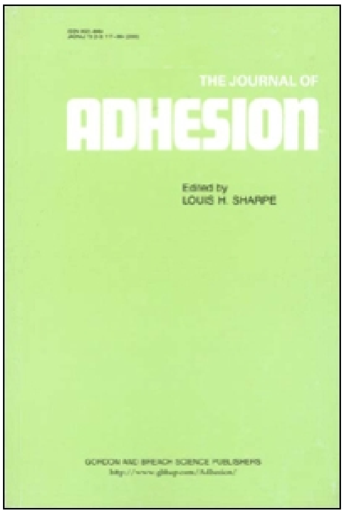

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Elementary Mechanisms in the Interaction of Organic Molecules with Mineral Surfaces†

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Model systems are used to reproduce the actual situations encountered during the interaction of organic molecules with mineral solids under controlled experimental conditions.

The role of local electrical fields produced by surface heterogeneities and the influence of the electronic properties of the functional groups of the organic molecule and of the surface are demonstrated and discussed.

This study enables modelling of the basic mechanisms in the organic molecule-mineral solid bond and of the polymerization process of the organic film.

The results given here may be used to produce theoretical models of predictive nature in the field of adhesion and structural bonding.

KEY WORDS Adhesion; metal oxides; acrylonitrile; electrochemistry; chemisorption; acid-base reactions.

INTRODUCTION

Although the problems of structural bonding and the adhesion of organic films to mineral surfaces are generally well-mastered in the

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field of industrial applications, they still raise a number of questions from the design point of view.

Precise answers to these questions would clearly ensure better control of the use of adhesives and improve the laws of behaviour of assembled materials.

Unfortunately, such an approach cannot be made using samples taken from industrial materials, owing to their complexity and also to the lack of reproducibility of such samples which would, anyway, be difficult to describe suitably at an atomic or molecular scale.

It is, therefore, necessary to deal with the problem posed under simplified conditions enabling the production of models which can be experimentally controlled. We can then make a serious approach to the following questions:

- the mechanisms of interation between organic molecule and mineral substrate in terms of surface physico-chemistry,
- the mechanisms of polymerization and possible changes in the resulting polymer in terms of molecular chemistry,
- the behaviour of the mineral organic compound in terms of solid state physics.

The purpose of this article is to describe the results achieved with the system Acrylonitrile–oxidizable metal. The first part will be devoted to a methodological explanation and a brief description of the experimental equipment used. The second part will describe the mechanisms governing the organic molecule/mineral solid bond. In the third part, we shall discuss the influence on this bond of the condition of the mineral surface (electronic properties and chemical composition). A set of results concerning the laws of behaviour of assembled materials will be evocated in the conclusion.

I METHODOLOGY—INSTRUMENTATION

I-1 The surfaces of true mineral solids

In practice, except for a few noble metals, the surfaces of mineral materials are nearer to those of insulating substances than those of metals. This is obviously the case for solid insulating substances but also applies to most metals whose surface is always either naturally or as a result of treatment covered by a layer with non-metallic properties (oxide, nitride, carbide, organic coating, etc.). It should also be noted that following the machining processes to which they have been subjected, the surface of these metallic materials is morphologically different from their volume: the external layer of the material is in a microcrystalline or even amorphous state, and its properties are very different from the solid in volume.[1]

It naturally follows, from the point of view of electronic properties, that there are considerable variations depending on the depth with respect to the surface of the sample, the density of the electronic states being either that of an insulator (perfect or not) or that of a metal.

Thus, it is not possible, in the case of a true mineral, to consider its surface properties as similar to those which it posseses in volume. Moreover, the main properties of this surface are very different from those of a perfect insulating substance: not only do stoichiometry faults produce localized levels which invade the forbidden band but electrostatic charges (positive and negative) localized on these defects, together with the presence of dangling bonds presenting emergent orbitals and, finally, impurities either included or resulting from chemical adsorption cause considerable roughness of the isopotential curves. Very intense local fields (range approximately 1 to 2 nm, $|\mathbf{E}| > 10^8 \mathrm{V \cdot m^{-1}}$) are caused by this roughness.[2]

In fact, the surface of a true mineral can be described as a mosaic of sites which either give or accept electrons to a varying extent, with positive or negative electrical fields associated with the existence of these sites.

I-2 Role of functional groups on organic molecules

We know that the polymerization of a monomer may be the result of addition reactions which can be described in terms of acid-base reactions as intended by Lewis.

In the case of a monomer with one extremity A of an acid nature (electrophil) and the other extremity B of a basic nature (nucleophil), the polymerization reaction can be written: $AB + AB \rightarrow ABAB$. This type of reaction (ion polymerization) is, in particular, extremely active when the monomer is a polar and polarizable molecule. The presence of outside agents (electrical field, chemical aggression, plasma aggression) accelerates the polymerization process. We can now see why during an interaction between polymerizable molecules and a true mineral surface (creation of an adhesive bond) we obtain an adhesive/substrate interface, characterized by very strong bonds immediately adjacent to a layer where the adhesive is extremely fragile: the active extremities of the molecules close to the mineral solid interact strongly with the antagonistic active sites of the surface rather than participating in the polymerization mechanism.

I-3 Experimental simulation of these phenomena

An attempt at modelling this seemingly complex situation involves the inclusion of all the parameters while, at the same time, creating conditions favourable to an unambiguous demonstration of their role.

