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DEPARTMENT OF ENVIRONMENTAL PROTECTION
FLORIDA
Pollution Prevention Program

Metal Working Tip Sheet

Heat Treating

Heat treating refers to the heating and cooling operations performed on metal workpieces to change their mechanical properties, metallurgical structure, or residual stress state. Heat treating includes stress relief treating, normalizing, annealing, austenitizing, hardening, quenching, tempering, and cold treating. Annealing, as an example, involves heating a metallic material to, and holding it at, a suitable temperature, followed by furnace cooling at an appropriate rate. Steel castings may be annealed to facilitate cold working or machining to improve mechanical or electrical properties, or to promote dimensional stability. Gray iron castings may be annealed to soften them, or to minimize or eliminate massive eutectic carbides, thus improving their machinability.

PROCESS DESCRIPTION

Heating, quenching, descaling, cleaning, and masking operations generate most of the waste in the heat treating industry. Table 1 lists the waste generating processes and waste characteristics.

Table 1 Waste Generating Processes

Process	Waste
Heat treating	Refractory material
Case hardening	Spent salt baths
Quenching	Spent quenchants
Descaling	Spent abrasive media
Cleaning and masking	Solvents, abrasives, copper plating waste

Heat Treating Other Than Case Hardening

Heat treating is performed in conventional furnaces, or salt bath or fluidized bed furnaces. The basic conventional furnace consists of an insulated chamber with an external reinforced steel shell, a heating system for the chamber, and one or more access doors to the heated chamber. Heating systems are direct fired or indirect heated. In direct fired furnace equipment, the work being processed is directly exposed to the products of combustion, which are generally referred to as flue products. Gas- and oil-fired furnaces are the most common types of heat treating equipment. Indirect heating is performed in electric and radiant tube heated furnaces. Tubes for the latter can be electrically heated or fired with gas or oil. The heating operations of stress relieving, normalizing, annealing, austenitizing, and tempering *do not* generate hazardous waste. Refractory materials (furnace lining) are the only wastes generated, and they are disposed as nonhazardous waste.

Salt bath furnaces are commonly used to obtain better thermal control and more rapid heating. They consist of pots of molten salt heated by direct resistance methods (an electric current is passed through the salt) or by indirect fossil fuel or electric resistance methods (the pot is placed in a furnace-like enclosure).

In the fluidized bed furnace, gas is passed up through a bed of dry, finely divided particles, typically aluminum oxide. The turbulent motion and rapid circulation of the particles in the furnace provide heat transfer rates comparable to those of conventional salt bath equipment. The parts to be treated are submerged in a bed of fine solid particles held in suspension by an upward flow of gas. Heat input to a fluidized bed can be achieved using:

- Internal resistance heated beds. The particles and gas are heated by sheathed internal resistance heated elements.
- External resistance heated beds. A fluidized bed contained in a heat resisting pot is heated by external resistance elements.
- Direct resistance heated beds. Electrically conducting material, such as carbon powder or silicon carbide, is employed as the bed material.
- Internal combustion gas fired beds. An air/gas mixture is used for fluidization and ignited in the bed, generating heat by internal combustion.
- External combustion heated beds. A fluidized bed, contained in a heat resisting pot, is heated by external gas firing.
- Submerged combustion fluidized beds. Combustion products pass directly through the mass to be heated.

Dragout loss of fluidized bed particles ,which are removed by agitating, gas blowing, and bouncing, can be minimized by water spraying. Recovered particles can then be reused after being dried, screened, and returned to the bed.

Case Hardening

Case hardening processes supply a quantity of carbon or nitrogen for absorption and diffusion into the steel. These processes are carried out in either gas phase furnaces or in salt bath furnaces that are similar to the furnaces that are used for other heat treating processes. Case hardening performed in liquid media is the major source of waste.

The salt baths in liquid carburizing, liquid nitriding, and liquid cyaniding processes are considered hazardous when spent. Typical baths contain molten sodium, potassium cyanide, and cyanate salts. In carburizing processes, after the workpieces are heat treated, they are quenched for the purpose of hardening. The quenching media becomes contaminated with the cyanide used in case hardening and must be disposed as hazardous waste. Spent quenching oil and wastewater generated in the cyanide heat treating cycle become hazardous waste because cyanide salts are transferred to the oil bath or water bath as a result of dragout.

Gas carburizing burns natural gas in a sealed furnace and produces no hazardous waste. Gas nitriding employs ammonia gas to supply the nitrogen and produces no solid hazardous waste.

