

Cathodic delamination of methyl methacrylate-based dry film polymers on copper

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Studies of the bond degradation between a laminated organic coating and a copper substrate have been carried out using electrochemical techniques. The failure of the bond is attributed to a cathodic reaction which occurs under the coating. The rates of delamination are shown to be affected by delay time after exposure, temperature, applied potential, composition of the electrolyte, and surface abrasion prior to application of the coating.

Introduction

If a metal is discontinuously covered with an organic coating, or if a coated metal is damaged, the resulting system is vulnerable to deterioration when subsequently exposed to

an aqueous corrosive environment. The coated metal behaves more readily as a cathode, i.e., an electron-accepting site, and the exposed metal serves as the complementary anode, an electron-generating site. The cathodic reaction may produce products beneath the coating which adversely affect the bond between the metal and the organic coating and thus may cause delamination [1-3]. This phenomenon has been termed *cathodic delamination* because the same effects may be obtained if the metal is polarized cathodically by means of an external potential. Cathodic delamination is an especially annoying problem with coated pipelines and painted ships that are protected from corrosion by means of an external potential.

Corrosion of ferrous metals and its control with organic coatings have been extensively studied [4]. Very little has been reported for copper. In the present study copper was selected because of its wide use as a substrate in the fabrication of printed circuit boards. It was suspected that cathodic delamination processes were operative during the processing of circuit boards coated with photoactive polymers.

The dominant cathodic reaction in an acidic environment, where oxygen has been excluded, is



27

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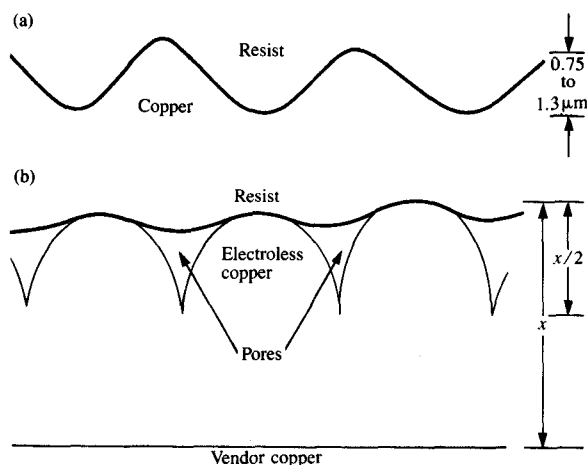


Figure 1

Schematic representations of interface profiles obtained using copper samples having different surface roughnesses. (a) Profile of a scrubbed copper surface laminated with resist; exhibits no crevices or separation at the interface. (b) Profile of an unscrubbed electroless copper surface laminated with resist; contains deep pores which are detrimental to adhesion. (From Ref. [15]. Published with permission of *Electronic Packaging and Production*.)

In most corrosion processes, oxygen is present and several cathodic reactions may be operable:



All of these reactions have in common the fact that the local pH is increased either by the consumption of H^+ ions or the generation of OH^- ions.

Other cathodic reactions may also play a role in certain circumstances. These include the change in valence state of an ion in solution, $\text{Cu}^{++} + \text{e}^- = \text{Cu}^+$; for example, the interaction of organic compounds or enzymes with hydrogen adsorbed on the metal surface, or reactions involving living organisms such as bacteria.

The most common cathodic reaction in corrosion in non-acid media is represented by Eq. (4). This is also the reaction most likely to occur beneath an organic coating permeable by oxygen [5]. The pH level at the delaminating front has been shown to be as great as 14, as measured by pH-sensitive electrodes inserted through the metal substrate from the back side [6].

The hydroxyl ions generated by the cathodic reaction appear to be the species that cause breakdown of the coating/substrate bond. The mechanism by which this breakdown occurs is unknown. In some cases, it appears that the high value of pH leads to dissolution of the thin metal

oxide at the boundary between the coating and the metal [7, 8]. In others, the polymer near the interface is attacked by a reaction similar to saponification [9]. It has also been proposed that surface energy considerations lead to a preference for a metal/water interface over a metal/polymer interface [10].

The generation of hydroxyl ions at the coating/metal interface requires the presence at the interface of oxygen, water, electrons, and cations [e.g., Eq. (4)]. The cations provide charge balance for the hydroxyl ions generated by the reaction. The oxidized metal surface at the interface also must be catalytically active for the oxygen reduction reaction to occur. The important question is "How do the species reach the interfacial region?" It is apparent that the electrons are provided by the metal. The other species, however, can reach the delaminating front either through the polymer coating or through the thin liquid layer in the interfacial region. Many literature references to the rates of diffusion of species through polymers are provided in the paper by Marsh et al. [11]. Research at Lehigh University has also shown that the diffusion of oxygen, water, and cations through organic coatings is sufficient to account for the delamination rates observed experimentally [12]. The prevailing evidence is that the reactant species are provided to the interface by diffusion through the coating.