In order to overcome the random nature of distribution of the active sites on the mineral substrate surface, we must on the one hand create a surface which is well-defined chemically (pure metal), and on the other hand give it an even acid or basic character; electrochemistry is well suited to this aim, the working electrode either emitting or receiving electrons, depending on its polarization (cathode or anode). Electrochemistry is also useful for creating intense even and isotropic fields, produced on the surface of the electrode by the formation of the double layer once the system is polarized above the null charge potential. As for the monomer molecule, it must have the necessary characteristics (acid and basic extremities and polarizability) while remaining sufficiently simple to be calculable, so as to enable the production of a model whose validity can be checked out by experimental results. As a first approach, the acrylonitrile (AN) seems well studied to this aim. A complete study of this molecule was therefore carried out, combining experience and theoretical chemistry.[3]

I-4 Study techniques

In parallel with electrochemistry performed in a strictly controlled organic environment[4] and used to follow the interacton kinetics activated by the double layer electrical field, we had to simulate the case of surface sites without an intense electrical field. For this we used the normal methods of the physico-chemistry of surfaces, the acrylonitrile molecule being in an ultra-vacuum environment in the gaseous phase: its interaction with the surface of the sample then results exclusively from the intrinsic properties of the two bodies.

In this latter case, we required spectroscopic techniques which were both sensitive and non-destructive: the association of UV photo-electron spectroscopy (UPS) and metastable de-excitation spectroscopy (MDS)[5] resulted in a good description of the chemisorption mechanism. In fact, the escape depth of the photoelectrons is approximately 2 nm. It is therefore possible to "see" the substrate through one or more chemisorbed molecular layers whereas the MDS, being sensitive to emergent orbitals only, gives electronic and structural data on the solid-vacuum interface.

Finally, UPS and MDS were associated with infrared absorption spectroscopy (IRAS) and Auger electron spectroscopy (AES) for the study of samples obtained after electrochemical treatment.

II RESULTS OBTAINED—INTERPRETATION

The acrylonitrile molecule was, therefore, subjected to three types of interaction with a polycrystalline metal surface:

- non-polarized metal surface;
- negatively-polarized metal surface (basic character imposed), the molecular being situated in the cathode double-layer field;
- positively-polarized metal surface (acid character imposed), the molecule being situated in the anode double-layer field.

In all three cases, the metal was a transition metal offering a high density of occupied states below the Fermi level.

II-1 Chemisorption of acrylonitrile on nickel

Before each measurement, the nickel surface is cleaned by ion bombardment. The acrylonitrile is introduced into the experimental chamber in gaseous form; exposure to acrylonitrile is measured in

Langmuirs ($1L = 10^{-6}$ Torr · s) and carried out at pressures between 10^{-8} and 10^{-7} Torr, the basic pressure of the installation being 10^{-10} Torr. The sample is maintained at ambient temperature.

The interpretation of the experimental data[6] shows that like molecules of the type C_2H_2, C_2H_4 and C_6H_6[7] and CH_3CN,[8] the acrylonitrile molecule is absorbed flat on the surface of the metal (Figure 2b) without modifying the metallic nature of this surface from the point of view of electronic properties. The covalent bonds between the molecule and the surface result from electronic exchanges: on the one hand between the π and anti-bonding orbitals of the vinyl extremity and the d-levels of the nickel; and on the other hand between the π orbitals of the CN group and the bottom of the valence band of the metal.[9]

This situation is obviously unfavourable for any subsequent polymerization process. Moreover, the energy of the molecule + surface bond is low enough to enable the adsorbate to be desorbed by heating at moderate temperature ($T \sim 600K$).[10]

II-2 Interaction of acrylonitrile with a negatively-polarized surface

The surface of polycrystalline nickel is used as a cathode in an electrolytic cell containing organic solution (solvent: acetonitrile; salt: perchlorate of tetraethylammonium; the acrylonitrile acting as a co-solvent). The potentio-dynamic characteristics (I(V) curves) in Figure 1 show the changes of Faradaïc current with respect to electrode potential: in the presence of acrylonitrile an inhibition peak appears, showing an irreversible modification of the surface of the electode. This irreversible modification has its origin in two important phenomena: on the one hand the oxide layer which initially covers the surface of the electrode is reduced (visible result on the I(V) curve without acrylonitrile); on the other hand, in the presence of acrylonitrile a polymer film is deposited on the electrode; identified by IRAS in polarized light, this film is composed of polyacrylonitrile chains (PAN) perpendicular to the plane of the electrode, the pendant nitrile groups being themselves oriented in this direction (Figure 2c); the direction of this orientation (nitrogen atom pointing towards the outside of the film) is controlled by MDS: the AN—Ni bond is therefore made by means of the carbon in the β-position to the CN and polymerization results

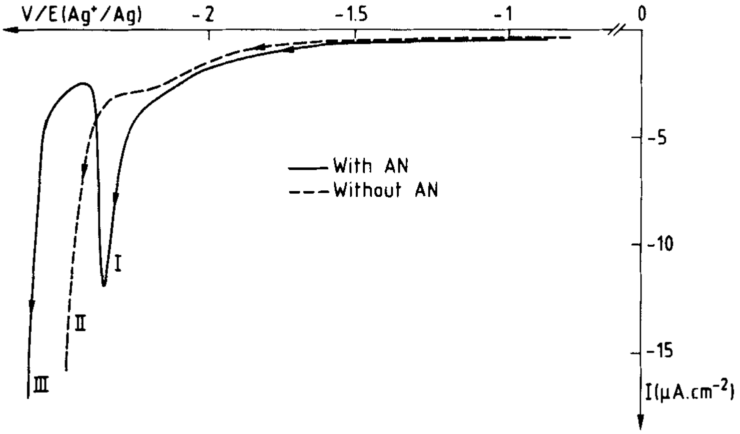

FIGURE 1 Interaction of AN with a negatively-polarized metal. In the presence of AN, the Faradaïc current shows an inhibition peak located between the reduction region of the oxide (I) and that of the intense Faradaïc current (III).

from an addition reaction involving the vinyl doublet of the molecule.[11]

II-3 Modelling of the interaction between acrylonitrile and a cathode

Negative polarization of the electrode corresponds to the formation of a double-cathode layer. An intense electrical field ($|\mathbf{E}| \sim 10^7\,\mathrm{V \cdot cm^{-1}}$) oriented towards the surface of the electrode in a direction perpendicular to its plane results from the antagonism of positive ion/cathode charges (double electrochemical layer).

