EFFECT OF THE SEALING PROCESS ON WETTABILITY AND WEAR PROPERTIES OF ANODIZED ALUMINUM LITHOGRAPHIC PLATES

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Abstract: Anodic coatings produced on a typical alumi-
num plate were sealed using four aqueous media. The wear
behavior and wettability of the anodized aluminum surface
sealed in sodium silicate solution differ markedly from
those sealed in the other media. These results are inter-
preted on the basis of different mechanisms of sealing.
Implications to lithographic plate manufacture are men-
tioned.

INTRODUCTION

Anodized aluminum has long been used in the litho-
graphic printing industry as a plate substrate because of
its light weight, ease of graining and surface treatment,
and economy in moderate and long term use (Salgo, 1962).
The anodizing process converts the soft aluminum metal
surface to a hard yet porous coating which is almost the
same as that of a lithostone. A sealing treatment is
generally carried out after anodization to improve the
hydrophilicity and corrosion resistance of the anodized
surface. The sealing treatment involves immersing ano-
dized plates in a boiling distilled water or in a hot
aqueous solution such as nickel acetate solution, potas-
sium dichromate solution, or sodium silicate solution.
Severn and Burring (1978) studied the water wettability of
anodized aluminum plates sealed in distilled water. They

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found that the water wettability decreased rapidly with increase in sealing reaction time until the contact angle reached a maximum value of 60° after about two minutes. Longer reaction times gradually increased the wettability; the contact angle became constant at approximately 10°. Similar behavior was observed by the present authors and their colleagues (Hughes et al, 1983) for coatings sealed not only in distilled water, but also when sealed in nickel acetate and potassium dichromate solutions. They also observed a significantly different behavior in the case of the anodic coating sealed in sodium silicate solution. No reduced water wettability was found. Wear studies of the coatings sealed in these media showed that the silicate-treated coatings also wear differently from the coatings sealed in the other solutions.

This paper represents an extension of the previous paper (Hughes et al, 1983) and considers alternate sealing mechanisms to explain these differences. Implications to the manufacture of lithographic printing plates are considered.

EXPERIMENTAL

Preparation Of Aluminum Plate

The aluminum used in this study was an 1100 alloy expressly anodized in a proprietary manner by the manufacturer for use as a lithographic plate. The anodic coating was removed by immersing the plate in an aqueous solution containing 2% CrO_3 and 5% H_3PO_4 at 95°C for five to ten minutes, according to ASTM Standard B137. The metal was then etched in an 8% NaOH solution, desmutted in a 30% HNO_3 solution, chemically grained in a $H_3PO_4-HNO_3$ solution, and thoroughly washed with distilled water immediately before anodizing. The anodization was carried out in 15% H_2SO_4 under various conditions of electrolyte temperature and anodizing voltage. The thickness of the anodic coating was varied by controlling the anodizing time. A commercial electrolysis grade lead was used as the cathode. Electrolyte circulation was accomplished by bubbling compressed air through the anodizing solution. The temperature of the anodizing solution was controlled by an external water bath. After anodization, the panels were immersed in a 5% $NaHCO_3$ solution for ten seconds to neutralize residual acid, thoroughly washed with distilled water, and finally stored in a desiccator until testing.

Sealing Process

Four aqueous solutions were utilized for sealing the anodic coatings. They were distilled water, nickel acetate solution, potassium dichromate solution, and sodium silicate solution. The distilled water sealing reaction was carried out at the boiling point of water. The nickel acetate solution contained 6 g/L of nickel acetate and 8 g/L of boric acid; pH was 5.6; sealing temperature was 90 $\pm$ 5°C. The potassium dichromate solution contained 15 g/L of potassium dichromate and 3 g/L of sodium hydroxide; pH was 6.9; sealing temperature was 90 $\pm$ 5°C. The sodium silicate solution contained 53 g/L of sodium silicate (Na_2O : SiO_2 = 1 : 3.3); pH was 11.4; sealing temperature was 90 $\pm$ 5°C. All of these solution concentrations are typical in the anodization industry.

Wettability Measurement

Wettability measurements were made by placing a drop of doubly distilled water on the specimen surface and measuring the contact angle by means of a NRL Contact Angle Goniometer Model A-100. A container of doubly distilled water was placed in the environmental chamber of the apparatus to establish high humidity and to minimize the rate of water droplet evaporation. Contact angle measurements were made two minutes after a water drop of 5 μL was placed on the sample surface. The average value of four different droplets was taken as the contact angle.

RESULTS

Surface Topography Of Anodized Aluminum

Graining is considered to be a very important process in the lithographic printing plate manufacture to improve the water holding capacity of the plate, and is generally accomplished by either a mechanical, chemical, or electrochemical method. Scanning electron micrographs in Figure 1 show the surface topography of a chemically grained metal surface and two anodized aluminum surfaces. The surface topography of a brush-grained metal surface prior to and after anodization is illustrated by the electron micrographs in Figure 2. These photographs indicate that the anodizing reaction converts the soft metal surface to a hard coating without greatly changing the surface topography of the underlying metal substrate. Accordingly,