Diffusion of water through most polymers exposed to an aqueous solution is initially rapid, but the diffusion of oxygen and cations under similar circumstances is relatively slow. Thus, one might expect a delay before cathodic delamination begins. Delay times are not observed with very thin coatings but are commonly observed with coatings more than $25 \mu\text{m}$ thick. It has been shown theoretically that the delay time before delamination proceeds at a uniform rate can be described by the equation $t = (1/6 D)b^2$, where t is the delay time, D is the diffusion coefficient of the rate-limiting species, and b is the coating thickness [13].

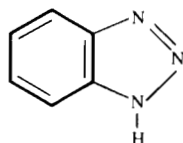
The diffusion coefficients of alkali metal ions such as Li^+ , Na^+ , K^+ , and Cs^+ in aqueous solution are different because of the waters of hydration associated with the ions. Lithium ions diffuse at a relatively slow rate and cesium ions diffuse at a relatively rapid rate. It might thus be expected that diffusion of the alkali metal cations through polymer films would differ when exposed to a potential gradient. We might also expect that cathodic delamination rates will differ if the ionic diffusion is rate-determining. Indeed, large differences in cathodic delamination rates are observed when the coated metal is exposed to equimolar solutions of LiCl , NaCl , KCl , and CsCl [14].

Physical barriers can also affect the rate of solution transport to reactive sites. For example, if the surface onto which the polymer is applied is rough and has crevices, the rate of solution transport may be faster than if the polymer is attached to a smooth surface. Hamilton [15] has studied the effect of surface morphology on the adhesion of

laminated dry film photoresist to copper surfaces. **Figure 1** presents schematic representations of two interface profiles obtained using copper samples having different surface roughnesses. Hamilton found that a surface scrubbed with pumice yields the best photoresist performance in printed circuit fabrication. Fullwood [16] has also shown the effect of the roughness of copper surfaces on the fine-line circuit reproduction using dry film photoresists. He concludes that pumice scrubbing yields the best results.

The catalytic activity of metals for the cathodic reaction can be controlled under some circumstances. For example, the introduction of small amounts of cobalt into the oxide film on the surface of zinc decreases the activity of the surface for the oxygen reduction reaction [17].

The surface activity of copper—the metal of interest for use in circuit boards—is often controlled by an inhibitor, benzotriazole (BTA), which has the following structure:



Cuprous oxide is normally a protective surface for copper, but it is readily attacked by Cl^- , SH^- , OH^- , NH_4^+ , and to a lesser extent CO_2 . BTA can affect the properties of cuprous oxide films by stabilizing the film. The copper oxide-BTA layer interferes with the anodic and/or cathodic reactions of the corrosion process. Copper oxide-BTA films form in an acidic or neutral solution, and the type of film formed is dependent on the pH of the BTA solution. At pH values of 3.5 to 4, thick, shag-carpet-like films are formed, while at pH > 4, thin, compact, highly protective films are formed [18]. Roberts [19] reports that the BTA film forms primarily on Cu_2O , not CuO . However, upon aging, the final layer is a mixture of Cu_2O -BTA and CuO -BTA. The Pourbaix diagram shown in **Figure 2** may be used to predict the best conditions for forming Cu_2O . Copper in NaHCO_3 solution (pH = 8.1) at 25°C yields a potential of +0.12 V vs the normal hydrogen electrode (NHE). The Pourbaix diagram shows that the stable form of copper under these conditions is Cu_2O . In fact, we have found that an alkaline pretreatment of copper in an NaHCO_3 solution prior to BTA application yields a significantly more corrosion-resistant Cu_2O -BTA layer than if no pretreatment is used, as measured using potentiodynamic scans in 0.3% NaCl to calculate corrosion rates.

A joint project was initiated between IBM and Lehigh University to study cathodic delamination of dry film polymers on copper in highly alkaline solutions. Some of the experimental results are reported here.

Experimental procedures

Copper was coated with a dry film methyl methacrylate polymer. Prior to lamination of the polymer, either the