Given the dipolar moment of the CN group, the acrylonitrile molecule is oriented in such a way that its CH_2 extremity interacts with the metal surface (Figure 3b). Moreover, polarization of the vinyl bond under the inductive effect of the dipolar moment of the CN group is reinforced by the electrical field, such that the CH_2 extremity of the molecule begins to lack electrons, which reinforces its acid character in the sense intended by Lewis. The acid-base reaction between molecule and electrode can then occur, leading to the establishment of a chemisorption bond (Figure 3c). The transfer from the electronic pair from ex-vinyl bond to the CH extremity of

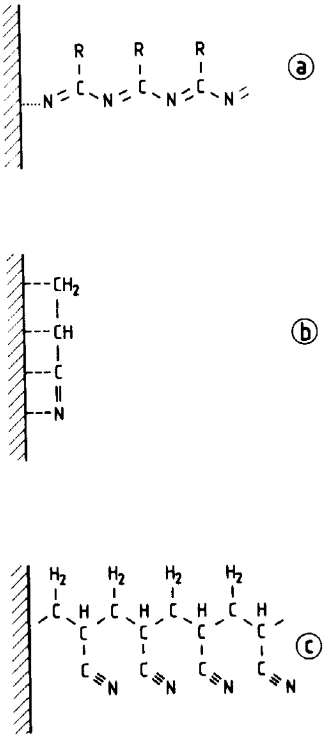

FIGURE 2 Different forms of AN/Metal interaction. a—Metal polarized positively (anode). b—Metal non-polarized (classical chemisorption). c—Metal polarized negatively (cathode).

the molecule results in a shift of the basic character, initially located on the surface of the electrode, such that the acid-base reaction can be propagated from monomer to monomer and leads to the formation of polymer (PAN). Figure 3d illustrates this mechanism. As the film thickens, the surface of the electrode moves towards the solution: functioning of the cell (from the electro-chemical point of view) is ensured with respect to Faradaïc current by hole conduction from CN group to CN group, owing to the existence of π electrons; the monomer supply of the reactional area (double-layer) results from diffusion of the acrylonitrile from the solution.

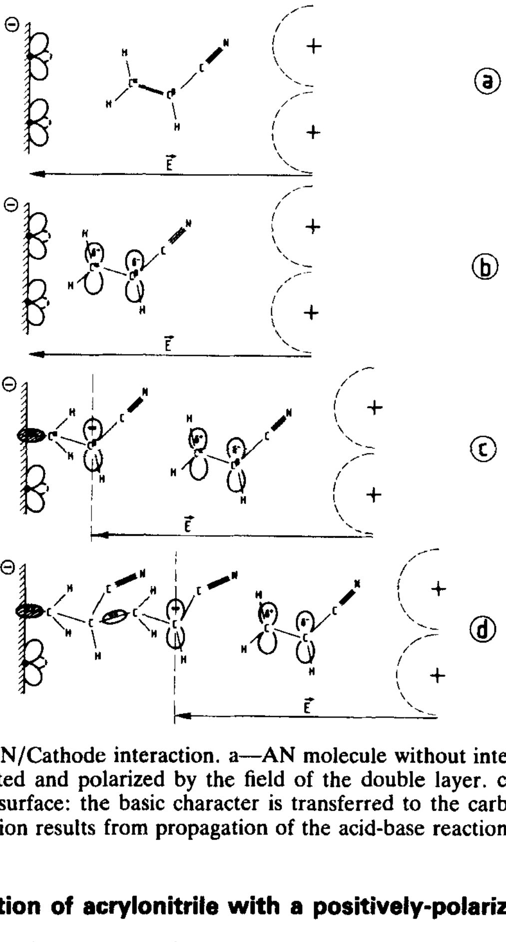

FIGURE 3 AN/Cathode interaction. a—AN molecule without interaction. b—AN molecule oriented and polarized by the field of the double layer. c—AN molecule bonded to the surface: the basic character is transferred to the carbon in α of CN. d—Polymerization results from propagation of the acid-base reaction.

II-4 Interaction of acrylonitrile with a positively-polarized surface

Returning to the diagram in Figure 3b, the electrode now occupies the space previously occupied by positive ions, the double-layer in this case being formed by the accumulation of negative ions in front of the anode; as for the electrical field of this new configuration, it is the same direction and the same orientation as on Figure 3b. We can see immediately that if an interaction is to occur between molecule and surface, it will necessarily involve the nitrogen atom from the CN group. As in the previous case, the reaction will be acid-base type, as described by Lewis: in fact the electronic lone pair of the nitrogen atom is the cause of a basic character as defined by Lewis, while positive polarization gives the electrode an acid character.

However, unlike the previous case (propagation of the basic character of the cathode to the CH extremity of the vinyl bond), the nitrogen-metal bond can occur without the carbon atom in the CN group lacking electrons, *i.e.* taking on a marked acid character. Under these conditions, the polymerization process can only occur by opening of a π bond in the CN group under the effect of an attack of this bond by an oxidizing radical.[12] We can therefore predict, on the one hand, a much slower reaction speed than that which occurs on the cathode, and on the other hand a resulting polymer built around a skeleton composed of —C=N— conjugate bonds. Experimental results confirm these assumptions: it requires several minutes on the anode to create a 100 nm thick film (whereas on the cathode, one second is enough to achieve this thickness); moreover, electron spectroscopies (UPS and MDS) indicate the presence of a broad valence band, characteristic of an organic semi-conductor, attributable to conjugate —C=N— bonds. Finally, infrared absorption spectroscopy can be used to identify the nature of the R radicals in a pendant position on the skeleton: these are —CH=CH_2 (from the acrylonitrile) —CH_3 (from the acetonitrile) and —O—CH_3 and —O—CH=CH_2, resulting from attack of the π bond by an oxidizing radical.

