

TECHNICAL BULLETIN



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"Caustic Etch"

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CAUSTIC ETCHING

Wrought aluminum is supplied in the mill finish condition which can give variable appearance after anodizing. Caustic etching before anodizing reduces these variations and makes the appearance of the aluminum surface more attractive to the customer.

Over the years, many changes have occurred in etch composition and practices. This Technical Bulletin reviews the historical development to provide context for current technology, and discusses the influence of process variables on the appearance of the etched surface.

Development of etches

Prior to 1960, etch formulations were very simple, consisting of 50-100g/l NaOH, and were operated at about 60°C. There were a number of problems.

1. As the etch bath was used, aluminum and impurities would build up in solution, and a brighter “spangle” appearance would develop. The Al^{3+} content was limited to about 50g/l, and zinc to about 5ppm.
2. The etch rate decreased as the aluminum content increased.
3. As the ratio of Al^{3+} to $\text{NaOH}_{\text{free}}$ approached one, there was the chance that aluminum compounds would precipitate from the solution, particularly if it was cooled, producing a hard, chemically-resistant scale.

Typical practice was to operate these etches using partial dumping to control the Al^{3+} concentration at between 50 and 100% of that of $\text{NaOH}_{\text{free}}$. The appearance of the metal surface varied over this range, but that variation was reduced by controlling etch time or temperature.

In the 1960s, more complex formulations were developed to minimize the effects of metal ion build up in solution. Thus, for example, 50g/l NaOH and 40g/l NaF at 60°C was claimed to produce a smoother, whiter finish. Also, 50g/l NaOH, 40g/l NaNO_3 with 1g/l tataric acid at 60°C had very good smoothing power, and tolerance to Al^{3+} was increased to about 80g/l. Additives found to control the effects of zinc included CuSO_4 /triethanolamine, NaNO_3 or NaNO_2 ; the latter two also tended to give a more matte finish. It was appreciated that the most economical way to operate an etch was to dump solution when it had the highest Al^{3+} content and the lowest $\text{NaOH}_{\text{free}}$. Additives such as tartrates, gluconates and heptonates complexed the Al^{3+} allowing up to 100g/l Al^{3+} in 50g/l $\text{NaOH}_{\text{free}}$, and reducing hard scale formation.

Partial dumping was still necessary, and because of the higher viscosity of these solutions due to their Al^{3+} contents, more etch was being lost by drag-out. This led to the development of the “long-life” or “never-dump” etches in the early 1970s. The concept was to operate with the Al^{3+} content sufficiently high that the viscosity was at the point where the amount of Al^{3+} lost by drag-out equalled the amount of aluminum dissolved in the etch. Thus, for example, if metal dissolution was 100g/m², then the drag-out would have to contain 100g Al^{3+} per m² of load surface area. These etch formulations contained Na_2S to precipitate Zn as ZnS , higher levels of complexant, and often increased $\text{NaOH}_{\text{free}}$, eg 110g/l $\text{NaOH}_{\text{free}}$, 130g/l Al^{3+} , 25g/l sodium gluconate, and 2g/l $\text{Na}_{\text{free}}\text{S}$. The elimination of partial dumping led to a greater consistency of finish. Effectively, “continuous dumping” was being used as etch solution was being dragged out to the rinse. This put demands on effluent treatment with associated sludge disposal costs.

To reduce the impact on effluent treatment, it was necessary to obtain the same matte finish with less metal dissolution. A further development in the late 1980s addressed this, which involved operating at even higher levels of Al^{3+} (with more complexant present). However, with the associated high viscosity, these high Al^{3+} levels would be depleted by drag-out, so surfactants were added to reduce drag-out, and a static rinse was introduced to provide solution to replenish the etch of evaporation losses.

Today, the long-life etch is the norm for Europe. A uniform, very matte appearance without sign of die-lines can be produced with metal dissolution of about 75g/m². However, environmental considerations are much more significant with tight controls on effluent and sludge; in some countries anodizing sludge is considered to be a hazardous waste.