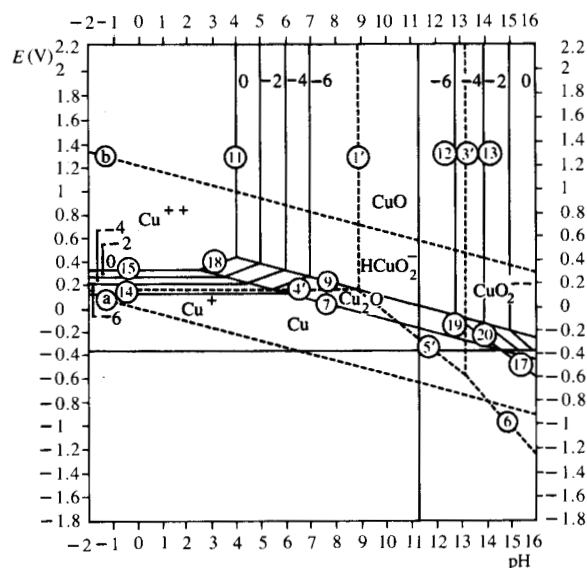


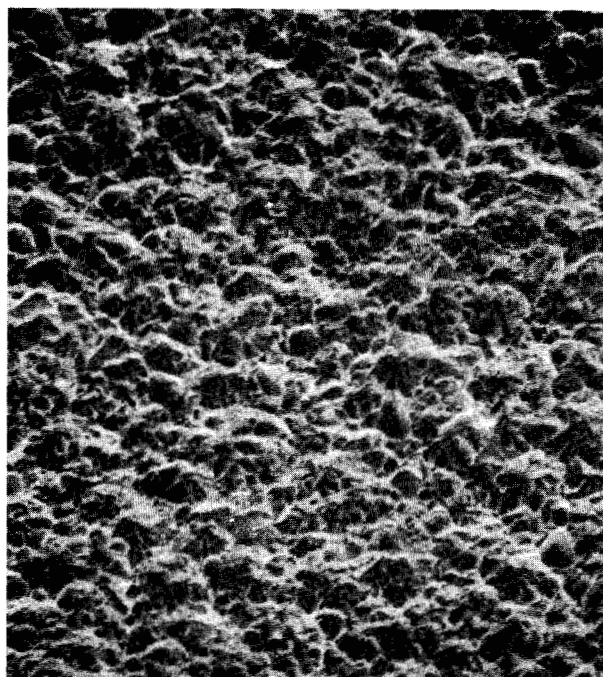
Figure 2

Potential-pH equilibrium diagram for the copper/water system at 25°C, considering the solids Cu , Cu_2O , and CuO . $\text{Cu}(\text{OH})_2$ is not considered.

copper was in an untreated condition or the surface was abraded using a pumice slurry. The slurry was made up using 25% by volume of 4F pumice from Hess Pumice Products and deionized water. The average pumice particle size was 5.8 to 15.3 μm . The copper surfaces were abraded in a pumice scrub machine. Four techniques were used to measure the surface roughness after various numbers of passes through the pumice scrub machine: scanning electron microscopy (SEM), Tally Surf, reflectance, and cross section. **Figures 3, 4, 5, and 6** show the results of these measurements.

More than 24 measurements were made with all four measurement techniques on samples prepared with various amounts of pumice scrubbing. In all cases, the surface became smoother with increased pumice scrubbing. **Figure 6** best shows the effect pumice scrubbing has on smoothing the copper surface. Photomicrographs of the photopolymer surface which was peeled from the copper surfaces of **Fig. 6** indicated that the photopolymer was in contact with the copper mainly at the peaks, **Fig. 6(a)**, but made more intimate contact with the copper in **Fig. 6(b)**. In some instances, the copper surface was inhibited by dipping in a solution of BTA at pH 5.5.

The effect of an applied cathodic potential was determined by making a 1-mm-diameter opening in the polymer to the underlying copper specimen with the sharp tip of a pointed tool. The specimen was immersed in the electrolyte and its



(a)



(b)

Figure 3

Scanning electron micrographs of a copper surface, magnification $\sim 500\times$, angle 30° : (a) unscrubbed surface; (b) after 16 scrubs with pumice.

potential was held constant by means of a simple integrated circuit potentiostat constructed according to the

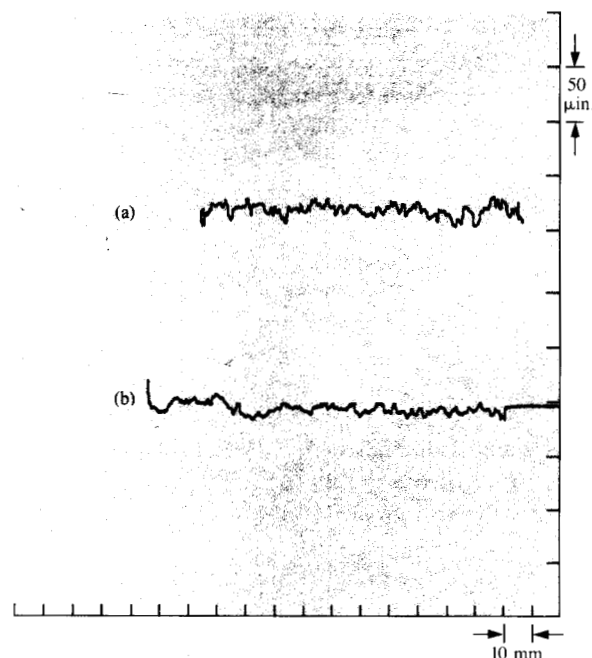


Figure 4

Comparative surface roughness measurements of a copper specimen: (a) unscrubbed surface (center-line average of trace heights $27\text{ }\mu\text{in.}$); (b) after 16 scrubs with pumice (center-line average of trace heights $21\text{ }\mu\text{in.}$). Accuracy is ± 2 percent.

specifications of Baboian, McBride, Langlais, and Haynes [20]. A vertically positioned remote junction filled with 5% Na_2SO_4 and equipped with a Vycor glass tip or a porous ceramic tip allowed the potential to be monitored without exposing the reference electrode to the harsh alkaline environment often used in the cell. The Vycor tip had a short lifetime when exposed to hot alkaline solution, so the ceramic tip was used with the hot alkaline solutions.