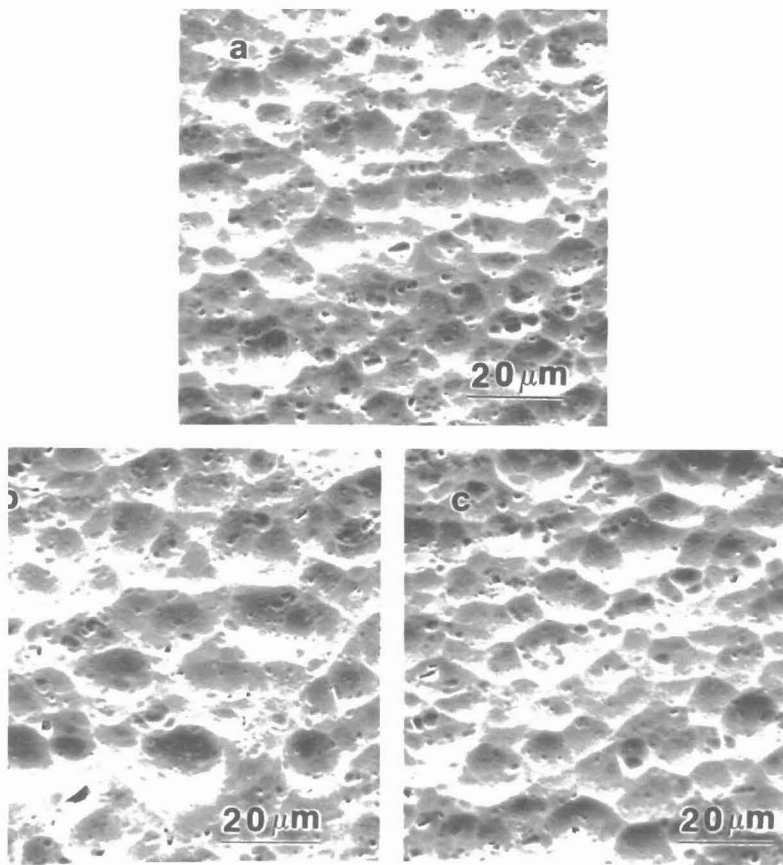graining is normally carried out prior to anodization in
plate manufacture.

FIGURE 1. Surface topography of (a) a chemically grained
aluminum metal surface, (b) an anodized aluminum surface
produced in 15% H_2SO_4 at 30°C and 15 V for 45 minutes,
and (c) an anodized aluminum surface produced in 15%
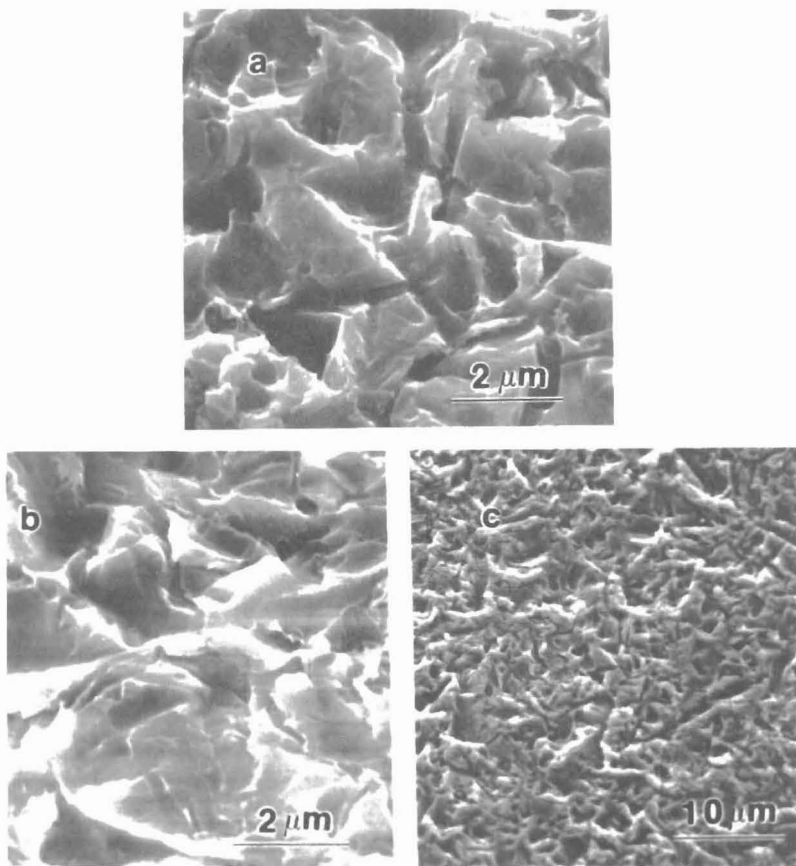H_2SO_4 at 20°C and 15 V for 20 minutes.

FIGURE 2. Surface topography of (a) a brush-grained alumi-
num metal surface and (b) and (c) an anodized aluminum
surface produced in 15% H_2SO_4 at 20°C and 20 V for 30
minutes at two magnifications.