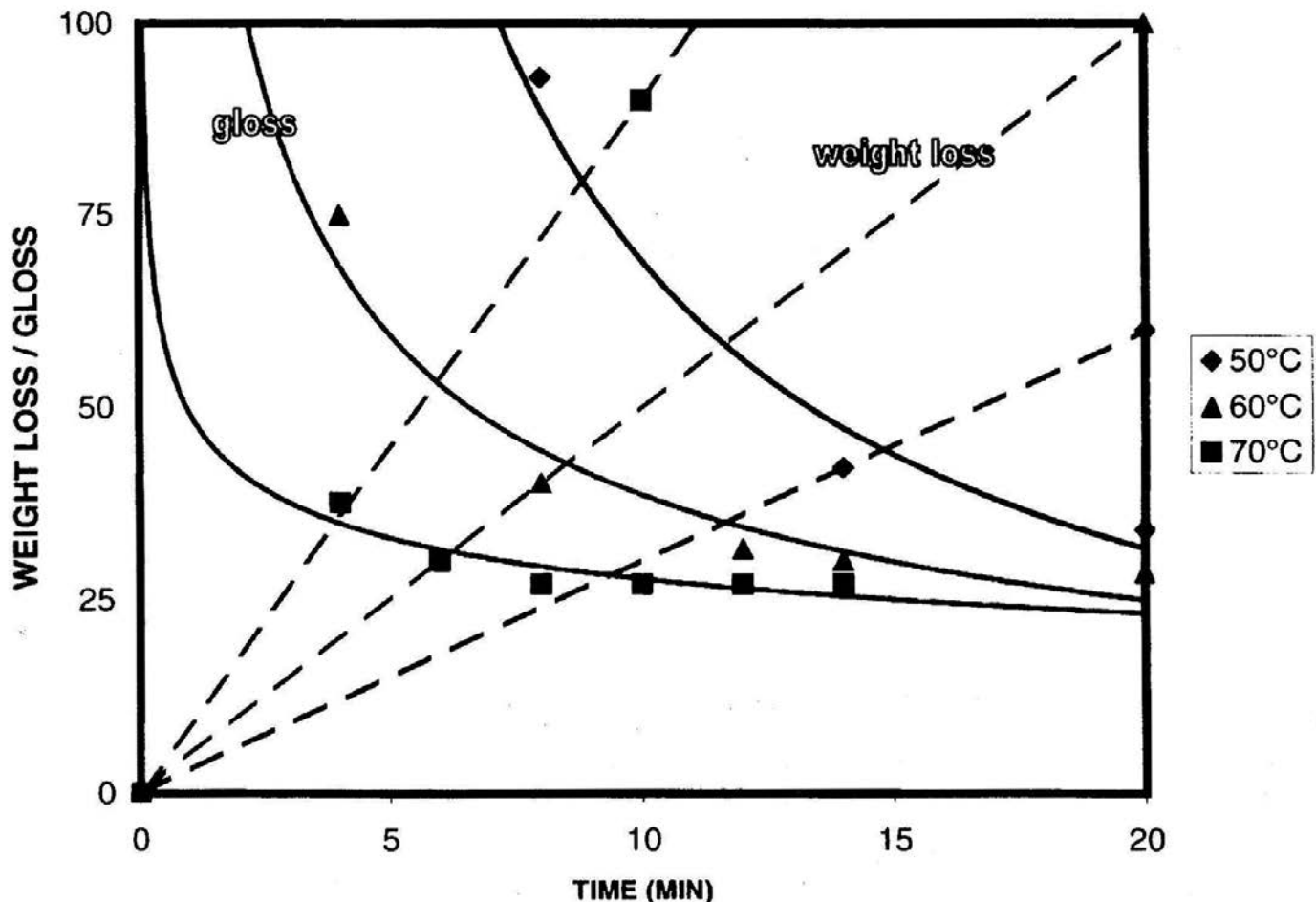
Etch development in Japan has been different, and provides a route to minimize the environmental issues by eliminating waste at the source. However, the Japanese market does not demand high matte finishes and will tolerate some residual die lines. A typical Japanese etch contains 65g/l $\text{NaOH}_{\text{free}}$ and 50g/l Al^{3+} at 60°C, and is operated with metal dissolution of 50g/m². The etch is continuously recirculated through a crystallizer where aluminum hydroxide is precipitated, while the NaOH is recovered back to the etch tank. This controls the etch composition. The $\text{Al}(\text{OH})_3$ can often be sold as a by-product. Also, because the solution has a relatively low viscosity and is relatively dilute, drag-out is reduced and so is the amount of waste. There are only few examples of recovery etch systems claimed to produce successfully very matte finishes by operating at high Al^{3+} contents facilitated by additives.

Effect of process variables on appearance

One of the drivers of historical etch development has been to obtain a uniform, matte finish with minimum metal dissolution. As described above, certain additives affect this. Other important additives remain the proprietary information of chemical suppliers. However, also important are the effects of NaOH and Al^{3+} concentrations, solution temperature, and process time. In general, more matte finishes are obtained by plants that operate their etch solutions at temperatures greater than 60°C, with higher Al^{3+} contents, often over 100g/l, and at ratios of Al^{3+} to $\text{NaOH}_{\text{free}}$ greater than one. However, it may be difficult to achieve all these criteria using a recovery etch system.

Even with long life etch formulations, the specific conditions to achieve a given finish may vary depending on the additives present. The effect of etching time is, in some respects, more complex. Certainly, plants achieving more matte finishes tend to etch for longer times, often about 15 minutes. But, it is important to consider also the need to be able to produce a consistent finish, and to avoid over-etching. The graph exemplifies changes in weight and gloss (arbitrary units) that occur during etching. The weight loss increases linearly with time, while the gloss decreases rapidly at first, but then tends to plateau. Higher etch temperatures lead to more rapid weight loss, and quicker reduction in gloss.

THE EFFECT OF ETCH TIME ON WEIGHT LOSS AND GLOSS FOR DIFFERENT ETCH TEMPERATURES



Weight loss is important in controlling process costs. It represents lost metal which cannot contribute to the value of the final product. It also represents material that may go to waste as a sludge with associated treatment and disposal costs.

However, in order to control the product, it is important to operate the etch near or on the plateau. Under these circumstances, slight changes in process conditions from load to load will not have a major effect on product appearance. On the other hand, if the etch time is very short, then it is much more likely that the gloss will be changing rapidly, and product consistency will be more difficult to achieve and maintain.