

Adhesion Mechanisms of Enamel–Varnishes on Copper: Adhesion Promoter Versus Corrosion Inhibitor

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ABSTRACT: The role of adhesion promoters, copper oxidation, and thermal aging in the adhesion mechanism of enamel on copper winding wires is investigated. Evidence is presented on the predominant role of the copper oxide at the interface in the wire–enamel adhesion phenomena. The oxidation process and the copper oxides stability at the interface are seen to strongly depend upon the thermal aging of the wire and the nature of both the enamel and the pro-

moter. Atomic force and scanning electron microscopy analyses show that so-called promoters act more efficiently as corrosion inhibitors than as adhesion enhancers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 952–958, 2003

Key words: adhesion; adhesion promoters; additives; coatings; metal–polymer complexes

INTRODUCTION

Polymer coatings on metal have come to play an important role in various technological applications, including winding wires, whose electrical, mechanical, and surface properties are being constantly improved. The enamel–copper adhesion in winding wire is assumed to be a key parameter that may influence a large set of properties such as the dielectric strength, flexibility, windability, and chemical resistance of the wire. This implies that the adhesion should be strong and resistant to scratching, peeling, delamination, and aging. Adhesion is a complex phenomenon related to physical effects and chemical reactions at the interfaces. Therefore, the nature and structure of the interface ultimately determine the quality of the copper–enamel system. Adhesive forces are set up as the enamel is applied and cured to the bare wire and during the enameling process. The magnitude of these forces obviously depends on the nature of the copper surface and the binder. They may be broadly categorized into two types: the primary forces corresponding to covalent bonds in the energy range of 15–170 kJ and the secondary forces including hydrogen bonds, dispersion, dipole, and induction forces with a much lower energy in the range of 0.5–12 kJ.¹ All these forces are assumed to participate in the adhesion of polymer coatings such as enamel on copper, even if the actual

mechanism of enamel attachment is not yet fully understood.²

More generally, adhesion between metals and polymers is known to be a balance between wetting, chemical, or physicochemical bonds formed at the interface and the bulk features of the adherents.³ The nature of these “links,” the eventual diffusion of metal into the polymer side, and the role of metal surface oxide are still open to discussion.^{4,5} Furthermore, to improve such adhesion, adhesion promoters are now frequently used. It has been shown, for example, that —NH groups can form coordination complexes⁶ with copper surfaces (Fig. 1). These copper–azole complexes seem to act as corrosion inhibitors rather than adhesion promoters.⁷

In the present article, the adhesion of poly(vinyl acetoformal) (PVF) enamel on round copper wire has been characterized. The role of adhesion promoters, copper oxidation and thermal aging have been investigated and a new comprehensive mechanism is proposed and discussed. Although a huge amount of literature is dedicated to planar polymer–metal interfacial adhesion, polymer-coated wire geometry is definitely studied less. Furthermore, almost no experimental studies appear in the literature on PVF–copper adhesion. One of the tasks of the present work is thus to stimulate further work on that domain from other groups in the world research community.

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EXPERIMENTAL

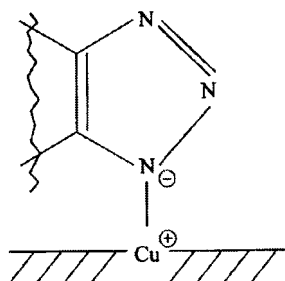


Figure 1 The coordination complex between the azole compound and the copper surface.

NEXANS as a PVF-based enamel, was used to produce winding wires with an initial diameter of 1.5 mm. The average diameter increase was found to be 70 μm . Formtenal[®] is mostly composed of PVF polymers, whose structure is presented in Figure 2, in a mixing of reactive diisocyanate monomers in organic solvents including cresol and xylene. Two types of Formtenal[®] enamel were studied in order to understand the adhesion phenomena⁸ at the enamel-copper interface.