Salts that contain barium compounds are sources of hazardous waste. These salts are used in high temperature applications such as hardening high speed steel, hot work steels, and other air hardening tool steels.

Quenching

Quenching is an integral part of liquid carburizing, liquid cyaniding, and liquid nitriding. When the surface of the steel absorbs a sufficient quantity of carbon or nitrogen from a hot molten salt bath, the part is often quenched in mineral oil, paraffin base oil, water, or brine to develop a hard surface layer. Tool steels that are liquid nitrided are not normally quenched, but air cooled.

Quenching, a cooling operation in metal heat treating, can be accomplished by immersing hot workpieces in water, oil, polymer solution, or molten salt, depending on the cooling rate required. In spray quenching, streams of the quenching liquid are applied under pressure to hot workpieces. Fog quenching is the application of a fine fog, or mist of liquid droplets, and the gas carrier as cooling agents. Gas quenching cools faster than still air and slower than oil. Water and brine are the quenchants most commonly used for carbon steel. Oil quenching is less drastic than water quenching and produces less distortion.

Parts should never be transferred directly from a cyanide containing carburizing bath to a nitrate-nitrite quench bath. This can result in a violent reaction and may cause an explosion.

Quenching is a significant source of waste in the heat treating industry. The waste consists of spent quenching media in the form of spent baths and wastewater that are generated when quenched workpieces are washed to remove remaining salt or oil after the quenching operation.

Descaling

The intense heat of air or atmosphere in furnaces may cause an oxide scale to form on the surface of workpieces. This scale must be removed before additional processing can take place. Descaling can be accomplished by sandblasting or by pickling. In pickling, the workpieces are immersed in a hot acid bath to clean the surface of all impurities. The acid dissolves the metal oxide and ferric oxide rust and scale. The workpieces are then rinsed in water to remove the acid.

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Parts Cleaning and Surface Masking

Supportive operations in heat treating (such as parts cleaning and surface masking) generate hazardous waste. Masking by plating prevents carburizing or nitriding of metal workpieces or selected parts of workpieces during the heating cycle. Plated deposits of bronze or copper are the most common coatings. Nickel, chrome, and silver are also effective, but higher costs restrict their use to special applications. When the application does not permit the retention of protective plate on the finished part after heat treating, selection of the coating is important from the standpoint of subsequent stripping. Copper and silver are the easiest to strip. Because of the cost and the ease of stripping, copper is most widely used for plating.

WASTE DESCRIPTION

Spent cyanide baths, quenchants, abrasive media, refractory material, and plating, and wastewater created in the parts cleaning operations, generate the most waste in the heat treating industry. The following sections characterize waste from case hardening baths and pots, quenching baths, parts cleaning, and masking operations.

Case Hardening Baths and Salt Pots

Significant waste is generated in heat treating operations where cyanide containing baths are used. In normal bath maintenance, sludge collected at the bottom of the pot is removed daily. When disposed, this sludge is treated as hazardous waste. As the bath media is depleted, bath pots corrode. To minimize corrosion of the pot at the air-salt interface, salts are completely changed every three to four months.

Quenching

Cyanide salts adhering to parts contaminate the quenching bath, rendering the bath a hazardous waste when spent. Salt that remains on the parts after the parts reach room temperature must be washed off, usually in water.

Waste is generated in the following forms:

- Residue (salt sludge) from oil baths used for quenching cyanided, liquid carburized, and nitrided parts
- Spent water and brine quenchants used for liquid cyanided, liquid carburized, and liquid nitrided parts
- Quenching process dragout waste from other than case hardening

Dragout in the form of oil is removed from the parts by hot water washing. Oil is one of the most commonly used quenchants in the heat treating industry, therefore the quantity of waste oil that must be handled as a hazardous waste is substantial.

Parts Cleaning and Masking

Additional sources of hazardous waste in the heat treating industry are parts cleaning and masking operations. Solvent cleaning, aqueous cleaning, and abrasive cleaning wastes are generated for disposal or treatment.

The most popular masking operation is copper plating. The hazardous wastes generated in this process are identical to metal finishing industry wastes.

REFERENCES

For more information on the types of hazardous waste generated in plating operations see US Environmental Protection Agency, *Guides to Pollution Prevention: The Fabricated Metal Industry*.

If waste generated is expected to be hazardous, and information regarding storage and handling is needed, check with the Florida Department of Environmental Protection, Hazardous Waste Management Section (850) 488-0300.