Ink And Water Wettability

The wettability of anodized aluminum surface by water after sealing was determined for each of the aqueous environments at 1, 2, 5, 10, 20, 30 and 60 minutes of sealing. The data previously reported (Hughes et al, 1983) are plotted in Figure 3 in terms of the contact angle of the water droplet with the anodized surface. Coatings sealed in distilled water, nickel acetate, and potassium dichromate solutions exhibited reduced hydrophilicity after short sealing times and good water wettability after longer sealing times. The sodium silicate sealant was unusual in that excellent water wettability was exhibited at all sealing times. All the sealing treatments produced small water contact angles, i.e. good water wettability, at sealing times in excess of ten minutes.
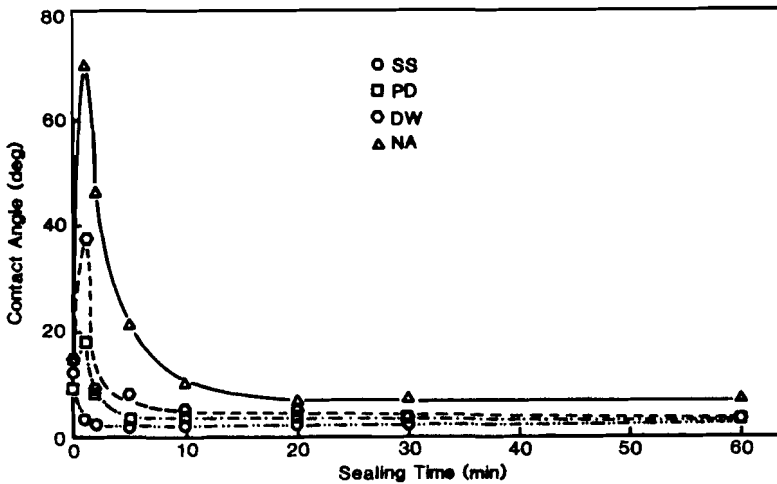

FIGURE 3. Contact angle of water with anodized aluminum surfaces sealed in sodium silicate solution (SS), potassium dichromate solution (PD), distilled water (DW), and nickel acetate solution (NA) for times up to 60 minutes. Note: Figure is reproduced from Hughes et al (1983).

The tendency of a red ink (GPI GA80-1421) to wet the anodized and sealed aluminum surfaces was determined concurrently with the contact angle measurements. Ink, when applied with a hand roller, readily stuck to any of the aluminum surfaces when dry (Figure 4). When the treated surface was wet with distilled water prior to the application of ink, the results varied with the sealing treatment; ink wet all but the silicate-treated surfaces to some extent (Figure 5). Ink did not wet the anodized surfaces that were sealed in sodium silicate solution even at sealing time as short as one minute. When the surface was wet with a press-ready commercial fountain solution, ink wet none of the sample surfaces whether sealed or not (Figure 6).

sealed in boiling distilled water   sealed in sodium silicate solution

0 min   1   2   5   0 min   1   2   5

10   20   30   60   10   20   30   60

sealed in nickel acetate solution   sealed in potassium dichromate solution

0 min   1   2   5   0 min   1   2   5
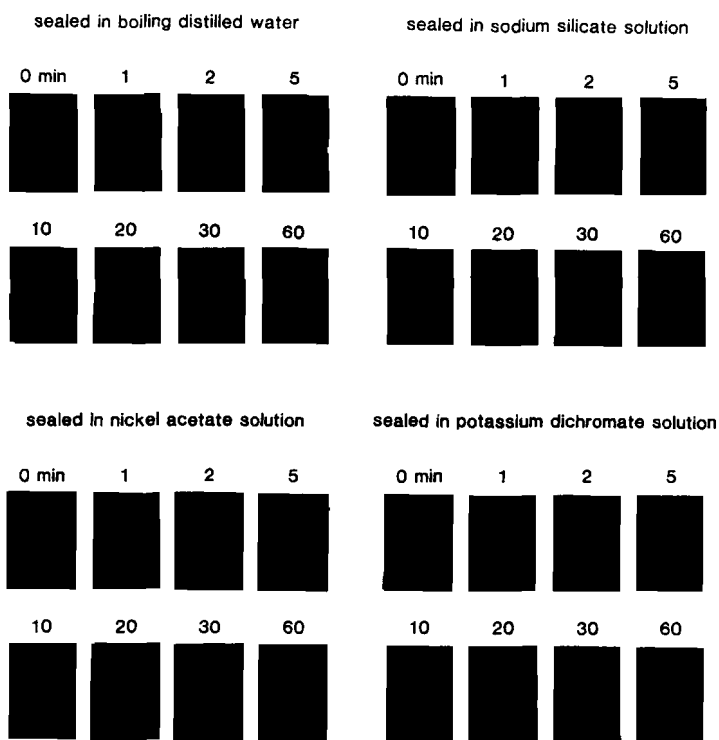
10   20   30   60   10   20   30   60

