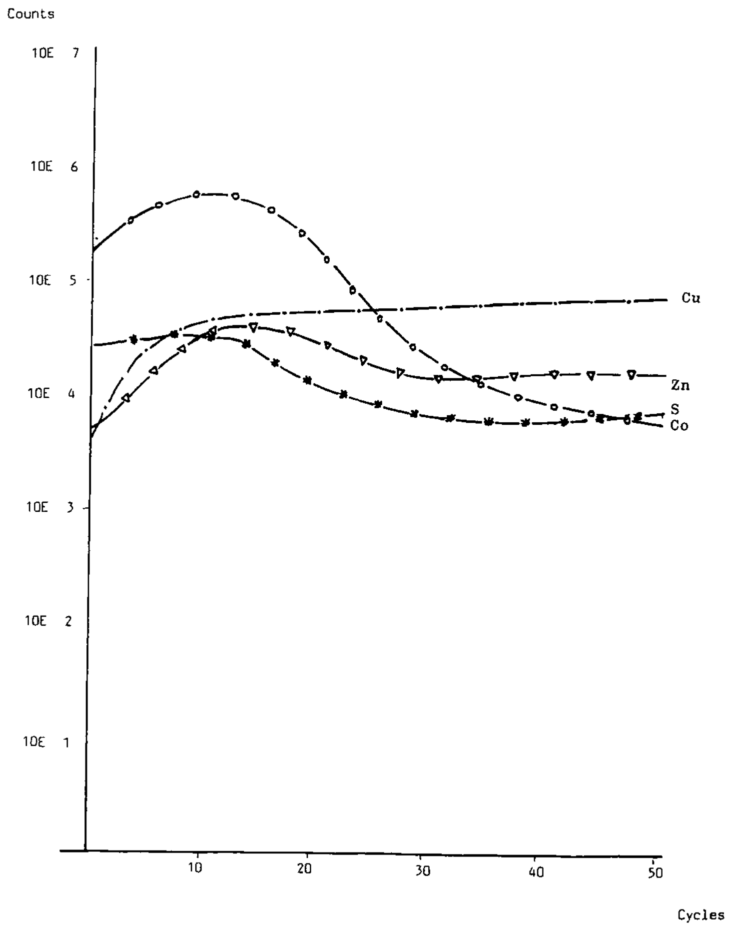

FIGURE 4 SIMS, Promoter, Cobalt MBT.

TABLE IV
XPS depth profile—cobalt accelerator complex bonding promoter

				Maximum Remaining free		Ratio
Etch time (minutes)	Cus %	ZnO %	CoS %	Cu %	Zn %	Cu/Zn
3	23.2	7.6	8.4	0	25.0	—
8	14.0	16.8	8.4	22.0	24.5	0.9:1
15	5.6	12.4	2.0	55.5	19.1	2.9:1
25	2.4	6.4	0	71.6	15.9	4.5:1
40	1.8	5.6	0	74.1	15.1	4.9:1