The copper samples were generally used as $50 \times 50\text{-mm}$ squares whose edges and electrical contact area were shielded from the electrolyte by a thick layer of silicone sealant in the experiments carried out at 73°C . The electrical contact to the copper was made by drilling a small hole in the corner of the sample, inserting the stripped end of an insulated wire into the hole, filling the hole with conductive paint, and allowing the conductive paint to dry thoroughly before coating with a silicone sealant. The sealed sample and reference and auxiliary electrodes were immersed in a beaker containing the test electrolyte. A thermostat was inserted in the beaker, which was placed in a water bath and sealed with a stopper to prevent evaporation. Room temperature experiments were conducted on copper sections which were restricted in area by clamping a glass cylinder to the surface with the aid of a rubber "O" ring and a ball and socket clamp, as shown in Figure 7.

The delaminated area was determined by pressing adhesive tape to the surface repeatedly until all the delaminated material was removed. The delaminated area was circular in shape, as shown in the example in **Figure 8**, and the boundary between the unaffected area and the delaminated area was very sharp. In many cases, the amount of delamination could be judged before the stripping of the adhesive tape by a slight change in the optical properties of

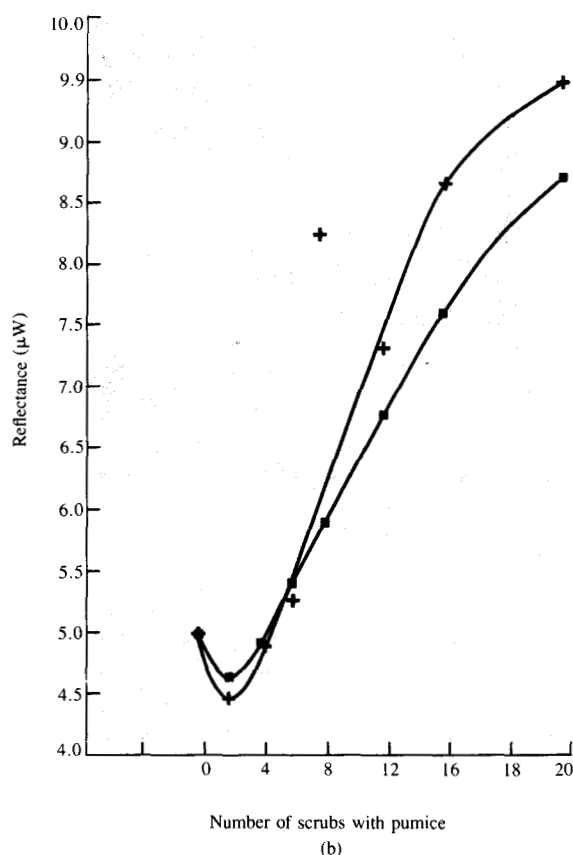
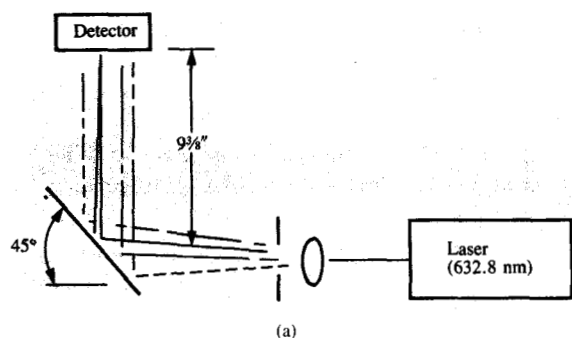


Figure 5

Effect on reflectance of number of scrubs with pumice: (a) system for measuring reflectance; (b) reflectance data.

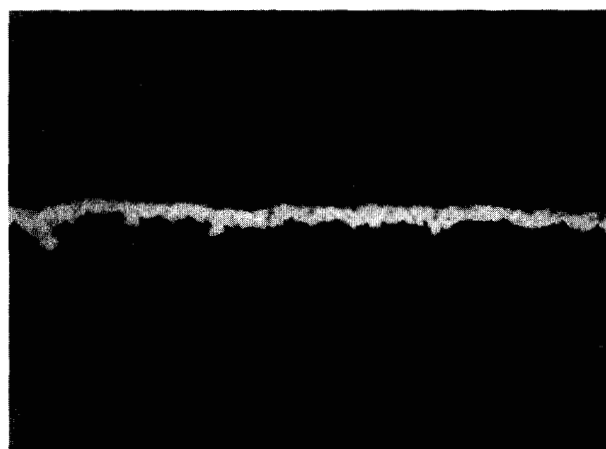
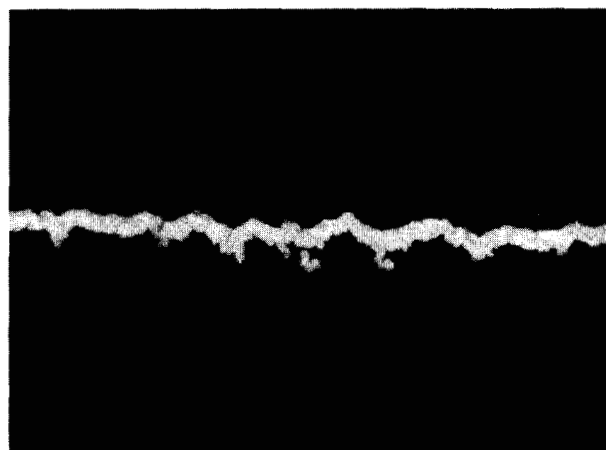