II-5 Summary of results

In this way, using electrochemistry and physico-chemistry of surfaces techniques, it has proved possible to reproduce experimentally the various situations encountered on actual material.

These results are summaraized in Figure 2: in the absence of a local electrical field (sites with low potential roughnesss), the molecule is chemisorbed on the flat, is unsuitable for any subsequent polymerization process and the molecule-surface bond is weak (Figure 2b). However, in the presence of intense electrical fields (sites with high potential roughness) only one extremity of the molecule is involved in the bond with the substrate, the other extremity being available for polymerization processes.

Molecule-surface adhesion is governed by an acid-base reaction, as described by Lewis which, as we shall show here later, produces a strong bond. Depending on the direction of the local electrical field, acrylonitrile is adsorbed either by the carbon from its CH_2 extremity (Figure 2c) or by the nitrogen from its CN group (Figure 2a). Finally, reproduction of the initial conditions at each stage of the polymerization (in particular direction and orientation of electrical field) produces parallel polymer chains, whose abounding depends on the number of available sites on the surface of the electrode and the steric bulk of the molecules. This creates favourable conditions for filling of the volume occupied by the film with useful material for adhesion.

III INFLUENCE OF THE ELECTRONIC PROPERTIES OF THE SURFACE

The results given in the previous chapter show that adhesion of the organic molecule to the metal results from an acid-base reaction, as described by Lewis, *i.e.* on the sharing of an electronic pair supplied by one of the two elements. For a given organic molecule, we can therefore see that the electronic properties existing on the surface of the mineral material will play an important role in the quality of the bond achieved and, as a result, in the qualities of the polymer film.

For the purpose of the study which follows, there are two types of consideration to be taken into account:

- this research should stay close to actual problems (which therefore means priority examination of cases in which the mineral is constituted from a common and therefore oxidizable metal);
- the possibility of unambiguous interpretation of the results obtained with respect to the nature and structure of the film.

We therefore chose to favour cathode studies (electrochemistry on reduction) which, as we have seen above, lead to the generation of PAN films which can be easily characterized. In this context, various types of situations may be encountered:

- transition metal (with tight-binding electrons) with non-stoichiometric oxide (this is the case of iron)
- transition metal with stoichiometric oxide (such as nickel);

- alloy of transition metals with passivating surface segregation (stainless steel A316L)
- metal with free electrons coated with a fairly thick layer of oxide (with a wide forbidden band) which is fairly disturbed (aluminium can be used for this study).

III-1 Interaction of acrylonitrile with a negatively-polarized iron surface

In the initial state, the surface of the electrode is covered with various oxides,[13] reduced once cathode polarization is established, in accordance with the reactions:

$$Fe_nO_m + 2me^- \rightarrow nFe + mO^{--}$$

The oxygen thus released is discharged from the double-layer by the electrical field; this mechanism helps to create a uniform layer of pure iron on the surface of the electrode, whose electronic properties are shown in Reference 14.

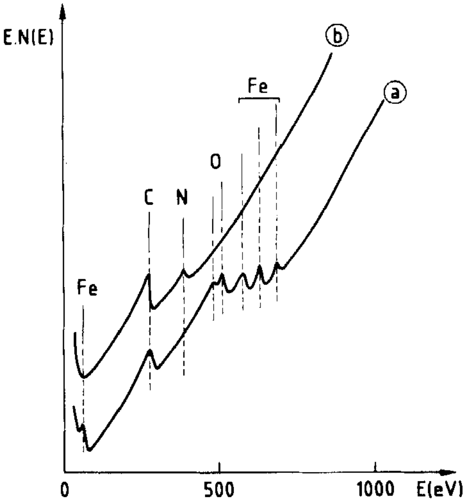

FIGURE 4 AN/iron interaction (cathode area). a—Initial chemical composition of the surface (AES). b—Chemical composition of the surface after electrolysis (AES). c—Curve I(V) in the presence of AN (0.5 M). d—Curve I(t) in the presence of AN (0.5 M) for V = −2.8V.

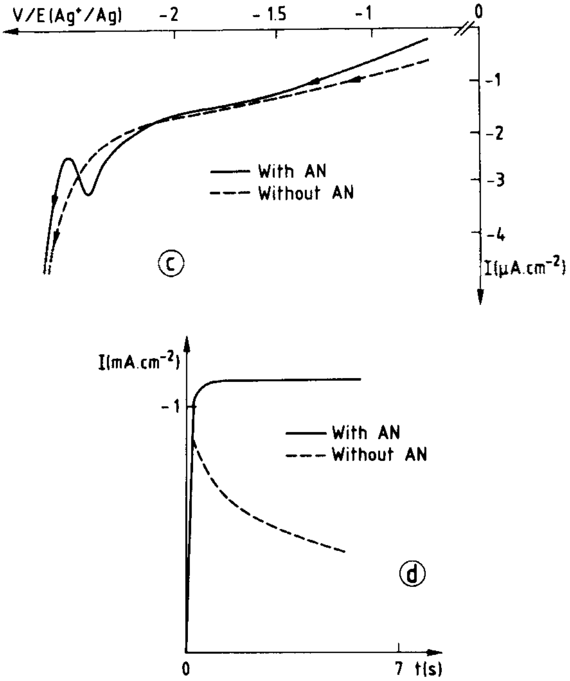

FIGURE 4 (*continued*)

The electrode is composed of Armco iron, mechanically polished (final particle size 1 μm), then coated by cathode bombardment with a film of iron of the same quality, approximately 1 μm thick. Following exposure to the air of the laboratory, the surface showed traces of atmospheric contamination detected by AES (Figure 4a). The potentio-dynamic characteristic (curve I(V) in Figure 4c) obtained during an electrolysis shows three separate areas: after a period of reduction of the oxide (I), there appears a Faradaïc activity inhibition peak, indicating modification of the surface of the electrode (II) and, finally, at (III) a region of intense Faradaïc activity which favours rapid growth of the thickness of the film. It is, however, interesting to note that the Faradaïc intensity is independent of the thickness of the film, as shown by the potentio-static characteristic in Figure 4d: the thickening film does not offer any particular resistance to passage of current. However, as shown in Figure 4b obtained by AES on the elctrode after electrolysis, the film of polyacrylonitrile covers the entire surface as the characteristic Auger lines of the iron have disappeared.