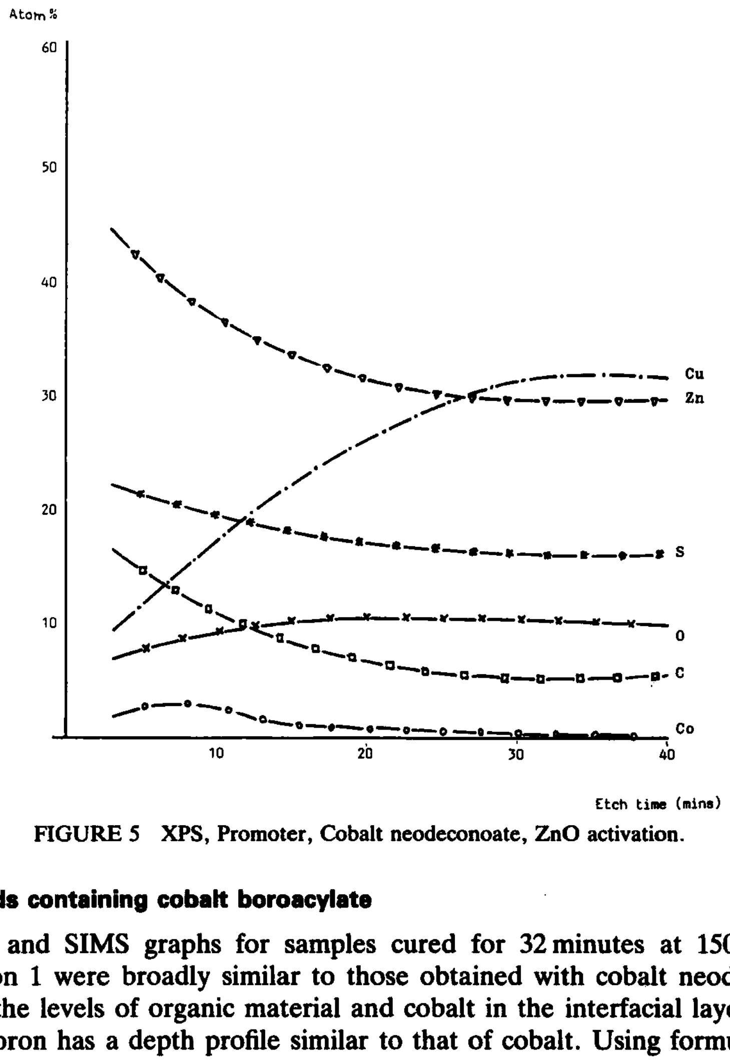

FIGURE 5 XPS, Promoter, Cobalt neodeconoate, ZnO activation.

Compounds containing cobalt boroacylate

The XPS and SIMS graphs for samples cured for 32 minutes at 150°C using formulation 1 were broadly similar to those obtained with cobalt neodecanoate although the levels of organic material and cobalt in the interfacial layer appear higher. Boron has a depth profile similar to that of cobalt. Using formulation 3, replacing zinc oxide with magnesium oxide shows magnesium to be incorporated in the interface with a profile similar to that of cobalt. This can be seen in Figures 7 and 8. In its absence from the compound, zinc is only detected after 25 minutes etching, *i.e.*, *ca.* 45 nm, contrasting with the control where it was detected on the top surface of the interfacial layer. Boron is also present with a comparable profile. Table VI is based on the data given by Figure 7. This, taken in conjunction with Figure 8, leads to the following picture of the interfacial layer. The upper surface of the interface is essentially organic, based on squalene. Copper sulphide increases slowly as the organic material declines and continues to increase to a maximum after 25 minutes etching, probably about 45 nm depth. The cobalt content reaches its maximum before this; boron and cobalt go together. The bulk metal is, unlike the control, not reached with 40 minutes

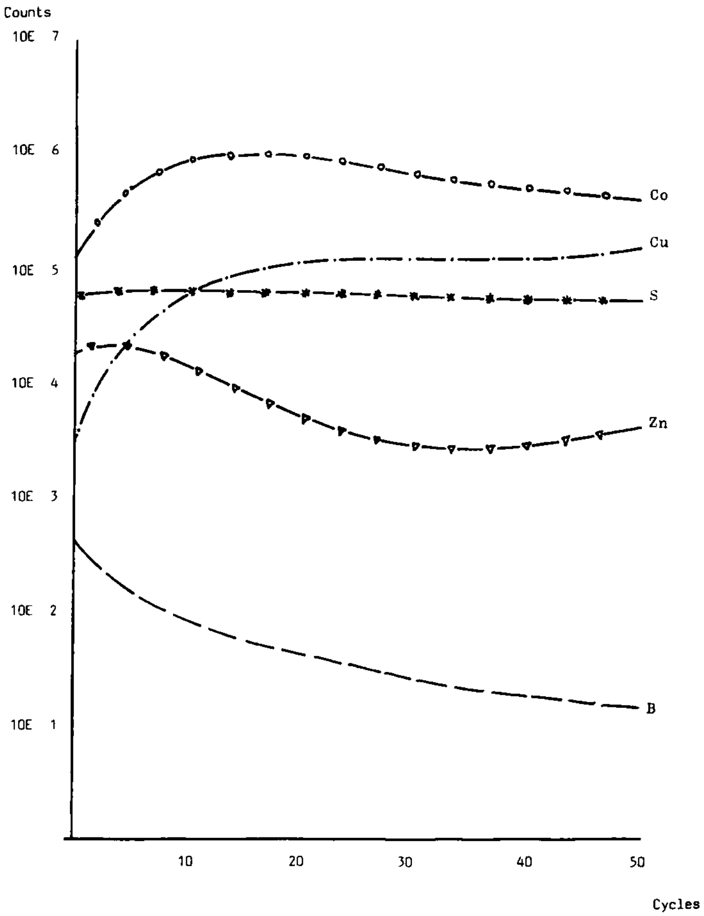

FIGURE 6 SIMS, Promoter, Cobalt neodeconoate, ZnO activation.