Figure 6

Cross section of a copper surface, magnification $\sim 650\times$: (a) unscrubbed; (b) after 16 scrubs with pumice.

the delaminated region. However, the adhesive tape test was always used in quantitative measurements of the degree of delamination.

Electrolytes used in the delamination experiments were chosen to facilitate an understanding of the mechanisms involved in the separation of the polymer from the copper substrate in solution. Test solution compositions included NaOH solutions at various pH values, as well as KOH, LiOH, and Ba(OH)₂ solutions. The role of the cation in the cathodic delamination process was studied by comparing 12.5 pH solutions of LiOH, NaOH, and KOH and 11.7 pH solutions of KOH and Ba(OH)₂. Potentials cited are with respect to a saturated calomel reference electrode.

Results

Data from a typical set of experiments on cathodic delamination are shown in **Figure 9**. Each datum point

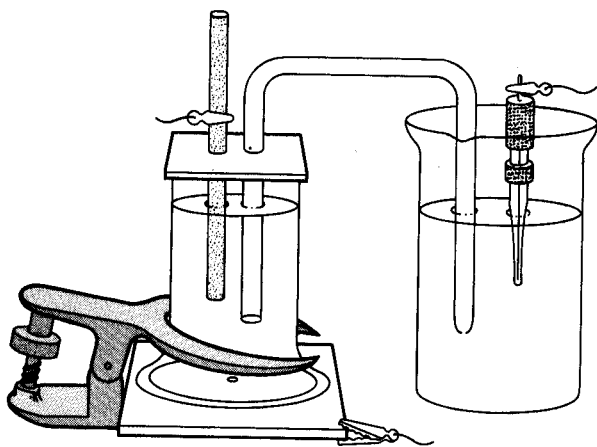


Figure 7

Apparatus used in the cathodic delamination studies.

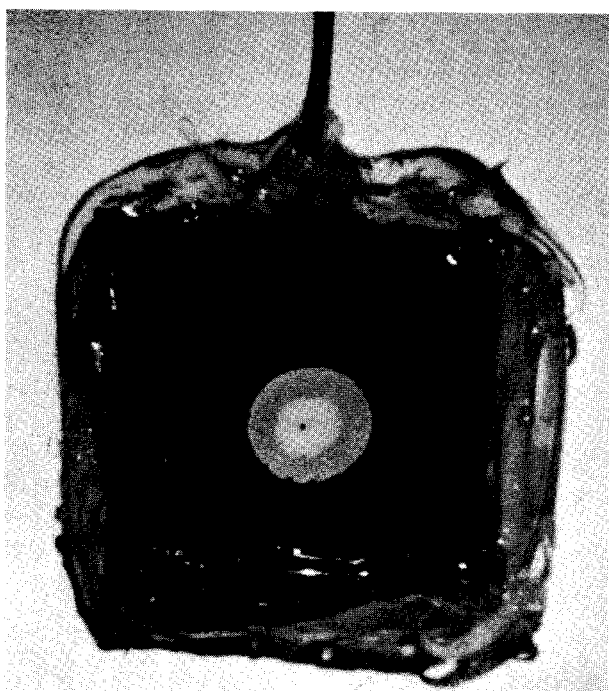


Figure 8

Example of delaminated (circular) area in a test coupon.

represents a separate experiment. It can readily be seen that the delaminated area increases linearly with time during its early stages. The slope of this curve is the delamination rate in cm^2/h . This linear behavior was noted in all experiments in which multiple points were obtained at different times.

The effect of the applied potential was examined by measuring the delaminated area after a fixed exposure time. Data obtained for a solution of NaOH are given in **Figure 10**. Similar sets of experiments were carried out on samples having surfaces treated in various ways. In all cases the shape of the curve was similar to that shown in Fig. 10.

It is generally recognized, as mentioned previously, that the cathodic delamination occurs because the oxygen reduction reaction, $\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$, occurs under the coating adjacent to a defect [8]. In order to determine whether this reaction is the determining one in the delamination of the polymer from copper, experiments were carried out in a 12.5 pH KOH solution with an applied potential of -0.8 V under conditions where oxygen was removed by bubbling pure argon through the solution. No significant delamination occurred after the specimen had been polarized for five days. This experiment, along with others carried out in various electrolytes in the absence of oxygen, gave convincing proof that oxygen is an essential component in the delamination process.