Formtenal[®] 19016 OA 20 contains a polymerization catalyst (which acts on blocked polyisocyanates, allowing the beginning of the polymerization at a lower temperature) and an alkyd-triamino-triazine additive as an adhesion promoter. Formtenal[®] 19016 NC 20 is a bare varnish without any additive or adhesion promoter.

In the magnet wires industry thermal class 120 corresponds to a lifetime of 20,000 h at 120°C. Although our enamel wires were supposed to withstand 120°C, we decided to increase the annealing temperature to 150 and 180°C to study the aging effect.

Adhesion measurements

The first method we thought about to study such polymer-metal interfacial adhesion was the classical and widely used peel test.^{9,10} However, we also wished to preserve the cylindrical geometry of the wire to be as close as possible to our system. We then started adhesion measurements using the semi/quantitative *fiber pull-out*¹¹ test, in which a droplet of the resin is deposited and cured around the copper wire before the shear stress required to pull the resin out of the wire is measured. Unfortunately, the adhesion was

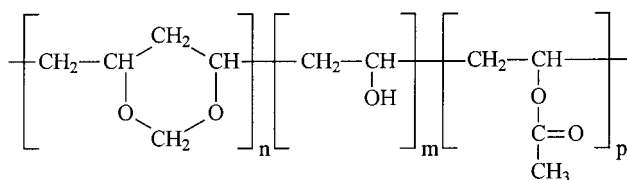


Figure 2 The poly(vinyl acetoformal) (PVF) structure.

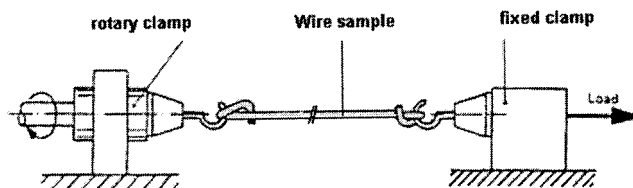


Figure 3 A schematic view of the twist peel test.

so strong that it was impossible to pull out the polymer droplet without breaking the wire. We then decided to use the more qualitative *twist peel test* that is extensively used in the winding wire industry for characterizing the adhesion strength of enamel on bare copper.² In the twist peel method one end of the wire, on which a notch was formed in the lengthwise direction by a cutter, is fixed to a clamp that can be axially displaced. The wire is then stretched toward the horizontal direction by applying a weight to the fixed clamp, as illustrated in Figure 3. The length of the sample and the weight depend upon the wire diameter as defined IEC Norms.¹² The other end of the wire is twisted toward the diameter at a speed of 100 rpm until the insulating film is peeled off. The adhesion strength is then represented by the number of revolutions needed to delaminate the enamel-copper joint. This test allows a comparison between different samples but it does not give the absolute adhesion energy needed to peel off the coating.

Atomic force microscopy (AFM) analysis

The topographic information of the copper and enamel surface down to submicron dimensions was obtained with an AFM instrument after peeling the interface. Observations were performed in contact mode using a Nanoscope III Multimode AFM (Digital Instruments, Santa Barbara, CA) with a V-shaped Si_3N_4 cantilever (Nanosensor, Germany) with a tip radius of curvature (R) of around 50 nm. All pictures were taken in air (22°C, 45% relative humidity) with a scanning frequency of 2 Hz.

Scanning electronic microscopy (SEM) analysis

SEM was used to provide topographical and elemental information of the joint after delaminating the copper-enamel interface. The SEM images were analyzed for copper and carbon quantification using energy dispersive X-ray spectroscopy (EDS). A Philips XL20 SEM microscope was used under a voltage of 5 kV. Sample surfaces were coated with a thin layer of gold to eliminate charging effects.

RESULTS AND DISCUSSION

In the present study the situation is more complex than in the general case where promoters are depos-

ited or created directly on the copper surface but added directly in the varnish formulation. This means that the alkyd-triamino-triazine additive might also react with the hydroxyl group of the PVF polymer or the isocyanate monomer contained in the enamel. As a preliminary study, we checked whether the glass-transition temperatures (T_g) and the shape of thermogravimetric curves were the same for both modified and nonmodified systems. This points out that the differences that may appear between these two resins should involve adhesion promoters only.