TABLE V
XPS depth profile—cobalt neodecanoate bonding promoter

Etch time (minutes)	Cus %	ZnO %	CoS %	Maximum Remaining free Cu %	Zn %	Ratio Cu/Zn
3	17.8	13.2	4.4	—	36.8	—
8	32.8	16.6	6.4	1.7	30.7	0.05:1
15	30.0	19.0	5.8	9.7	27.0	0.36:1
25	23.2	20.8	4.0	21.4	21.4	1:1
40	28.2	20.8	3.4	19.6	22.1	0.88:1

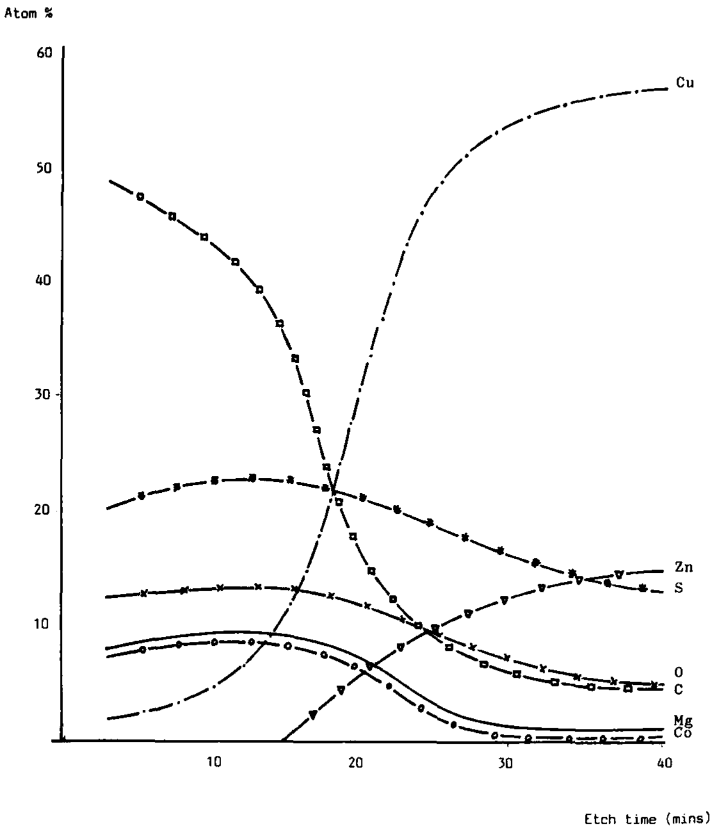

FIGURE 7 XPS, Promoter, Cobalt boroacylate, MgO activation.

etching indicating that the interfacial layer is either thicker or more dense than the control.

Figure 9 shows the XPS depth profile of a coupon, the same as the above sample, but steam aged for one hour at 121°C. Etching was extended to 90 minutes to reach nearer the bulk metal. Obvious differences with the unaged system (see Figure 7) are the much lower initial concentration of carbon and sulphur, the fact that zinc is now seen at the surface and that cobalt is not seen until after about 10 minutes etching. Making the previously-described assumptions gives the results shown in Table VII. Two important features stand out.

There is now a significant concentration of zinc oxide (or hydroxide) at the surface of the interface and an even larger one beneath the copper sulphide layer. There is no sign of cobalt beneath the copper sulphide layer. If one considers the amount of organic matter, indicated by the carbon content, on moving outward from a base line given by 40 minutes etching shown in Table VIII, it is obvious that the organic layer is already substantially reduced after three minutes etching and this is then comparable with the unaged specimen after 25 minutes etching.