FIGURE 4. Tendency of an ink to wet the anodized aluminum surfaces sealed in sodium silicate solution, nickel acetate solution, potassium dichromate solution, and distilled water for various times. The aluminum surface was dry.
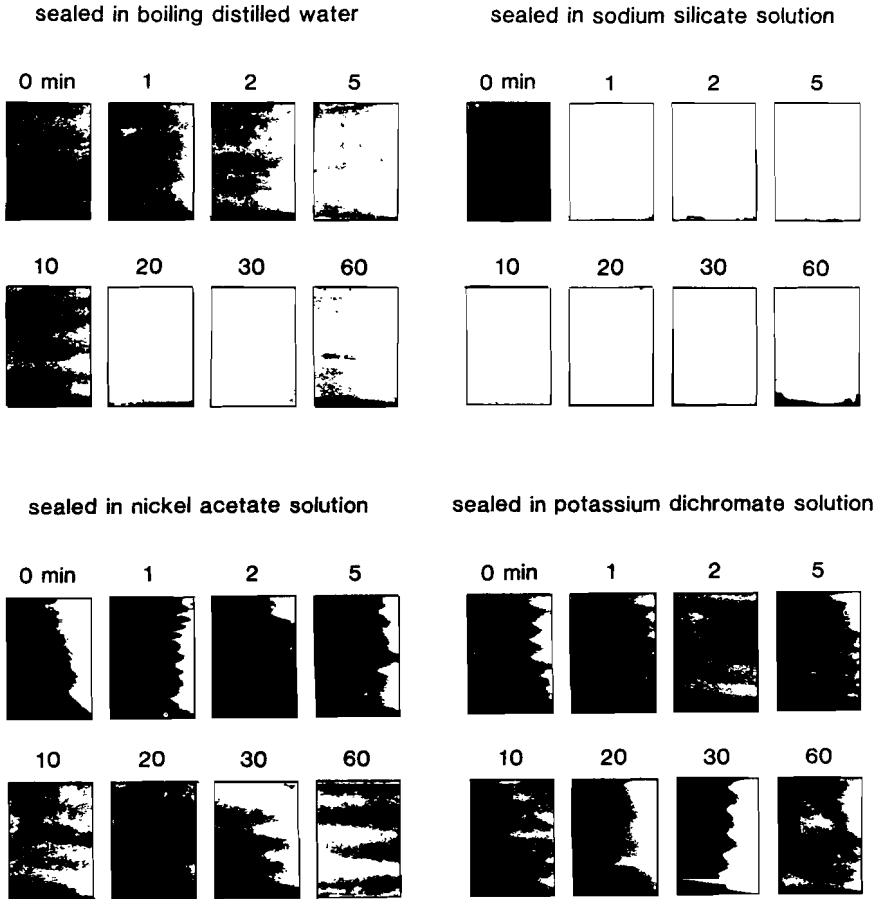
sealed in boiling distilled water

sealed in sodium silicate solution

0 min 1 2 5

10 20 30 60

0 min 1 2 5

10 20 30 60

sealed in nickel acetate solution

sealed in potassium dichromate solution
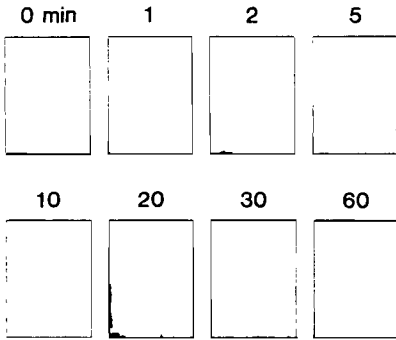
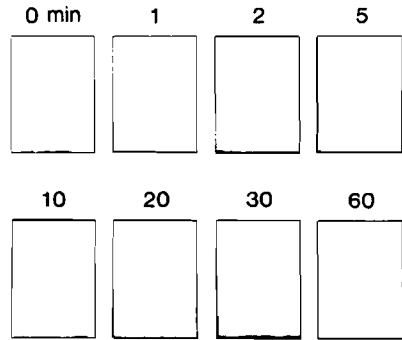0 min 1 2 5

10 20 30 60

0 min 1 2 5

10 20 30 60

FIGURE 5. Tendency of an ink to wet the anodized aluminum surfaces sealed in sodium silicate solution, nickel acetate solution, potassium dichromate solution, and distilled water for various times. The aluminum surface was wet with distilled water before the application of ink.
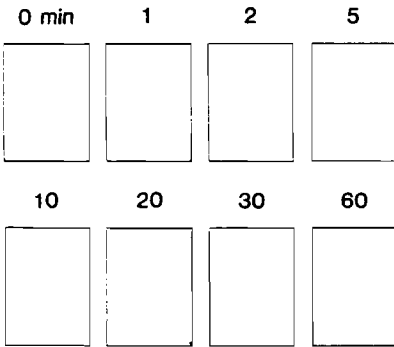
sealed in boiling distilled water   sealed in sodium silicate solution

0 min   1   2   5   0 min   1   2   5

10   20   30   60   10   20   30   60

sealed in nickel acetate solution   sealed in potassium dichromate solution

0 min   1   2   5   0 min   1   2   5

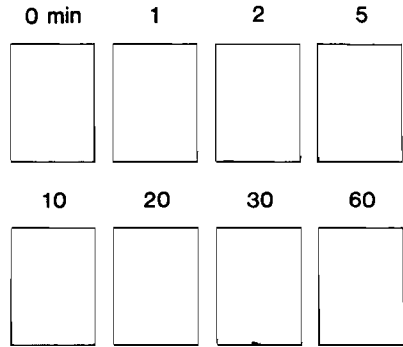10   20   30   60   10   20   30   60

FIGURE 6. Tendency of an ink to wet the anodized aluminum surfaces sealed in sodium silicate solution, nickel acetate solution, potassium dichromate solution, and distilled water for various times. The aluminum surface was wet with a commercial fountain solution before the application of ink.