The results of the adhesion strength for both systems as measured using the twist peel test method are presented in Figure 4. In standard conditions, the adhesion was found to be 340 turns for the adhesion promoters containing the enamel Formtenal® 19016 OA 20 compared to 308 turns for the bare reference 19016 NC 20. The standard deviation for the twist peel test values was lower than 2%. The 10% increase of adhesion observed in the system containing the promoter is then relevant. After thermal aging at 180°C for 2 h in air, the adhesion strength was measured again. In both cases the adhesion strength significantly decreased as shown in Figure 4. The adhesion strength decreases from 340 to 187 turns for the 19016 OA 20 system whereas it decreases from 308 to 237 turns for the 19016 NC 20 enamel. Therefore, it appears that thermal aging strongly affects the adhesion of enamel on copper. It is interesting that such an effect seems to be enhanced by the presence of an adhesion promoter in the enamel.

The deterioration of the adhesion strength as a function of the thermal aging conditions was investigated for the Formtenal® 19016 OA 20 system, as shown in Figure 5. At 120°C in air, the adhesion strength seems to not be affected and remains constant at about 340 turns. At 150°C in air, the adhesion strength decreases slightly with the annealing time. The peel test measurement goes from the initial value 340 down to 275

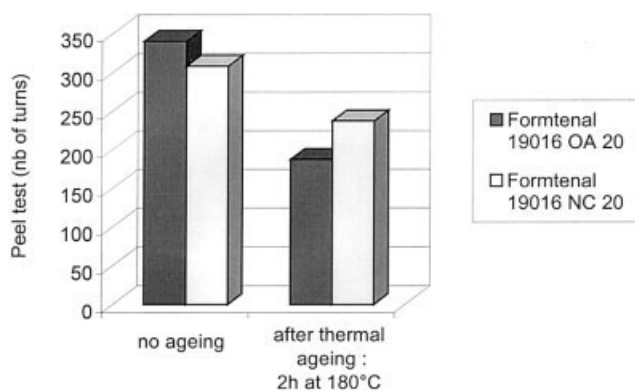


Figure 4 The adhesion strength of Formtenal® enamel on copper using the peel test method. The adhesion quantification is given in terms of the number of turns needed to delaminate the assembly.

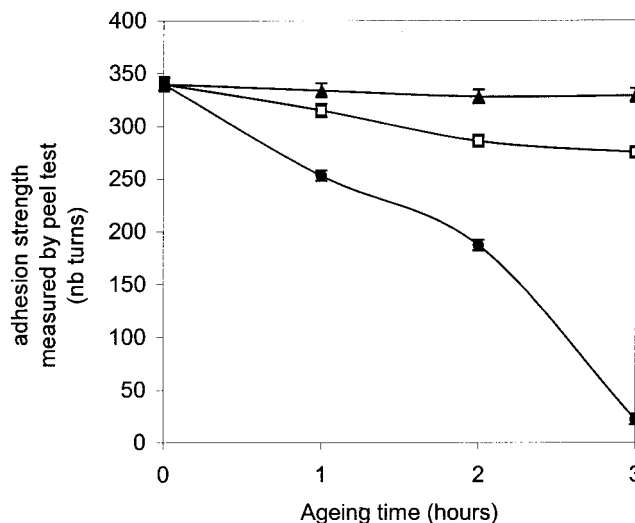


Figure 5 The evolution of the adhesion strength of Formtenal® 19016 OA 20 on copper after aging at (▲) 120°C, (□) 150°C, and (●) 180°C.

turns, corresponding to a decrease of 23%. The largest degradation of the adhesion strength is observed during the thermal aging at 180°C in air. The adhesion strength decreases strongly from 340 turns to less than 50 in a few hours. Therefore, the adhesion of enamel on copper clearly depends upon the temperature and the annealing time, as illustrated in Figure 5. Below 150°C, the peel test measurement does not significantly decrease and the adhesion strength is still high. Above 150°C and particularly at 180°C, the thermal treatment dramatically affects the adhesion of the enamel on the copper wire.