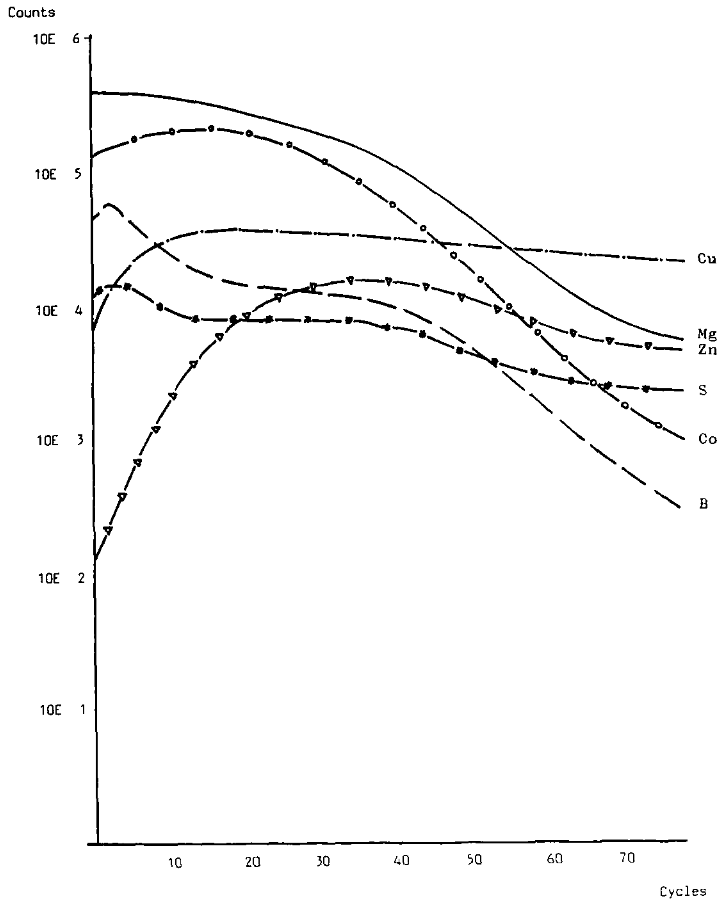

FIGURE 8 SIMS, Promoter, Cobalt boroacylate, MgO activation.

TABLE VI
XPS depth profile—cobalt boroacylate bonding promoter MgO used as activator

Etch time (minutes)	Cus %	ZnO %	CoS %	Maximum Remaining free Cu %	Zn %	Ratio Cu/Zn
3	3.2	0	13.2	—	—	—
8	9.0	0	15.6	—	—	—
15	14.4	0	28.6	—	—	—
25	33.0	9.8	5.8	32.2	4.1	7.8:1
40	26.0	16.0	2.0	41.3	7.5	5.5:1

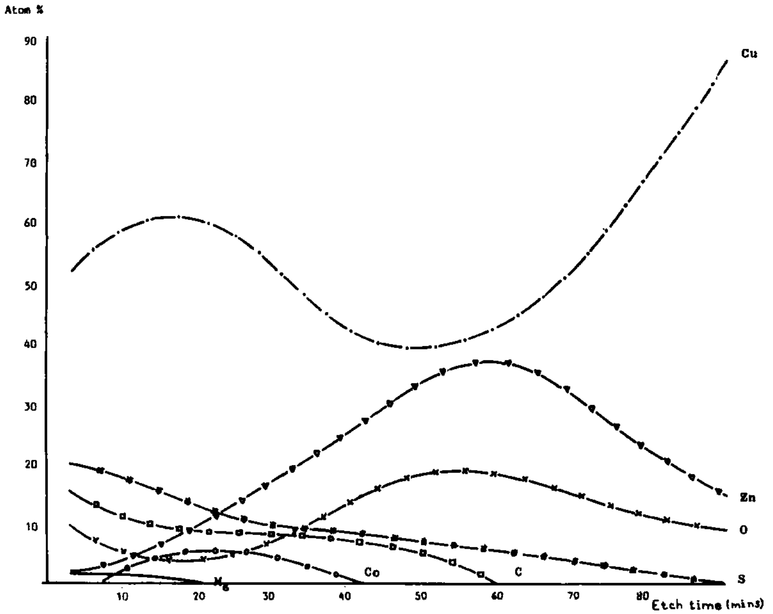

FIGURE 9 XPS, Promoter, Cobalt boroacylate, after steam ageing.