Figure 11 shows that the rate of delamination is also a function of temperature.

It was shown earlier [14] that the rate of the delamination process is strongly a function of the cation present in the electrolyte. For example, the delamination rates of polybutadiene, epoxy, and alkyd coatings on steel immersed in solutions of alkali chlorides decrease in the order of CsCl, KCl, NaCl, and LiCl when the electrolytes are all of the same molar concentration. The effect of electrolyte was studied in the case of this polymer on copper in LiOH, NaOH, and KOH at a pH of 12.5 and $\text{Ba}(\text{OH})_2$ and KOH at a pH level of 11.7. These results are summarized in **Figure 12**, where it will be noted that the rates of delamination decrease in the order KOH, NaOH, LiOH, and $\text{Ba}(\text{OH})_2$.

Various procedures are used to protect the copper against deterioration while it is in storage before use. Two methods that were tested included samples that were abraded with pumice only and those that were treated in a solution of BTA. The results of two sets of delamination experiments with the pumiced and nonpumiced samples are shown in **Figure 13**. The upper pair was polarized at -1.2 V and the lower pair was polarized at -0.5 V . It will be noted in both cases that the abraded samples exhibited lower delamination rates than the nonabraded samples. It will also be noted that the samples polarized at -1.2 V yield curves that extrapolate to zero delamination at zero time, whereas the samples polarized at -0.5 V yield curves that extrapolate to a value of 6 to 10 hours at zero delamination. This time has been characterized previously as the "delay time," and it decreases in magnitude as the applied potential is increased.

The effect of BTA treatment and aging time at 80°C in air prior to the delamination test with applied potential is shown in **Figure 14**, where two differences may be recognized. First, the rate of delamination without aging at

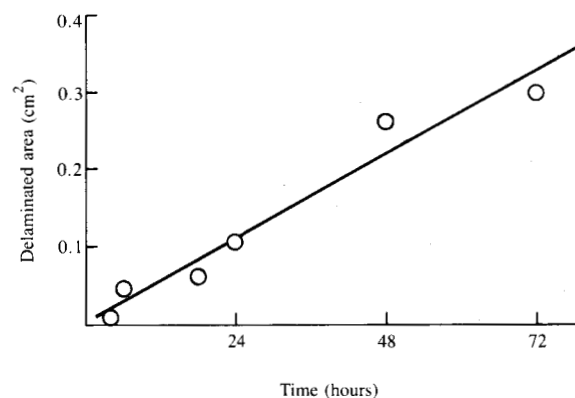


Figure 9

Delaminated area as a function of time upon immersion in NaOH (pH = 12.5) at an applied potential of -0.8 V.

80°C is greater in the case of the two samples that were not treated with BTA and significantly lower for the two samples that were treated with BTA. Furthermore, it will be noted that aging of the samples at 80°C increased the rate of delamination for samples that received no BTA treatment and decreased the rate of delamination for samples that were treated with BTA. Aging in either air or argon at 80°C for times longer than approximately two hours led to defects in the coating which showed up as blisters after several hours' exposure to KOH (pH = 12.5) at 73°C under an applied cathodic potential.

Discussion

The utility of this study can readily be seen when one considers pattern copper plating. Such plating is used extensively in the printed circuit industry for electroforming circuits onto an organic laminate structure, such as epoxy-glass. The process involves applying an organic masking material, such as a dry film photoresist, to a thin copper layer previously laminated to the epoxy-glass. The photoresist is exposed with a light source through an appropriate mask. It is then developed to yield channels in the photoresist for subsequent pattern plating. The most common dry film photoresists are methyl methacrylate-based polymers.

Pattern copper plating (electroforming through a mask) is usually carried out electrolytically in a copper/acid ($\text{CuSO}_4/\text{H}_2\text{SO}_4$) solution or a copper pyrophosphate/ammonium hydroxide ($\text{Cu}_2\text{P}_2\text{O}_7/\text{NH}_4\text{OH}$) solution. Some printed circuit manufacturers use electroless copper pattern plating based on $\text{CuSO}_4/\text{HCHO}/\text{NaOH}$ solutions.

In the case of copper pyrophosphate plating the pH level is generally ~ 8.5 , whereas in electroless copper plating the pH level is in the range of 11 to 12.

The results of this study show that methyl methacrylate-based polymers do cathodically delaminate from a copper

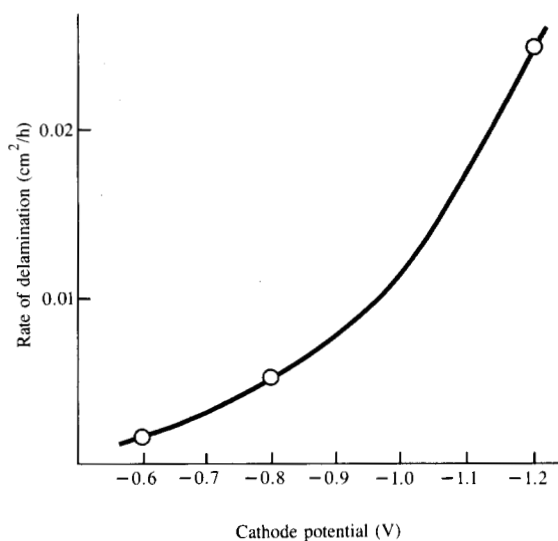


Figure 10

Rate of delamination as a function of cathode potential upon immersion in NaOH (pH = 12.5) at room temperature.