As the thermal index¹³ of PVF is commonly 120°C, we assume that thermal degradation of the enamel will arise from such aging at 180°C. This bulk effect would definitely contribute to the large drop of the adhesion. However, we also have to consider the evolution of the copper–enamel interface during the thermal aging under different conditions, where the copper oxidation and the adhesion promoter are supposed to play a key role in the adhesion mechanisms.

The oxidation of copper is very fast in an air atmosphere. Hence, it is very difficult to observe a pure Cu surface. The main oxide types on the Cu surface are CuO, Cu₂O, Cu(OH), and Cu(OH)₂. According to Mishra and Weimer,¹⁴ the polished Cu has mainly Cu₂O on its surface, which appears very quickly on the Cu surface. The Cu₂O oxide is converted to CuO by a longer oxidation process in air. It seems that CuO cannot be obtained by a direct oxidation of the Cu surface but results from the oxidation of Cu₂O.

The formation of the oxide layer on the copper surface was studied with AFM as presented in Figure 6. A copper plate sample was cleaned with sulfuric acid in order to remove oxides on the surface,^{14,15} and

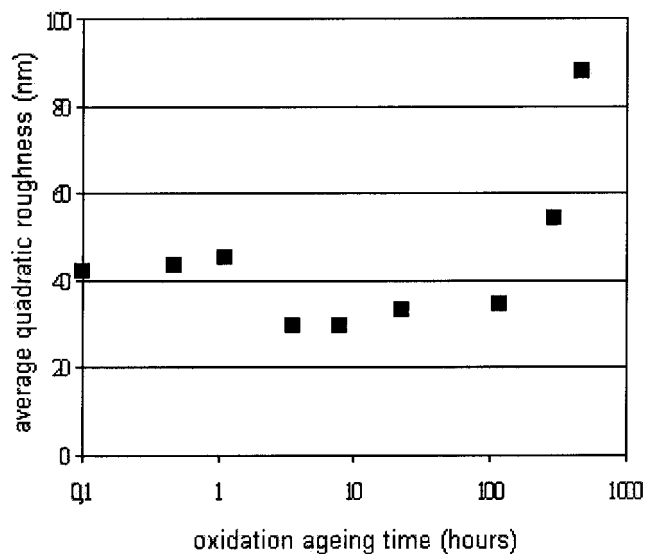


Figure 6 The evolution of the root mean square roughness of a macroscopic copper surface in air as a function of the oxidation time at 25°C.

Cu oxidation in air was followed by AFM during more than 20 days at room temperature. The root mean square (RMS) roughness obtained by AFM changes with time, corresponding to the oxidation process. The formation of Cu_2O seems to be quite slow during the first hours where the average roughness is still in the range of 40 nm. Then the oxidation process is greatly accelerated, resulting in the increase of the roughness of the surface from about 30 to 90 nm. The formation of Cu_2O on the Cu surface is obviously enhanced when the temperature is increased. The roughness of a Cu surface was also measured after a thermal treatment at 180°C. After 5 h at 180°C, a weak Cu_2O layer was formed at the surface of the sample and the average roughness was calculated from Figure 7 to be 145 nm. The AFM topographic picture presented in Figure 7 shows the peculiar morphology of the oxide layer. Indeed, it was easily removed by gently wiping off the surface with a filter paper, showing the low cohesive nature of the oxide layer.^{16,17}

We may conclude that thermal aging of wire at a relatively high temperature affects not only the coating structure but also the copper-coating interface by enhancing the oxidation process of the copper surface. Moreover, the formation of a low cohesion Cu_2O and CuO layer at the copper- enamel interface is assumed to strongly influence the adhesion strength.

