Kirk-Othmer Encyclopedia of Chemical Technology.

METAL SURFACE TREATMENTS, PICKLING

Pickling is a term used to describe metal-cleaning operations designed to remove oxides from metal surfaces. These oxide films may be the result of in-process operations such as heat treating, hot rolling, forging, chemical passivation and etching, or simply environmental corrosion. Among the terms commonly used to describe these oxide layers are scale, rust, smut, white corrosion, and black or blue oxide. Although in some cases the oxide films may be removed using alkaline solutions of various compositions, pickling solutions are predominantly acidic, and most often very strongly acidic.

A number of pickling formulations are available. The proper choice is dictated by the chemistry of the base metal as well as of the oxide film itself. Whereas no single pickle formula is generally effective on all metal alloys, sulfuric acid is probably the most versatile of all the acids. The mechanism by which the acid solutions attack and remove the oxide film varies with the metal, metal oxides to be removed, and the acid used. In some cases oxides are removed by the acid, such as sulfuric acid, penetrating film imperfections such as cracks in the oxide layer, then attacking the base metal. Hydrogen gas is formed at the oxide–metal interface. The pressures thus generated blow off the oxides. Many acids, eg, hydrochloric acid, dissolve the base metal as well as the oxide layer. Pickle inhibitors are therefore available for most pickling acids. These inhibitors minimize or prevent the acid from attacking the base metal, yet allow effective removal of the oxides.

The speed of the pickle reaction is also dependent on the concentration and temperature of the pickle, the degree of agitation of either the metal part or the pickle solution, the alloy being pickled, and the acid used. Pickling solutions may be applied by either spray or immersion techniques. However, because of the noxious fumes emitted, there must be adequate ventilation. Sometimes, particularly when spraying techniques are used, an enclosure to contain the fumes and mist is employed.

1. Metals and Alloys

1.1. Carbon and Low Alloy Steels

Sulfuric acid and hydrochloric acid are the predominant pickling acids for ferrous alloys and some stainless steels having less than 10% chrome and nickel (see Steel). However, organic acids, such as citric acid and tartaric acid, are seeing more use because these latter are nontoxic and less hazardous. Sulfuric acid is generally used at 10–15 vol % of 66°Bé acid at 65–83°C; hydrochloric is generally used at 20–40 vol % of 20°Bé acid at ambient up to 55°C. Pickling inhibitors are often used with these acids to minimize base metal loss, severe etching, and pitting without significantly affecting the rate of oxide removal. Metal loss can be reduced by 97–99% by using an inhibitor formulated specifically for the pickling acid.

1.2. High Chrome–Nickel Stainless Steels

Probably the most common descaling or pickling solution is a combination of about 10% by volume nitric acid with 1–4% hydrofluoric acid at about 49°C. For heavy oxide films, this mixed acid pickle may be preceded by a 20% by volume sulfuric acid pickle. Because scale is generated upon annealing, a molten oxidizing salt

bath is used to condition the scale and minimize the concentration and temperature required for the mixed acid treatment. Hydrochloric acid is rarely used for stainless steels, particularly for descaling or deoxidizing finished parts, because of its propensity to cause localized pitting. Sulfuric acid fortified with chloride salts or organic acids may be used successfully for removal of thin oxides on certain alloys.

1.3. Aluminum Alloys

Oxide removal on aluminum is generally accomplished using solutions of nitric (20–25% vol %) or sulfuric acid (5–10 vol %), containing various amounts of fluoride ions to control the etch and speed of oxide removal. Chromic acid has also been used as an etch retardant in sulfuric acid, but for ecological and health reasons use of chromic acid is becoming rare. Nonetching oxide removers, or bright dip solutions, consisting of fluoride compounds such as hydrofluoric acid or hydrofluorosilicic acid, formulated with organic compounds such as tragacanth gum or certain surfactants, are also effective.

1.4. Copper and Copper-Containing Alloys

Either sulfuric or hydrochloric acid may be used effectively to remove the oxide film on copper (qv) or copper-containing alloys. Mixtures of chromic and sulfuric acids not only remove oxides, but also brighten the metal surface. However, health and safety issues related to chromium(VI) make chromic acid less than desirable.