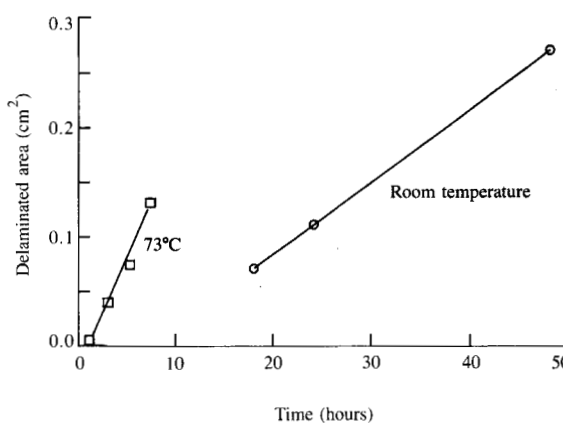


Figure 11

Delaminated area as a function of immersion time in NaOH (pH = 12.5) at two different temperatures and an applied potential of -0.8 V.

surface, with the rate of cathodic delamination being a function of time, pH, applied potential, temperature, surface morphology, and corrosion-inhibiting condition of the copper surface.

In the case of electrolytic copper plating, in a copper pyrophosphate bath, pH ~ 8.5 , the circuit board is the cathode. In an electroless copper plating bath the circuit channels consist of alternating anodic and cathodic sites, with a resultant mixed potential. In order to achieve good

circuit line definition it is important to suppress cathodic delamination of the photoresist. As we have seen above, cathodic delamination can be suppressed by selecting the lowest pH level, plating time, potential, and temperature. Also, the nature of the cation is an important factor. Another factor which can slow the delamination is an increase in the photoresist thickness, with a consequent decrease in the diffusion rate through the photoresist. Surface morphology and corrosion inhibition of the underlying copper surface can also suppress cathodic delamination.

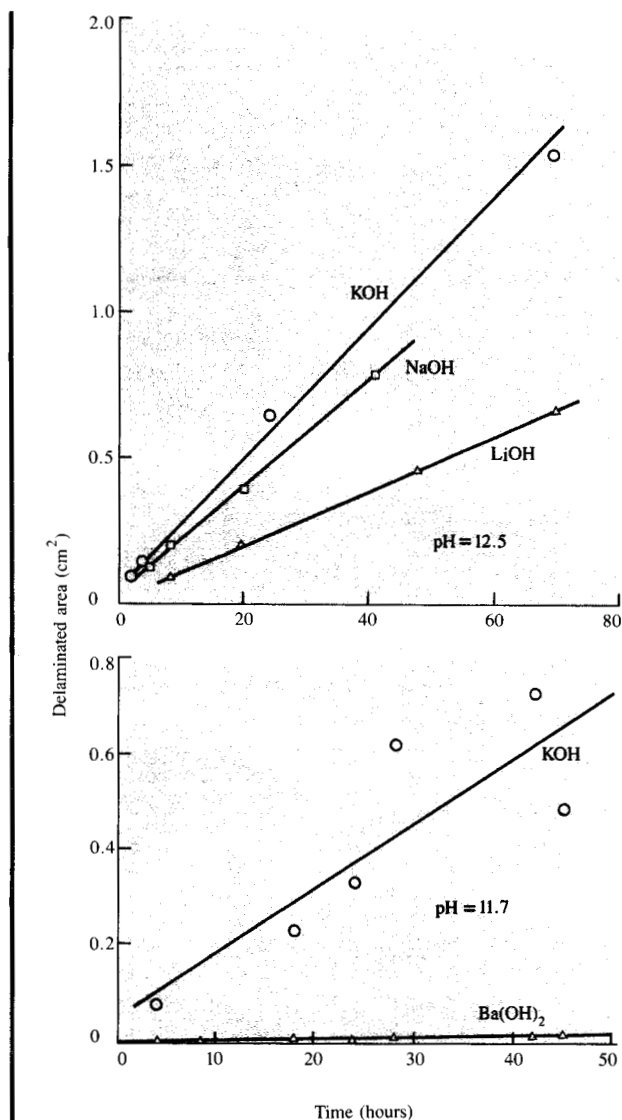


Figure 12

Delaminated area as a function of time upon immersion in different solutions. Specimens were treated with BTA and immersed at room temperature, under an applied potential of -1.2 V.