It appears then that a better understanding of the adhesion mechanisms of copper- enamel systems would certainly come through a careful examination of the interface versus various aging conditions (time, temperature, etc.). We analyzed the different delaminated surfaces available in the copper- enamel system after performing a peel test as illustrated in Figure 8. AFM observations of both the internal and external

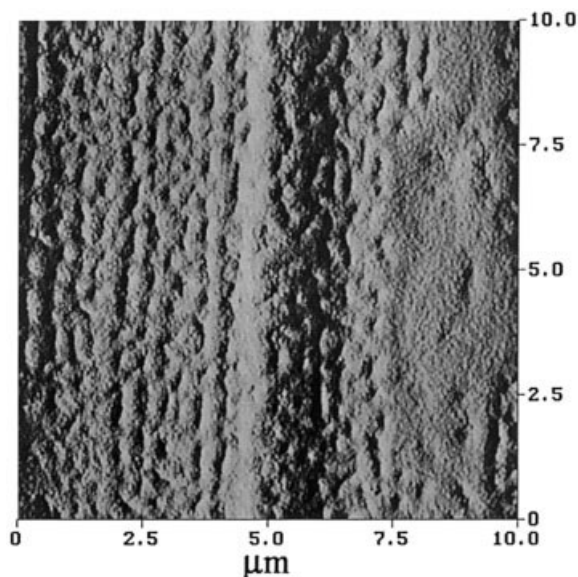


Figure 7 An AFM picture of the macroscopic copper surface obtained after oxidation in air for 5 h at 180°C.

surfaces of the enamel together with the copper one were investigated. The AFM pictures are presented in Figure 9 for the bare and formulated coatings.

The AFM pictures of the external surfaces are very similar for both types of enamel (Formtenal® 19016 NC 20 and 19016 OA 20). The computed RMS roughness was approximately 5 nm for both external coatings [Fig. 9(a,b)]. Slight differences appeared on the copper surfaces of each wire as seen in Figure 9(c,d), but the bigger variation probably shows up on the internal enamel surfaces [Fig. 9(e,f)]. The topographies presented on these last two pictures are very different and suggest a much more irregular surface for the 19016 NC 20 sample than for 19016 OA 20. Indeed, the RMS value is 26 nm for the 19016 OA 20 enamel and 74 nm for the Formtenal® 19016 NC 20 internal surface. A careful examination of Figure 9(e) suggests that the pyramidal shapes seen in the topography are not specific features of the bare enamel internal surface but rather a “feedback imaging” of the pyramidal tip used in contact mode. Indeed, if some-

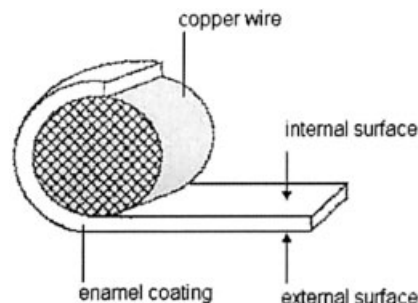


Figure 8 A schematic view of a delaminated enameled wire after peeling.