TABLE VII

XPS depth profile—cobalt boroacylate—one hour steam ageing MgO used as activator

Etch time (minutes)	Cus %	ZnO %	CoS %	Maximum Remaining free Cu %	Maximum Remaining free Zn %	Ratio Cu/Zn
3	33.8	9.0	—	38.0	—	—
8	31.6	8.0	2.2	44.7	1.7	26.3:1
15	20.4	2.4	6.0	54.4	6.1	8.9:1
25	12.2	12.6	10.2	48.5	10.2	4.7:1
40	20.8	25.2	3.8	31.2	11.9	2.6:1
60	9.0	33.4	—	38.8	18.9	2.1:1
90	—	7.0	—	89.3	3.7	24.1:1

TABLE VIII

Carbon content as a function of etch time

Etch time (minute)	40	25	15	8	3
Unaged carbon* (%)	7.5	11.7	31.2	36.4	42.1
Steam aged carbon (%)	6.0	5.3	8.3	9.8	14.9

* The mean of the results using ZnO and MgO as activator.

This is confirmed by the zinc and magnesium contents. All this confirms a greatly thinned, or much more easily removed, organic layer. Cobalt is also absent from the upper layer suggesting that it has been removed by the steam treatment and therefore was associated with the organic material.

THE INTERFACIAL LAYER MODEL

The model that emerges from these results agrees in most respects with the picture presented by Van Ooij.[1,2,4] Before reaction, the brass has a thin surface layer of zinc oxide. On reaction with a rubber/sulphur/accelerator compound without a cobalt bonding promoter, a fairly thin (*ca.* 45 nm) interfacial layer is formed containing copper sulphide, zinc oxide or sulphide and organic material. Into this layer projects remains of bulk substrate showing as free copper and zinc. The shapes of the copper and carbon depth profiles support the view that there is a dendritic growth of copper sulphide which is interlocked with the organic layer. A zinc oxide layer can be seen beneath the copper sulphide layer. Table III shows a high level for the maximum possible free copper and zinc.

This does not necessarily assert that after the etching times given the bulk metal forms an appreciable part, merely that if the bulk metal is penetrating into the interfacial layer it cannot be greater than the amount indicated and, moreover, since sulphur and oxygen are accounted for, the material is not present as sulphide or simple oxide. The addition of cobalt by the use of the cobalt accelerator complex causes some significant modifications to the interface. Whilst its depth stays almost the same, the amount of organic material taken into the interface is much increased suggesting a much stronger inter-penetrating cobalt sulphide-organic layer. Cobalt is present in the interface but was not detected in the zinc oxide layer on the bulk metal. (The level of free copper at the surface of the interface was very much reduced). Analysis of the cobalt profile suggests that it is present both in the organic phase and within the sulphide layer formed by both copper and zinc. The presence of cobalt in the sulphide layer and the reduction in the level of free copper should ensure improved adhesion on ageing by reducing both corrosion and the migration of zinc through the copper sulphide layer to form an overlayer of zinc hydroxide.

The interface found using cobalt neodecanoate or cobalt boroacylate is very different. The layer is very much thicker and higher levels of sulphur, oxygen and especially carbon are seen. This is particularly so in the case of cobalt boroacylate where an outer layer is observed with a high organic and sulphur content but only low copper sulphide content. Free copper is not present in the surface layers and zinc oxide or sulphide are only found in association with significant amounts of copper sulphide. The use of cobalt boroacylate gives a significantly higher cobalt level in the interlayer than either the neodecanoate or accelerator salts and boron is present with the cobalt. The picture of the interfacial layer after steam ageing also fits the previously-proposed model in which a thick zinc oxide or hydroxide layer forms under the copper sulphide layer. Steam ageing also removes the (mainly) organic layer at the surface of the interlayer. It is useful to speculate on the form in which cobalt is present in this interlayer. As the metal concentration is the same in each compound the concentration at the interface must reflect the ease with which they provide a source of cobalt for reaction. Cobalt is only seen in the presence of carbon and sulphur and this suggests that it is present bound to an organic molecule in a form such as Co-S-squalene rather than as cobalt sulphide. The steam aged interlayer, although it has lost cobalt from its outer surface, has a clear band of cobalt in the copper sulphide layer; cobalt is introduced as a squalene-soluble organo-metal and at some stage decomposition and reaction converts it to cobalt sulphide. It is in the latter form that it occurs in the copper/zinc sulphide layer. This suggests that its formation occurs at the same time as the formation of the other sulphides nearer to the original metallic substrate. The soluble material, together with the "vulcanised" squalene, which will not be of high molecular mass nor tightly cured, is easily removed by steam ageing. It appears that cobalt boroacylate, either because of solubility or migration to an interface, becomes more closely associated at a high concentration with the growing layer of cobalt/zinc sulphide.

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