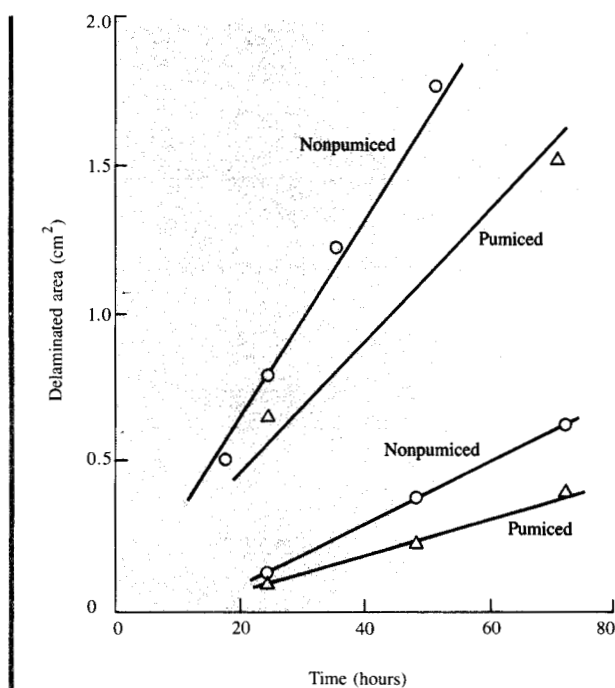
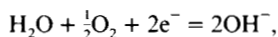


Figure 13

Delaminated area as a function of time for pumiced and non-pumiced specimens in KOH (pH = 12.5) at room temperature and an applied potential of -0.5 V (lower pair of curves) and -1.2 V (upper pair of curves). Specimens were treated with BTA.

Conclusion

This study has shown that polymethyl methacrylate coatings disbond from cathodically polarized copper. The mechanism of separation is cathodic delamination caused by hydroxyl ions generated according to the reaction



which subsequently degrades the coating/substrate interface. Evidence supporting this mechanism is the lack of delamination in the absence of dissolved oxygen.

The rate of cathodic delamination was found to be a linear function of time after the first few hours of exposure. At cathodic potentials less than -1.2 V, cathodic delamination exhibited a delay time prior to which no significant delamination occurred. This delay time was dependent upon the temperature and the applied potential and most likely corresponds to the time required for essential species to diffuse through the polymer coating to the disbonding site at the copper substrate. Cathodic delamination rates increased with increasing temperature in the range of room temperature to 75°C . Cathodic delamination rates also increased with increasingly negative applied potentials.

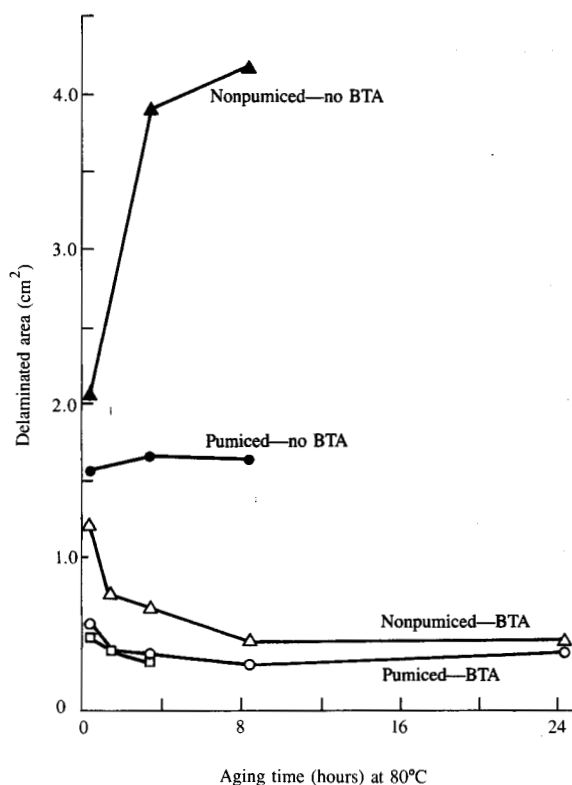


Figure 14

Delaminated area as a function of aging time at 80°C for various specimens immersed in KOH (pH = 12.5) at room temperature and an applied potential of -1.2 V, for a testing time of 16 hours.

The composition of the electrolyte had a significant influence upon the rates of delamination. For cathodic delamination, solutions containing potassium ions were more aggressive than lithium, sodium, or barium electrolytes of equivalent concentration in the order of K, Na, Li, Ba. This behavior is likely a consequence of the differences in the rates of diffusion of ions through the organic coating.

Surface morphology was also found to have a significant effect on delamination. Abrasion prior to coating application caused a reduction in the rate of cathodic delamination. The abrading smoothed the surface and decreased the depth of channels (Fig. 6), with a subsequent decrease in lateral diffusion of electrolyte to the delamination site, as visually observed through an ink test and the development of corrosion under the photopolymer from the edge of the line channels in a corroding medium.

As reported in the literature, BTA adsorbs onto the Cu_2O surface layer, forming a thin protective Cu_2O -BTA coating. This insulating coating decreases electron flow, interferes with the cathodic reaction (oxygen reduction), and prevents

OH^- formation. A decrease in the OH^- concentration at the coating/substrate interface then decreases the severity of the delamination process.

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