

Anode Polishing¹

FRANK C. MATHERS and ROBERT E. RICKS,² Indiana University

The purpose of this research was to test mixtures for use as baths for the anode polishing of metals. Although anode polishing is commercially done, there are some difficulties with, and some objections to, the solutions that are being used. As all have exceptionally high electrical resistance, they become excessively hot during operation. Sufficient heat is developed, unless a good cooling system is used, to char the glycerine which is used in one of the baths along with phosphoric acid. There is danger of an explosion, or at least there is a fire hazard, with the other most commonly used bath which is a mixture of perchloric acid and acetic acid anhydride.

What is needed is a bath of greater electrical conductivity containing constituents that do not char, or burn, or explode, if the temperature does become high. This research succeeded in finding a bath that did not char, burn, or have the possibility of exploding, but it still had a high electrical resistance.

A recent development in electrochemistry is anode polishing. Anodes are not dissolved appreciably in some solutions but become highly polished. Industrially, this is often a more economical method of polishing than any mechanical means. This is especially true of stainless steel, which polishes easily, and for some irregularly shaped articles the surfaces of which cannot be gotten in contact with a polishing wheel.

Anode polishing results³ from the selective dissolving of the elevations on the metallic surface and can only occur if the rate of dissolution of the elevations is greater than that in the depressions. This is effected when depressions are relatively anodically passive and the elevations relatively anodically active. An anodic film must form which is thinner in the elevations and thicker and more protective in the depressions. The electrochemical behavior of the metal ions anodically formed in the electrolyte governs the nature of this passivating film. This indicates that there is no universal solution and that many different baths would be satisfactory.

This theory explains why the salts formed at the anode must have high solubility and why the solution of these salts and the bath itself must have high viscosity. It also shows why agitation is undesirable; the anode film would be displaced. Such a passivating film and the high viscosity of the bath explains why the electrical resistance is so high. This causes very undesirable heating in most cases. This somewhat

¹ From a thesis by Herbert E. Ricks for the Ph.D. degree at Indiana University, 1942.

² Present address, Pennsylvania Salt Manufacturing Co., Philadelphia.

³ Pray and Faust, *Iron Age*, **145**, April 11, 33 (1940).

passive condition of the anode explains the relatively small loss in weight. If the anode loses much weight, etching or corrosion and not polishing results. If an insoluble solid salt forms at the anode, pitting of the anode is the result.

The solutions used⁴ are usually phosphoric acid and glycerine or perchloric acid and acetic acid anhydride.

Experimental

Electrolysis was carried out with anodes, 2x2 cm., of the metal or alloy being polished. The cathodes were lead sheets having an area about four times that of an anode. The anodes were cleaned before polishing by degreasing in carbon tetrachloride, dipping in concentrated hydrochloric acid and rinsing in distilled water.

Each electropolished anode was given a polish rating, by inspection, of from one to five (five being the most highly polished and one being the least polished).

The temperature, concentration of components in the bath, and current density were varied. The sample being polished was watched and if only etching or corroding occurred, the anode was replaced by another metal; if polishing occurred the anode was left for ten minutes or until no further polishing occurred.

Temperatures given were maximum temperatures, and were controlled by immersing the bath in cold water or by setting the bath on a hot plate having a bank of lamps in series with the hot plate so that the temperature could be varied. Amperes are per sq. cm. The quantities given are the proportions in which the chemicals were mixed in making the baths.

Stainless Steel

The best bath was 24 ml. of conc. phosphoric acid and 36 ml. of cyclohexanol, $C_6H_{11}OH$ (sometimes called hexahydrophenol). The current density was 0.38 amp. The temperature was 86°. The best time was 5 or, occasionally, 10 minutes. The bath did not char or darken from the high temperature as did the glycerine-phosphoric acid bath. This is an important advantage. The degree of polish was somewhat higher than could be obtained with the commonly used glycerine-phosphoric acid bath.

Other baths tested and their ratings are:

Sulfuric acid 20 ml., glycerine 15 ml., and 15 ml. of an equal molecular mixture of glycerine and tartaric acid, at 0.30 amp. and 40°; rating 4½ to 5.

Ammonium acetate 1 gm. and 8 ml. of cyclohexanol at 0.30 amp. and 84°; rating 4.

⁴The best general references with bibliography are: Tour, *Iron Age*, **145**, May 23, 56; May 30, 26 (1940); Shafer, *Metal Ind.* (N. Y.), **38**, 22 (1940); Tour, *Metal Finishing*, **38**, 321, 308 (1940).

Glycerine 10 ml., sulfuric acid 4 ml., and water 6 ml. to 0.24 amp. and 86°; rating 4 to 4½.

Pyrophosphoric acid 10 ml., and 10 ml. of cyclohexanol at 0.24 amp. and 105°; rating 4 to 4½.

Pyrophosphoric acid 10 ml. and 12 ml. of dioxan (trimethylene glycol) at 0.23 amp. and 97°; rating 4½ to 5.

Aluminum

The best bath was conc. sulfuric acid 12 ml. and glycerine 24 ml. at 0.25 amp. for 20 minutes. The rating was 5. The presence of water and hydrochloric acid increased the etching. A high current density was necessary and the time was usually 10 to 20 minutes.

Other solutions tried and their ratings are:

Carbowax 2 gm., hydrofluoric acid 4 ml., and aluminum nitrate 2 gm. at 1 amp. and 112°; rating 5.

Phosphoric acid 10 ml. and sulfamic acid, $\text{NH}_2\text{SO}_3\text{H}$, 3 gms. at 0.65 amp; rating 5.

Phosphoric acid 10 ml. and sulfuric acid 3 ml. at 0.67 amp. and 136°; rating 4 to 4½.

Copper

No entirely satisfactory solution was found. The best ratings were 4½. Phosphoric acid 24 ml. and cyclohexanol 36 ml. at 0.38 amp. and 100° for 5 minutes was perhaps the best one. Various baths such as (a) chromic acid and water; (b) ammonium acetate, glycerine and boric acid; (c) sulfamic acid and phosphoric acid; (d) acetic anhydride and sulfamic acid; and (e) pyrophosphoric acid and cyclohexanol, for 10-30 seconds rated about 4½.

Iron

Iron was difficult to polish, and no entirely satisfactory solution was formed. The best solution was phosphoric acid saturated with citric acid, at 0.22 amp. and 100° for 1 minute. The rating was 4½ to 5. Various combinations similar to those described for the other metals rated 4 to 4½.

Zinc

No satisfactory bath was found but the best result, rating 4½, was obtained with cyclohexanol, 20 ml., and phosphoric acid, 16 ml., at 0.35 amp. and 80° for 2 minutes. Various other combinations rated 4 to 4½.

Fused baths such as 10 gms. of NaNO_2 , 5 gms. of NaNO_3 , and 5 gms. of KNO_3 , were tried, but they always corroded the metals and did not produce a polish.

Conclusion

The presence of water and halogen ions caused etching rather than polishing.

The resistance of all polishing baths is high. This causes undesirable heating and, when easily decomposed organic compounds are used, serious blackening or charring results.

The most important development of this research was the successful use of cyclohexanol, a chemical that had never been used before in polishing baths. It seemed to be superior to glycerine in the two desirable ways: (1) It did not char when heated, and (2) it produced a little better degree of polish.

The cyclohexanol is insoluble in water which makes washing of the treated metal more difficult than when glycerine is used.