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ORGANIC COMPOUNDS IN ALUMINUM OXIDE FILMS ANODIZED IN AQUEOUS CARBOXYLIC ACIDS

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Organic compounds were isolated from brown-colored aluminum oxide films anodized in aqueous carboxylic acids. The isolated compounds were identified as the carboxylic acids utilized as electrolytes. The coloration is suggested to arise from free radicals in the organic compounds.

Aluminum anodic oxide films grow colored and show photo-luminescence when they are prepared by the anodization in aqueous carboxylic acids. These properties had been attributed to the exitation of electrons trapped in the vacancies of lattice in Al_2O_3 crystals or crystallites.1) However, it is unfavorable that the anodic films are composed only of Al_2O_3, since the film is formed as the result of the dehydration of Al^{3+} aquo-complex in the electric field and the dehydration is incomplete in aqueous acids.2) Thus, the anodic films should include hydrous aluminum oxide such as AlOOH or $Al(OH)_3$. They should also contain ligands of hard base such as carboxylete ion, since Al^{3+} dissociated by anodic polarization exchanges ligands when it is hydrated to form Al^{3+} aquo-complex.

In the previous paper,3) existence of organic substance with carboxylate group and free radicals was suggested by ir and esr for aluminum anodic films anodized in carboxylic acids. But complete confirmation of organic substance was impossible because the absorption spectra of the anodized films were overlapped partly with the absorption of hydrous aluminum oxide themselves. In this paper, we attempted isolation of organic compounds from the anodic oxide films and confirmation of their chemical constitution.

Experimental

Anodization Aluminum sheet samples, 10 × 5 cm, of 99.99 % purity were anodized at room temperature in 0.016 mol/l aqueous oxalic or malonic acid at a current density of 1.67 mA/cm^2. As the anodization proceeded, surface of the samples grew brownish and tarry spots appeared in places.

X-ray micro-analysis (XMA) and microscopic observation The anodized samples were cut off at the parts where tarry spots deposited and ground thoroughly. The obtained cross sections were examined both by XMA and a microscope. The XMA was performed for K_α-rays of C, Al, O, at the condition of accelerated voltage; 15 KV, sample current; 0.015 μA, and scanning rate; 10 μ/2cm/1min.

Isolation of organic compounds from the anodic films No organic solvent was possible to extract organic substances from the anodic films even if the powdered samples were heated in the boiling solvent[3). Therefore, a method was employed which dissolves the anodic films themselves to liberate organic substances from them. A 0.5 % H_2SO_4 solution was adopted to dissolve the films without the destruction of organic substances. Large amount of the anodic films was dissolved in the H_2SO_4 until saturated solution of profoundly dark brown color was obtained. The solution was poured into ethyl alcohol to precipitate almost all Al^{3+} and SO_4^{2-} ions as aluminum sulfate. Residual Al^{3+} ion was removed completely through cation exchange resin (Amberlite IR-120-B) without the color change of the solution. Thorough decoloration was observed when anion exchange resin (Amberlite IRA-400) was employed to remove residual SO_4^{2-}, suggesting that brown materials were anions. To avoid the absorption by anion exchange resin, cation-exchanged solutions were neutralized with aqueous ammonia. They were then concentrated under diminished pressure and the residues were added into ethyl alcohol to precipitate $(NH_4)_2SO_4$. The procedure was repeated until the amount of $(NH_4)_2SO_4$ became negligible. Small amounts (less than 3 mg) of the pale yellow residues remained finally in vessels were analyzed by means of ir, esr, and paper-chromatography.

Isolation of colored organic compounds from the anolytes after prolonged anodization Prolonged anodization in a vessel to separate anolyte and catholyte gave brown anolyte for both aqueous oxalic and malonic acids. The coloration of the anolytes is considered as the result of dissolution of the anodic oxide films because of their soluble property in acidic environment. Accordingly, the isolation of colored materials from anolytes was tried. The anolytes were concentrated under diminished pressure after Al^{3+} ion was eliminated through cation exchange resin (Amberlite IR-120-B). The residues were analyzed in the same manner as described above.

<u>Results</u>

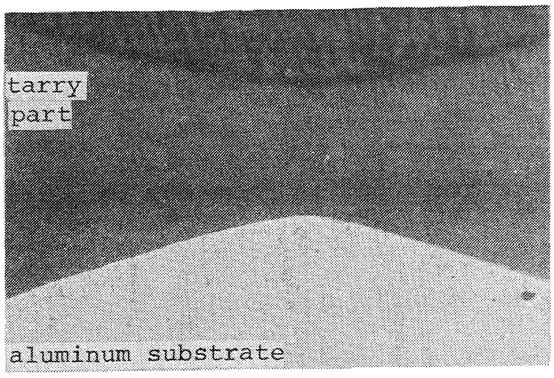

Photo 1, Cross section of tarry part

<u>Tarry matter</u> Photo 1 shows a cross section of the deposited tarry spots through microscope. The cross section consisting of homogeneous layer has developed up-and down-wards to the thickness extremely thicker than the other part. The downward development is considered as the result of the violent dissociation of aluminum substrate by a locally concentrated anodic current. The upward development is attributed to the volume increase by the conversion of $Al \rightarrow Al^{3+} \rightarrow$ hydrous aluminum oxide. No difference has been observed in relative concentrations of C, Al, and O between the tarry part and the other part by XMA as has been observed by ir in the previous paper$^{3)}$. Consequently, it has been proved that so-called " tarry matter " is not carbon compounds but the anodic oxide film itself. The appearance like tarry matter is attributed to the unusual growth of the anodic film by locally concentrated anodic current.

<u>Organic compounds isolated from the anodic films</u> Based on the result, the whole surface of anodized samples was subjected to the isolation of organic compounds. By the repeated precipitations, the solutions were decolorated, finally giving residues of pale yellow. Their ir absorption spectra, although they were somewhat blurred by impurities, were similar to the spectra of authentic oxalic and malonic acids, respectively. R_f values in paper-chromatography also gave the same results. UV absorption spectra revealed a peak

at 260 nm for the residue isolated from oxalic acid anodic film, and a peak at 210 nm for the residue from malonic acid anodic film. These values seem to support the above mentioned results. Their extended absorption to visible region are responsible to the coloration of the residues. Esr signal of $g = 2.005$ was detected for the colored substances.

Organic compounds isolated from the anolytes It was confirmed from ir and paper-chromatography that the pale yellow substances isolated from the two anolytes were oxalic and malonic acids, respectively. UV absorption peaks at $\lambda_{max} = 260$ nm ($\varepsilon = 50$) for the former and $\lambda_{max} = 210$ nm ($\varepsilon \doteqdot 100$) for the latter, gave the same results. The absorption bands extended to visible region are also responsible for the coloration of the substances. Esr signal of $g = 2.005$ and $\Delta H = 8$ gauss was clearly observed for the powdered isolated samples at room temperature. The intensity of the signal scarcely changed after a few months at room temperature. Consequently, the colored substances, which were identified as oxalic and malonic acids, respectively, have been proved to contain stable free radicals.

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