III-2 Interaction of acrylonitrile with negatively-polarized nickel surface

The nickel electrode is prepared in a similar way to that of the mechanically polished iron, followed by deposit of 1 μm of Marz nickel by cathode bombardment. Here again, cathode polarization helps to reduce surface oxide:

$$NiO + 2e^- \rightarrow Ni + O^{--}$$

However, unlike iron, nickel has a stable stoichiometric oxide (formation enthalpy $\Delta G = -101.2\,\text{kcal} \cdot M^{-1}$). The reduction kinetics of the oxide layer are, in this case, influenced by its thickness and the presence of stoichiometric faults which alter its stability: we then obtain results fairly close to those obtained with iron, which is

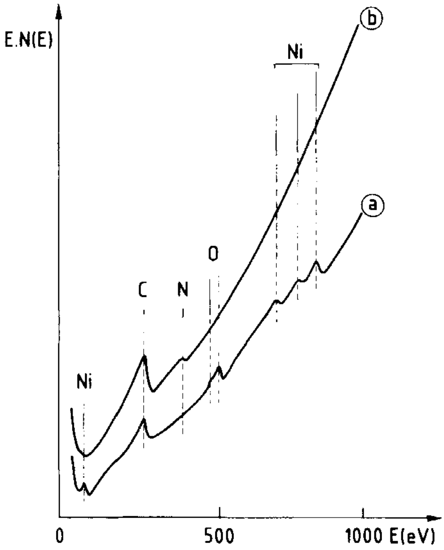

FIGURE 5 AN/nickel interaction (cathode area). a—Initial chemical composition of the surface (AES). b—Chemical composition of the surface after electrolysis (AES). c—Curve I(V) in the presence of AN (0.5 M). d—Curve I(t) in the presence of AN (0.5 M) for V = −2.8 V.

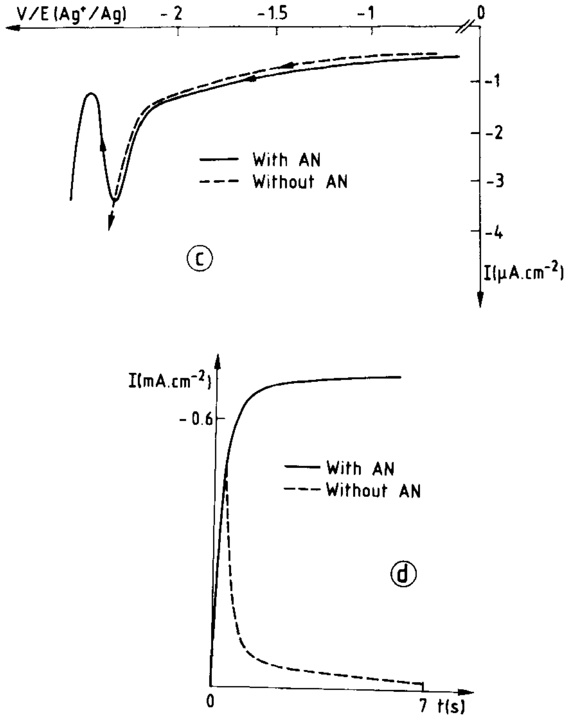

FIGURE 5 (*continued*)

explained to the extent to which electronic properties of these two metals are fairly similar.[14] In spite of surface contamination due to exposure to the air (Figure 5a), the potentio-dynamic (Figure 5c) and potentio-static (Figure 5d) characteristics are similar to those in Figure 4; similarly, the film of PAN obtained after electrolysis is total (Figure 5b). Following ion abrasion of the film (disappearance of the Auger line from the nitrogen and reappearance of Auger lines of the nickel), we note that the oxide initially present on the surface of the nickel has been completely eliminated: chemisorption of AN has occurred on the sites released by reduction of NiO.

However, if we compare the results achieved by MDS (surface electronic structure) from the three samples (Figure 6):

- one exposed to electrolysis without acrylonitrile (Figure 6a);

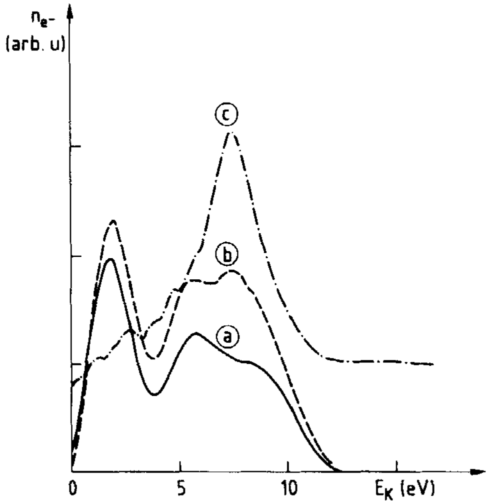

FIGURE 6 Modification by electrolysis of the surface of nickel with respect to thickness of the oxide (MDS spectrums). a—Crude nickel surface. b—Nickel surface (highly oxidized) after electrolysis. c—Nickel surface (slightly oxidized) after electrolysis.

- another exposed to electrolysis with acrylonitrile but initially very oxidized (Figure 6b);
- the third, exposed to the same electrolysis as the second, but initially only lightly oxidized (Figure 6c),

we note that sample no. 2 has hardly been modified by the presence of acrylonitrile in the electrolytic cell, whereas sample no. 3 shows an intense electronic emission band characteristic of the acrylonitrile CN group. In the case of nickel, therefore, there is a direct correlation between the possibility of reducing surface oxide and the possibility of obtaining an even, total and structurally well-defined film of PAN.