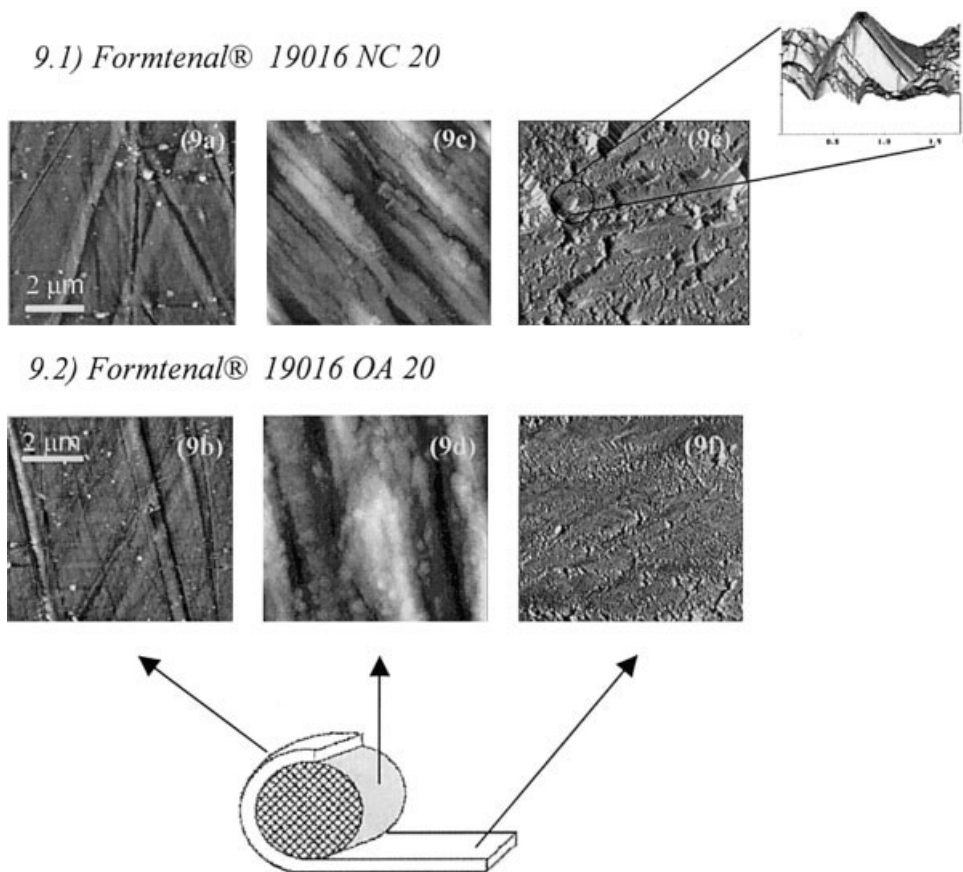


Figure 9 An AFM observation of the different surfaces of copper and enamel obtained after delamination. (e) The externalized area shows the pyramidal feedback image of the tip by the copper oxide with a measured pyramidal half-angle of 35°.

thing hard enough and sharper than the radius of the tip (around 60 nm) is present on the surface, it will image the tip (ceramic or metallic oxides are often used for imaging AFM tip).¹⁸ Furthermore, the computed half-angle of the pyramid visible in the externalized area of Figure 9(e) is 35°, in perfect agreement with the value given by the tip manufacturer. We may then conclude that small “scraps” of copper oxides

with very high modulus and sharp angles are present on the internal surface of the 19016 NC 20 enamel. Thus, the presence of promoter in the formulation seems to hinder the creation or diffusion of copper oxide in the varnish.

The presence of larger amounts of copper on the 19016 NC 20 internal surface [Fig. 9(e)] than on the 19016 OA 20 one [Fig. 9(f)] was confirmed by perform-

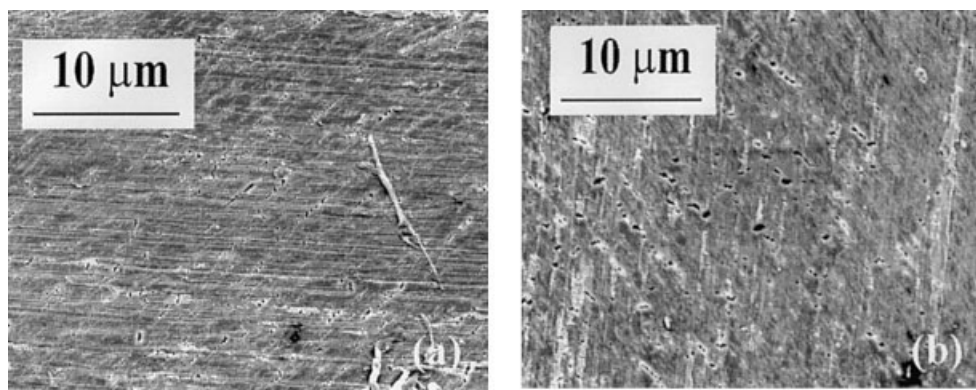


Figure 10 SEM pictures of the internal enamel surface after delamination for both bare and formulated coatings: (a) Formtenal® 19016 OA 20 and (b) Formtenal® 19016 NC 20.