Surface Topography Of Sealed Anodic Coatings

Scanning electron micrographs were obtained for anodic coatings that were sealed under various conditions. Close inspection of Figure 7 reveals that after the short time of only one minute of sealing with distilled water small grains began to grow on the coating surface. Within five minutes of sealing, the entire surface acquired a velvety appearance which did not change significantly as sealing treatment was continued for as long as 60 minutes. This finely textured surface was not observed for the same anodic coating sealed in sodium silicate solution as shown by the electron micrographs in Figure 8.

Effect Of Anodizing And Sealing Conditions On Surface Properties

Anodized aluminum plates formed in 15% H_2SO_4 at 20°C and 15 V for 20 minutes and at 20°C and 10 V for 140 minutes were reimmersed without an applied potential in the anodizing solution at a temperature of 35°C for 10 and 35 minutes, rinsed with distilled water, and sealed in distilled water and sodium silicate solution, respectively. The anodic coating was completely removed from the 140-minute sample after 35-minute immersion. The water contact angles with the anodized surfaces sealed in distilled water are shown as a function of sealing and reimmersion times in Figure 9 for the 20-minute anodic coatings and in Figure 10 for the 140-minute anodic coatings. It appears that reimmersion of the anodized sample in the sulfuric acid tends to destroy the reduced water wetting effect previously noted. The anodized surfaces of the 20-minute coating after 35-minute immersion were completely wet by distilled water at all sealing times. Sealing did not cause reduced wettability for the 140-minute anodized samples; and within ten minutes of immersion, these samples exhibited excellent wettability.

Wettability behavior of the anodized surfaces that were sealed in sodium silicate solution was similar to that shown in Figure 3 for all coatings studied, that is, reduced wettability did not occur.

Scanning electron micrographs were obtained for these coatings before and after reimmersion. No significant change of the surface topography of the 20-minute anodic coating was observed after ten minutes of immersion

(Figure 11a and b), whereas the surface structure was destroyed after a 35-minute immersion (Figure 11c). The surface structure of the 140-minute coating was already destroyed within ten minutes of immersion as shown by the photographs in Figure 12.
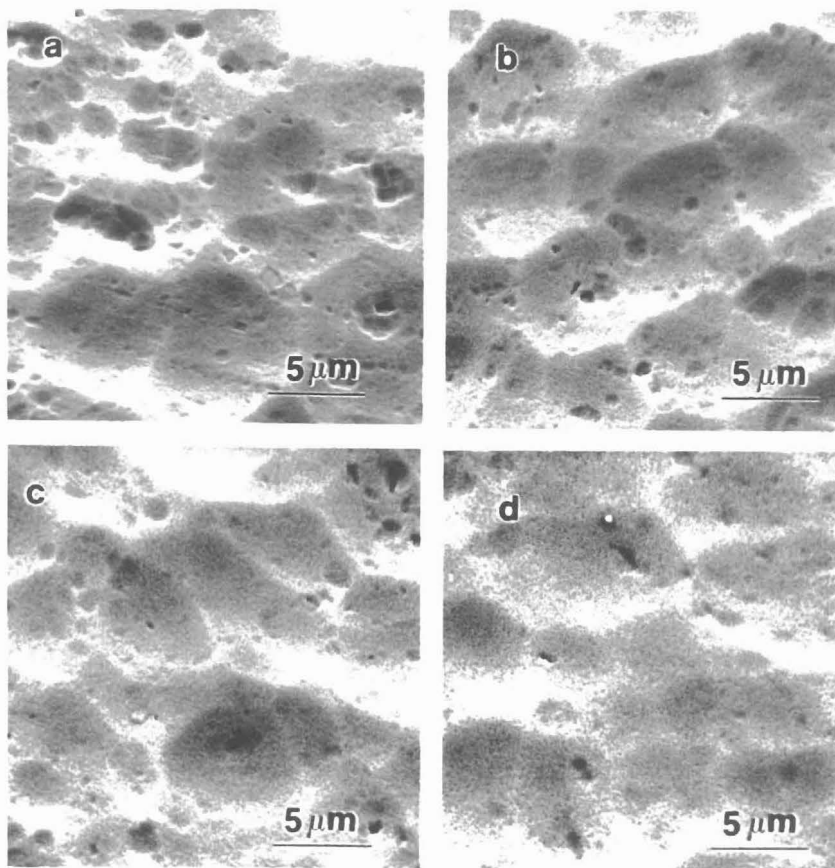