III-3 Interaction of acrylonitrile with negatively-polarized stainless steel

The stability of stainless steel A316L with respect to corrosion and oxidation is due to the surface segregation of one of its components (chrome) whose stoichiometric oxide (Cr_2O_3) is particularly stable (formation enthalpy $\Delta G = -168.8\,\text{kcal}\cdot\text{M}^{-1}$). Let us therefore consider two samples:

- STAINLESS STEEL 1, mechanically polished,
- STAINLESS STEEL 2, mechanically polished, then subjected to ion abrasion (Ar^+, $Ep = 3\,\text{keV}$, $Ip = 1\,\mu A$), designed to destroy its surface layer of natural oxide.

Both samples are subjected to the same type of measurements as the previous samples. The spectra shown in Figures 7a and b are Auger spectra obtained from STAINLESS STEEL 1 before and after electrolysis: oxygen is still present after electrolysis (reduction

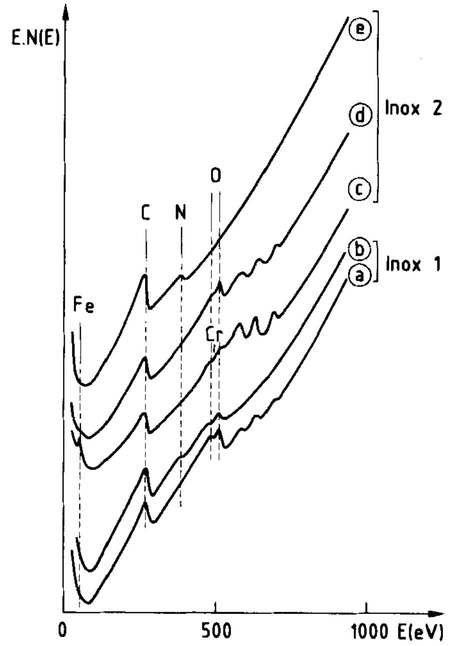

FIGURE 7 AN/Stainless steel interaction (cathode area). a—Initial chemical composition of the surface (as polished). b—Chemical composition of the surface of the sample after electrolysis. c—Initial chemical composition of the surface after ion abrasion. d—Chemical composition of the surface of the same sample after exposure to air (2 minutes). e—Chemical composition of the surface of the same sample after electrolysis. f—Curve I(V) in the presence of AN (0.5 M) of the 1st sample. g—Curve I(V) in the presence of AN (0.5 M) of the 2nd sample.

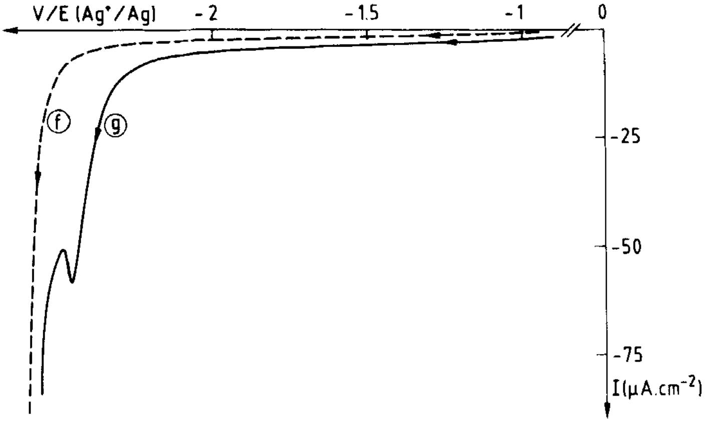

FIGURE 7 (*continued*)

has been very incomplete); however, the Auger line of the nitrogen indicates the presence of PAN, whereas the disappearance of Auger lines from the iron indicates that it is the areas of high iron concentration on the surface of the sample, which have above all been coated with PAN.

Let us now examine the potentio-dynamic characteristic (Figure 7f). The Faradaïc activity inhibition peak observed in the case of iron does not appear here, which confirms the results obtained by AES: the surface of the electrode is not completely modified by the deposit of a film of PAN during electrolysis.

However, the results obtained with STAINLESS STEEL 2 are quite positive, in that they show great similarity to those obtained with iron. Following ion abrasion, the surface of the sample contains only iron, chromium and carbon (Figure 7c). Brief exposure to air (corresponding to transfer of the sample from the ion abrasion apparatus to the electrolytic cell) causes the formation of a fine layer of oxide (Figure 7d) which can easily be reduced. An even and total film of PAN can then be obtained (Figure 7e), as is confirmed by the potentio-dynamic characteristic (Figure 7g): the Faradaïc activity inhibition peak appears, indicating complete modification of the surface of electrode.

Thus, as in the case of nickel, the presence of stoichiometric oxide with a strong formation enthalpy (therefore difficult to reduce) constitutes a block to the adhesion process.

III-4 Interaction of acrylonitrile with the surface of a negatively-polarized aluminium electrode

The situation is worsened in the case of aluminium, which has an oxide whose formation enthalpy is very high ($\Delta G = -258.2\,\text{kcal} \cdot \text{M}^{-1}$). An initial mechanically-polished sample AL1 shows a highly oxidized surface, contaminated by carbon (Figure 8a) which, following electrolysis, appears only thinly covered with PAN: the Auger lines of the aluminum and the oxygen are still clearly visible (Figure 8b). The potentio-dynamic characteristic (Figure 8f) shows no inhibition peak. Moreover, the Faradaïc