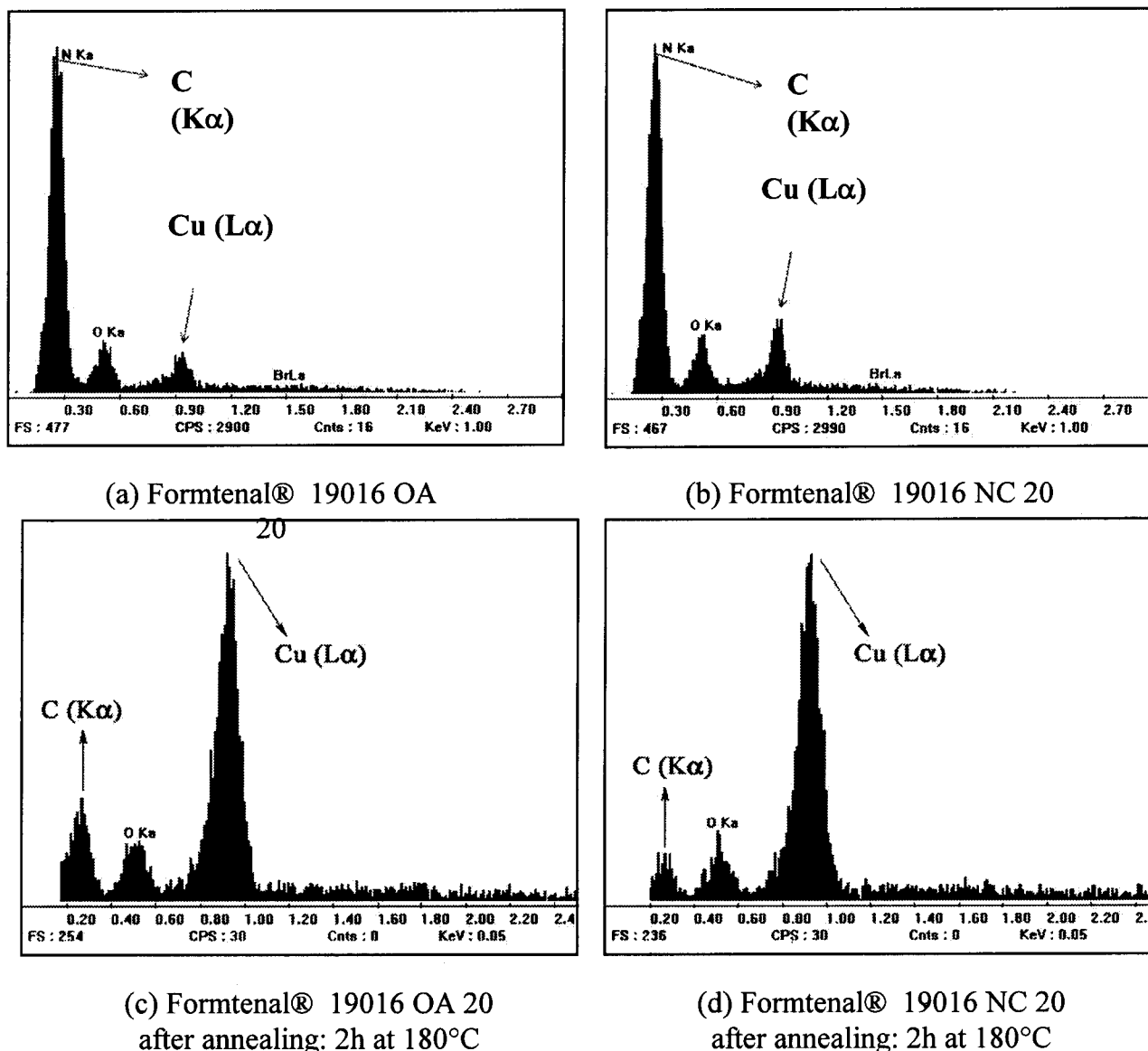


Figure 11 The carbon (C, $K\alpha$) and copper (Cu, $L\alpha$) atoms' peak quantification obtained by EDS analysis on the PVA enamel surface in contact with the copper wire.

ing chemical analysis in SEM using EDS. The pictures obtained by SEM for both samples are presented in Figure 10 whereas Figure 11 shows the different X-ray spectra. If we assume that the carbon peak ($K\alpha$) is constant as the principal component for both enamels, the amount of Cu on the sample, corresponding to the peak ($L\alpha$), can be determined by calculating the height ratio $Cu(L\alpha)/C(K\alpha)$. The calculation of this ratio for both enamel internal surfaces [Fig. 11(a,b)] indicates twice as much copper for the 19016 NC 20 than for the 19016 OA 20. This result suggests that the adhesion promoter contained in the Formtental® 19016 OA 20 may slow down the oxidation process at the enamel-copper interface by acting as a corrosion inhibitor, as previously suggested.^{19,20} Although the promoter may not directly improve the adhesion strength between

the copper and the coating, it hinders its decrease by preventing or limiting the formation of an oxidation layer at the interface.

EDS analysis was also performed after thermal aging on both samples, as shown in Figure 11(c,d). These results highlight the large increase of copper at the internal surface of both enamel surfaces compared with the nonannealed case. However, more copper is still found on the 19016 NC 20 surface. This result confirms the strong influence of temperature on the copper oxidation process, as mentioned before. We then assumed that a nonstable and porous¹⁶ copper oxide layer is formed at the copper-enamel interface during thermal aging. This layer is characterized by very low cohesive energy and would lead to a significant drop of the adhesion strength.

CONCLUSIONS