1.5. Zinc and Zinc Alloys

Zinc metal is highly reactive in acid solutions such as sulfuric, hydrochloric, and nitric dissolving rapidly at acid concentrations normally used to pickle steel and aluminum. Dilute (1–4%) solutions of these acids can be used with caution to remove zinc oxides. Sulfamic acid at concentrations of 2–6%, in conjunction with the proper proprietary inhibitor, can be effective in removing zinc oxides and corrosion by-products without attacking the zinc metal.

1.6. Magnesium Alloys

Heavy oxides are usually removed from magnesium alloys by using a concentrated (ca 20–25%) hydrofluoric acid solution. Because of its highly toxic and corrosive nature, extreme care must be taken when handling or using hydrofluoric acid solutions. Chromic acid at about 350 g/L containing small amounts (0.1–0.5 g/L) sulfate and chloride ions effectively removes surface contaminants and oxides without significantly attacking the base metal.

2. Alkaline Deoxidizers

In certain applications, and particularly when hydrogen embrittlement caused by acid etching must be prevented, highly caustic alkaline solutions together with complexing agents, eg, gluconates, citric acid, and EDTA, can be used to derust or remove light scale on steel alloys. These solutions are normally operated at concentrations of 120–360 g/L and at temperatures above 93°C. Even under these conditions, alkaline deoxidizers are significantly slower than acids in removing the surface contaminants.

3. Economic Aspects

The widespread use of chemical etchants to remove oxides and certain other foreign materials from metal surfaces stems primarily from the very low cost of the pickle. Also important is the high efficiency and versatility in cleaning simple configurations such as flat sheet or wire, as well as workpieces of intricate, complex design

where mechanical cleaning would be cumbersome and in many cases incomplete. Sulfuric and hydrochloric acids sell at about \$0.10–0.13/L, and caustic soda at about \$0.53/kg. The cost of pickling or chemical cleaning is thus only a fraction of a dollar for 90 m^2 (1000 ft^2), even when factoring ancillary costs such as energy, vendor margins, and disposal into the process. As an example, in a wire mill processing scaled steel wire at a cost of approximately \$4/m^2 (\$350/ft^2), the cost of cleaning off the oxide using 10% inhibited sulfuric acid is only about \$0.0004/m^2 (\$0.04/ft^2). This includes the cost of metal lost via dissolution by the acid; chemical cost, including a proprietary inhibitor at \$2.40/L; and waste treatment. Although the cost of pickling or oxide removal of such metals as aluminum, stainless steel, and copper alloys may be more expensive per square unit of metal treated, the cost of cleaning relative to the cost of the metal is similar.

4. Health and Safety

Acids such as sulfuric, hydrochloric, nitric, and especially hydrofluoric as well as strong alkalies such as caustic soda and caustic potash are extremely corrosive to animal and vegetable tissue. Extreme caution must be taken to prevent skin contact, inhalation, or ingestion. Violent reactions may occur when dissolving or diluting many of these chemicals with water.

Proprietary additives used with or formulated into acids and alkalies to impart desirable characteristics such as inhibition, improved wetting, and chelating may also contain toxic or carcinogenic chemicals. Producers of proprietary metal finishing chemicals are researching ways to replace and eliminate hazardous chemicals traditionally used in the pickling industry. As of this writing, however, new technology has not fully replaced the old. The Material Safety Data Sheet (MSDS) for each chemical or proprietary blend used in a process must be thoroughly read and understood before the process is put into practice.

BIBLIOGRAPHY

"Solvent Cleaning, Alkali Cleaning, and Pickling and Etching" in *ECT* 1st ed., under "Metal Surface Treatment," Vol. 9, pp. 1–9, by A. Mendizza, Bell Telephone Laboratories, Inc.; "Cleaning, Pickling, and Related Processes" in *ECT* 2nd ed., under "Metal Surface Treatments," Vol. 13, pp. 284–292, by S. Spring, Oxford Chemical Division, Consolidated Foods Corp.; in *ECT* 3rd ed., Vol. 15, pp. 296–303, by G. L. Schneberger, General Motors Institute.

General References

1. *Metals Handbook*, 9th ed., Vol. **5**, ASM International, Materials Park, Ohio.
2. K. Hacias, *Wire J. Int.*, 86–89 (Jan. 1995).
3. M. Murphy, ed., *Metals Finishing, Guidebook and Directory*, Vol. **90**, Metal Finishing, Hackensack, N.J., 1992.

KENNETH HACIAS
Henkel Corporation

Related Articles

Metal Surface Treatments, Case Hardening; Metal Surface Treatments, Cleaning; Metal Surface Conversion Treatments