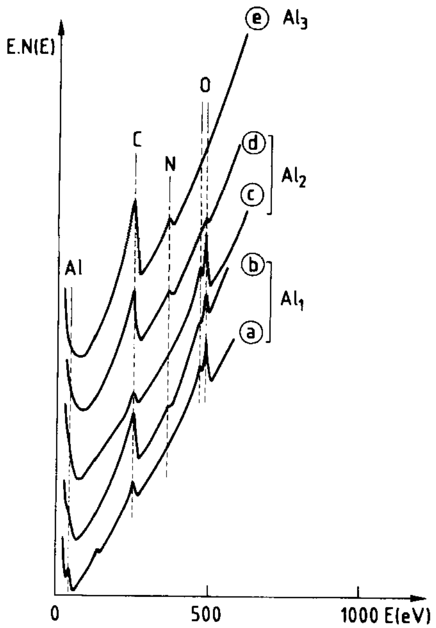

FIGURE 8 (AN/Aluminium interaction (cathode area). a—Initial chemical composition of the surface (as polished). b—Chemical composition of the surface of the same sample after electrolysis. c—Initial chemical composition of the surface after ion abrasion and exposure to air (2 minutes). d—Chemical composition of the surface of the same sample after electrolysis (0.5 M). e—Chemical composition of the surface of an identical sample after electrolysis (2.5 M). f—Curve I(V) in the presence of AN (0.5 M) of the 1st sample. g—Curve I(V) in the presence of AN (0.5 M) of the 2nd sample. h—Curve I(V) in the presence of AN (2.5 M) of the 3rd sample.

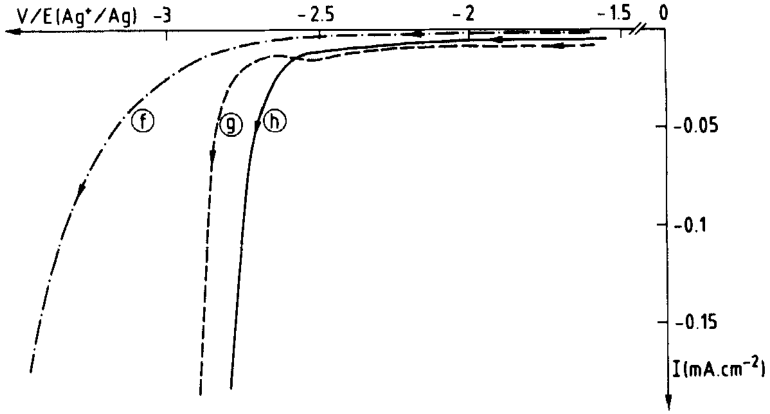

FIGURE 8 (*continued*)

activity of this electrode is very weak, indicating that its electrical resistance is high.

A second mechanically polished sample AL2 was subjected to ion abrasion until it was perfectly clean (*in situ* test by AES). The short exposure to air necessary for the transfer of the sample from the ion abrasion apparatus to the electrolytic cell caused the formation of a native oxide contaminated by carbon (Figure 8c). However, after electrolysis, the surface of this sample is almost completely covered with PAN (low intensity of aluminium and oxygen Auger lines (Figure 8d). Moreover, the potentio-dynamic characteristic (Figure 8g) shows, on the one hand, very high Faradaïc activity of the electrode (low resistance); in addition, there is a plateau in the area of the inhibition peak, if any.

We repeated this second experiment but under different conditions (concentration of AN in the solution 5 times higher than in all other experiments). This time, the surface of electrode AL3 was completely covered with PAN (Figure 8e) and a clear inhibition peak appeared on the potentio-dynamic characteristic (Figure 8h).

These results extend and complete those obtained with other metals. The thick and even oxide layer present on AL1 cannot be reduced: there is no film. Much thinner, the oxide layer on AL2 (native oxide) can be attacked locally by the reduction process, thus creating conditions favourable to the formation of PAN islands. In the case of AL3, the increase in the concentration of AN assists the polymerization reaction: the apparently complete coverage of the surface of the electrode results not from abounding of the PAN chains (as in the case of iron and nickel) but from the formation of adjacent organic aggregates grafted locally onto the substrate.

III-5 Interpretation of results

It is worthwhile interpreting all the results obtained.

As shown in Ref. 14, when uncoated, all the metals used show a high density of occupied electronic states at around their Fermi level which is obviously favourable to an acid-base type reaction, in which the metal plays the part of electron donor. However, their oxides, which are characterized by localization of electrons on the $2p$ levels of the oxygen, show only a very low density of occupied electronic states at the Fermi level (this is the case of iron and certain crystalline faces of nickel); this electronic localization may also lead to the establishment of a forbidden band ΔV, whose size increases with the formation enthalpy of the oxide (as an example ΔV O/Ni/111/ $\simeq 3$ eV; ΔV $Al_2O_3 \simeq 9.5$ eV). The wider the forbidden band and the less reducible the oxide, the less likely is the acid-base reaction.

It is now possible to suggest an energy diagram for the metal, oxide and electrolytic solution system (Figure 9).

Figure 9a shows, as an ordinate, the bonding energies of the active electronic levels with the non-polarized system. The electrons in the oxide layer are too bonded to be involved in an acid-base reaction with the LUMO (lowest unoccupied molecular orbital) of the acrylonitrile or with the unoccupied orbital of the ion $N(C_2H_5)_4^+$ of the supporting electrolyte: the system is stable. It is no longer stable when the electrode is polarized (Figure 9b):

- reduction of the oxide causes electronic re-occupation of the surface below the Fermi level;
- polarization of the vinyl bond of the AN in the double layer causes degeneracy of the LUMO and HOMO (highest occupied molecular orbital) and their shift;
- the unoccupied orbital of $N(C_2H_5)_4^+$ is lowered with respect to the vacuum level of the electode.