We have investigated the role of adhesion promoters, copper oxidation, and thermal aging in the adhesion mechanism of enamel on copper in winding wires. The copper oxidation at the interface seems to play a predominant role in the wire–enamel adhesion phenomena. The oxidation process and the copper oxides' stability at the interface are seen to strongly depend upon the thermal aging of the wire and the natures of both the enamel and the promoter. Our AFM and SEM analyses have shown that the adhesion promoter may play the role of an oxidation inhibitor at the copper–enamel interface rather than directly improving the adhesion strength.

At room temperature the presence of an adhesion promoter in the enamel results in a significant improvement of the adhesion strength, as measured by the peel test method. Such a result could be explained by the differences in the interface structure, which is composed of a copper surface and an enamel layer separated by an intercalated copper oxide layer. In the first case, the promoter prevents the formation of a large Cu oxide layer, leading to adhesive failure at the metal–enamel interface. Only a small amount of copper is then detected by EDS on the internal surface of the coating. In the second case, the oxide layer is probably thicker, leading to cohesive failure inside the copper oxide layer. Indeed, the EDS analysis shows a definitely larger amount of copper on the enamel's internal surface after delamination.

Thermal aging of the winding wire is seen to clearly affect the copper–enamel interface by enhancing the Cu oxidation process. However, it may also affect the enamel organic coating in volume, depending on its thermal index, leading to irreversible degradations of polymer bonds and polymer–metal bonds. We realized that the enamel–metal interface can be weaker from an adhesion point of view than the metallic oxide layer after annealing the wire.

Our conclusion is that the adhesion of enamel on copper in winding wire can be improved by using thermal resistant adhesion promoters/corrosion inhibitors, which would enhance the adhesion strength at the interface and limit the copper oxidation process.

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