FIGURE 7. Surface topography of anodic coatings formed at 20°C and 15 V for 20 minutes and sealed in boiling distilled water for (a) 1, (b) 2, (c) 5, and (d) 60 minutes.
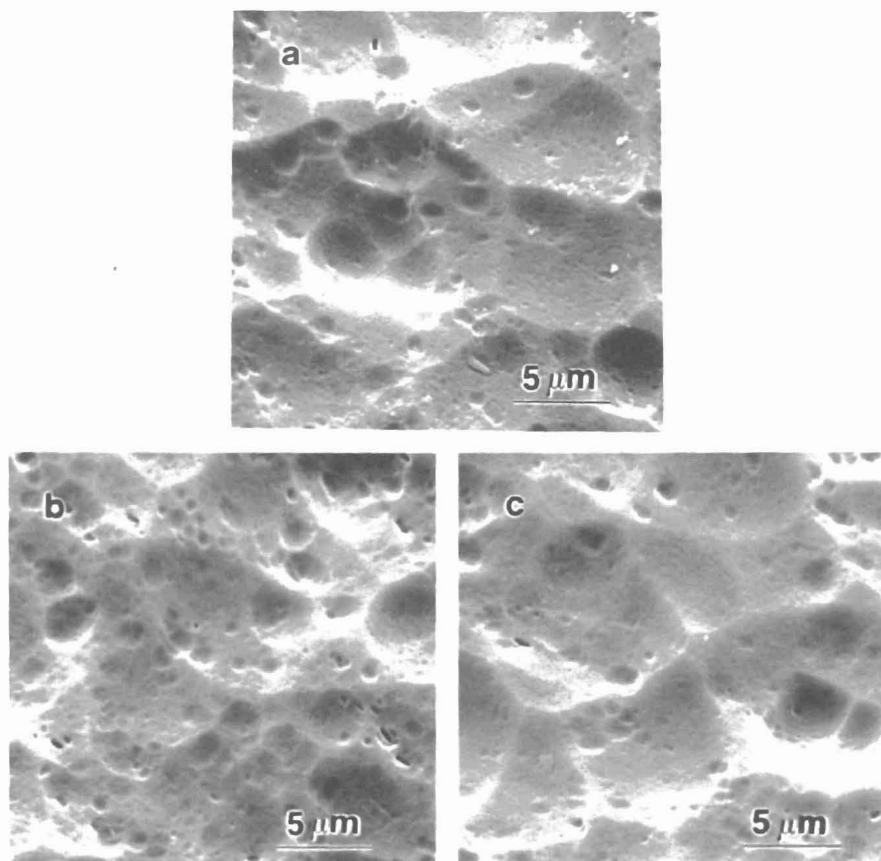
FIGURE 8. Surface topography of anodic coatings formed at 20°C and 15 V for 20 minutes and sealed in sodium silicate solution for (a) 2, (b) 10, and (c) 60 minutes.
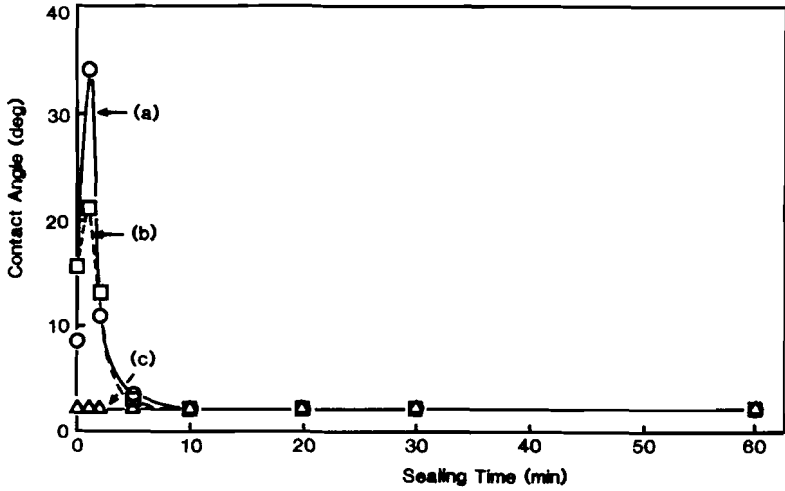
FIGURE 9. Contact angle of water with anodized aluminum surfaces sealed in boiling distilled water up to 60 minutes. Anodized aluminum was prepared in 15% H_2SO_4 at 20°C and 15 V for 20 minutes and reimmersed in the same electrolyte at 35°C for (a) 0, (b) 10, and (c) 35 minutes.
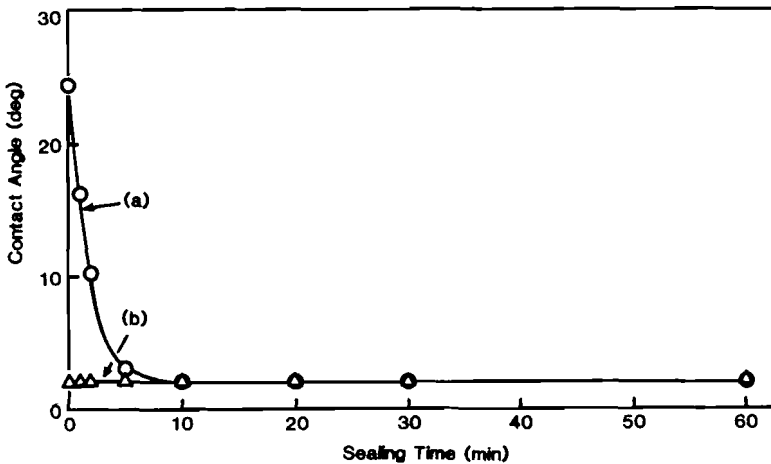

FIGURE 10. Contact angle of water with anodized aluminum surfaces sealed in boiling distilled water up to 60 minutes. Anodized aluminum was prepared in 15% H_2SO_4 at 20°C and 1C V for 140 minutes and reimmersed in the same electrolyte at 35°C for (a) 0, and (b) 10 minutes.