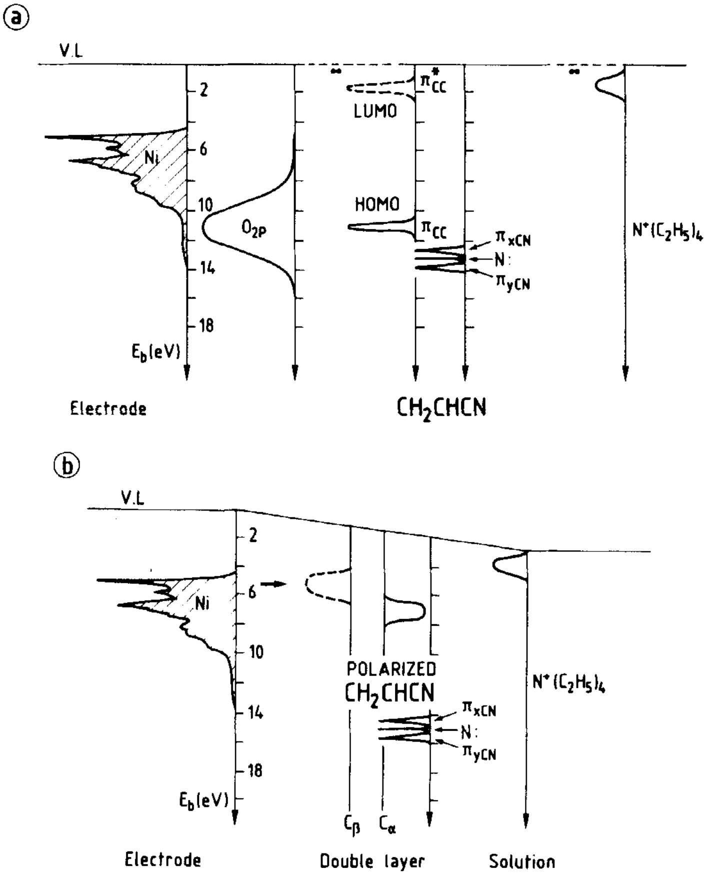

FIGURE 9 Energy diagram of the An–Ni system in the cathode area. a—System without interaction. The bonding energies are given with respect to the vacuum level. b—Polarized system. Establishment of the chemical bond (acid-base reaction) is shown by the small thin arrow; the Faradaïc transfer from the electrode to the $N^+(C_2H_5)_4$ ion is produced by tunnelling throughout the double layer.

Under these conditions, the acid-base reaction between metal and AN can occur, the resulting hybridation leading to a chemisorption bond. At the same time, the orbital resulting from the degeneracy of HOMO (and which is an electronic pair carrier) becomes, in turn, suitable for involvement in an acid-base reaction if a new AN molecule is available in its immediate vicinity (see Figure 3c and d).

This model has been established for a particularly simple case but its generalization can be very interesting for the technical applications: a preliminary study (experience, theory or bibliography) of the partners (mineral material and organic molecule) allows one to predict their ability for adhesion. It can also suggest and eventually help to determine what surface treatments can improve this ability, and how to modify the joining methods in order to benefit from the main properties of the organic molecule.

CONCLUSION

The results described in this article have been obtained by means of laboratory work designed to reproduce experimentally, and in a controlled and reproducible fashion, the various actual situations encountered during the production of organic coatings on mineral substrates and during the making of adhesive joints. They have enabled us to demonstrate the elementary mechanisms which govern organic molecule–mineral substrate bonds and the conditions necessary for optimization of the adhesion and reticulation processes.

Apart from the influence of the electronic properties of the monomer molecule, we have demonstrated the influence of the electronic states of the mineral surface and of the local electrical fields on the chemical reactions involved, and also on the properties of the resulting product.

The correlation between the elementary properties and the structure of the organic mineral system at atomic scale has been established and generalization methods proposed.[15–20]

Finally, results, as yet incomplete, show that the same approach can be adopted for a systematic study of the behaviour laws of such a system when subjected to a variety of stresses, and will be soon published.

References

1. J. C. Pivin, J. Perreau, C. Reynaud, J. Takadoum. J. of non-cryst. solids 86 (1986) 161.
2. G. Lecayon, C. Boiziau, *Proceedings of Adhecom,* 15–18th April 1986—Bordeaux (France), p. 259.

3. J. Perreau, C. Reynaud, G. Lecayon, Y. Ellinger, *J. Phys. B* **19,** 1497 (1986).
4. C. Boiziau, G. Lecayon, *Scanning Electron. Microsc.* **I,** 109 (1986).
5. C. Boiziau, *Scanning Electron. Microsc.* **III,** 949 (1982).
6. C. Reynaud-Matrat, Thesis, Université Paris-Sud-Orsay (France), July 1, 1986.
7. J. E. Demuth, D. E. Eastman, *Phys. Rev.* **B 13,** 1523 (1976).
8. K. Kishi, S. Ikeda, *Surf. Sci.* **107,** 405 (1981).
9. J. Perreau, *et al.*, *Surf. Sci.* **162,** 776 (1985).
10. C. Reynaud, C. Juret, C. Boiziau, *Surf. Sci* **126,** 733 (1983).
11. G. Lecayon, *et al.*, *Chem. Phys. Letts.* **91,** 506 (1982).
12. G. Tourillon, P. C. Lacaze, J. E. Dubois, *J. Electroanal. Chem.* **100,** 247 (1979).
13. J. C. Pivin, C. Roques-Carmes, G. Slodzian, *Int. J. of Mass Spectrom. and Ion Phys.* **31,** 293 (1979).
14. Landolt-Bornstein, *Numerical data and functional relationships in science and technology.* **III. 13,** C (Springer-Verlag, Berlin, 1984).
15. C. Boiziau, *et al.*, *Scanning Electron. Micros.* **IV,** 1187 (1984).
16. C. Boiziau, *et al.*, *ibid.* **IV,** 1385 (1985).
17. S. Leroy, *et al.*, *J. Molecular Structure* **128,** 269 (1985).
18. C. Reynaud, *et al.*, **11,** 159 (1985).
19. S. Leroy, *et al.*, *Materials Letts.* **3,** 239 (1985).
20. G. Lecayon, *et al.*, *Scanning Electron. Microsc.* (1986) (in press).