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FIGURE 11. Surface topography of anodized aluminum sur-
faces produced at 20°C and 15 V for 20 minutes and reim-
mersed in 15% H_2SO_4 at 35°C for (a) 0, (b) 10, and (c)
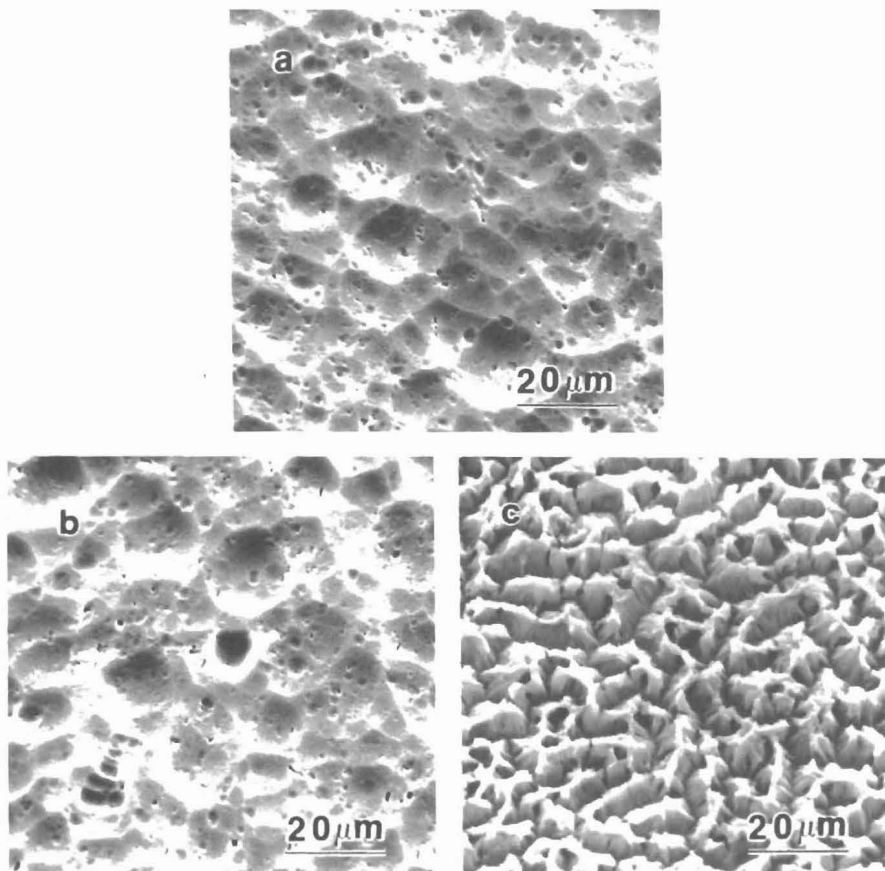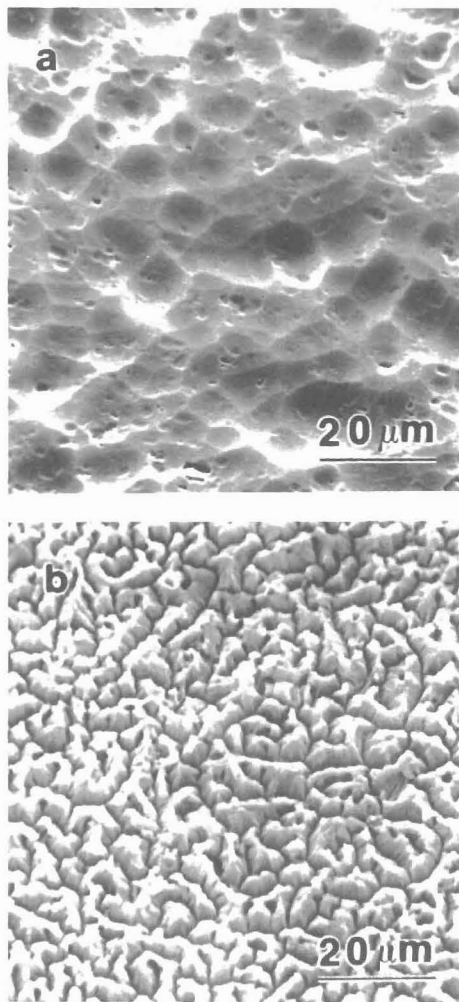35 minutes.

FIGURE 12. Surface topography of anodized aluminum sur-
faces produced at 20°C and 10 V for 140 minutes and
reimmersed in 15% H_2SO_4 at 35°C for (a) 0 and (b) 10
minutes.

DISCUSSION

Wear results of anodized aluminum sealed in distilled water, nickel acetate solution, potassium dichromate solution, and sodium silicate solution have been published (Hughes et al, 1983). An additional paper on the wear mechanism of unsealed anodic coatings has been submitted for publication (Chou and Leidheiser, 1986). Silicate-treated coatings exhibit high rates of wear throughout the entire wear range studied. The wear rate of coatings sealed in the other media is initially high and tends to decrease to a value typical of unsealed coatings. The excellent water wettability of coatings sealed in sodium silicate solution and their ability to debond ink in the presence of distilled water also distinguish these coatings from coatings sealed in the other solutions. It is proposed that the differences in wear and wettability behavior of sealed anodic coatings result from different mechanisms of sealing reaction.

Anodic coatings exposed to distilled water, nickel acetate solution, or potassium dichromate solution are probably sealed via a pore plugging mechanism (Barkman, 1965), according to the typical pore-structure model of anodic coatings on aluminum (Keller et al, 1953). The sealing reaction in these media involves dissolution of the anodically formed anhydrous alumina to aluminum ions and subsequent precipitation as a less-dense, more hydrophilic hydrated alumina. The precipitation process occurs most rapidly and earliest at the outermost oxide surface and, therefore, plugs pore mouths. The closure of pore mouths prevents water from penetrating into the pores, resulting in the observed temporarily higher water contact angles. This hydrophilic reaction product, as evident from the velvety appearance on the surface shown in Figure 7, simultaneously increases the overall wettability of the anodized surface. Competition between these two effects accounts for the reduced wettability at short sealing times, as shown in Figures 3 and 9.

Previous density measurements and wear results of unsealed anodic coatings formed on aluminum (Chou and Leidheiser, 1986) infer that the 140-minute coating has a greater pore diameter than the 20-minute coating. The reimmersion tests also support this inference; the larger-pored 140-minute coating dissolved faster. Nagayama et al (1972) observed that when an anodized aluminum specimen was reimmersed in the anodizing electrolyte without an

applied potential, the thickness of the oxide coating remained almost constant up to a certain time of immersion. Appreciable thinning of the anodic coating proceeded subsequently, as dissolution caused the pore mouths to merge into each other at the surface. Accordingly, the surface topography of the 20-minute coating after ten minutes of immersion (Figure 11) is indistinguishable from that of the original, intact coating. This result suggests that the chemical dissolution takes place primarily at the cell walls. Figure 11c shows that the pore structure is destroyed within 35 minutes of immersion. However, a 10-minute immersion is long enough to open the pore structure of the 140-minute coating (Figure 12), indicating that this coating has a greater pore diameter initially. Consequently, it needs a much longer time of sealing to close the pore mouths of the 140-minute coating and, therefore, the reduced wettability is not observed, as shown in Figure 10. Excellent wettability exhibited by the 20-minute coating after 35 minutes of immersion and by the 140-minute coating after 10 minutes of immersion when sealed in distilled water, is independent of sealing duration. The extremely rough surface of these samples (Figures 11c and 12b) probably explains this result.

As soon as the pore mouths are completely closed, the sealing reaction and hence the growth of the intermediate hydrated layer is controlled by diffusion of water into the anodic coating and diffusion of acid anions, which were incorporated in the anodic coating during anodization, out to the sealing solution (Wefers, 1973). This outer, hydrated layer which is soft accounts for the rapid wear in the early stages of wear testing (Hughes et al, 1983).

A finely textured surface (Figure 7) is characteristic of the coatings sealed in distilled water, nickel acetate and potassium dichromate solutions. However, the surface structure was not considerably changed in the case of coatings sealed in sodium silicate solution as shown in Figure 8. It is likely in the latter case that the sealing process proceeds via a surface modification mechanism proposed by Murphy (1967) rather than a pore plugging mechanism. As compared with the other nearly neutral media, the high pH of the silicate sealing solution facilitates a surface-layer formation of hydrated alumina on the cell walls by replacement of acid anions in the intercrystallite region by hydroxyl ions, and the high pH also

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inhibits the overall precipitation of pore plugging hydrous aluminum ions. Consequently, the pores remain open. The resulting modified microcrystallite agglomerates produce great strain in the coating and significantly reduce the wear resistance of the silicate-sealed anodic coating. Meanwhile, chemical dissolution of the cell walls by the highly alkaline sealing solution may further decrease the coating's resistance to wear. Accordingly, high wear rates were exhibited by silicate-treated coatings throughout the entire range of wear testing. Excellent water wettability of these coatings is expected because of the unplugged pore mouths and a hydrophilic modification that is limited to the cell wall surfaces.

PRACTICAL IMPLICATIONS

An imaged conventional lithographic printing plate is not selective to an oil ink in the absence of an aqueous phase, regardless of the hydrophilicity nature of the non-image area. Either anhydrous or hydrated alumina, that is, either unsealed or sealed anodic coatings on aluminum have a high energy surface which is readily wet by a low energy ink. In the presence of an aqueous phase, the high energy non-image area is preferentially wet by water, which acts as a barrier layer keeping the ink from reaching the non-image area. This water layer may also serve as a weak fluid boundary layer for ink release (Gaudioso et al, 1975). None of the conventional anodizing or sealing treatments changes these characteristics.

Sealing treatments, especially with sodium silicate solution, increase the hydrophilicity of an anodized aluminum surface and thereby help to ensure optimum differentiation between the image and non-image areas. The silicate-treated surface is able to debond ink completely even in the presence of pure water and consequently tends to widen the ink/water balance latitude at the press. This may be the reason why many commercial lithographic plates receive a silicate treatment of a proprietary nature. However, with the aid of a commercial fountain solution, both unsealed and sealed anodized surfaces are expected to run clean on the press (Figure 6), but are also expected to differ in ink/water balance latitude.

Improvement in hydrophilicity of anodic coatings by sealing unfortunately sacrifices the resistance to wear and hence the useful plate life. These opposing effects have to be taken into account when manufacturing a litho-

graphic printing plate.

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