The CAIROX® process for quality metal surface cleaning

Enhanced smut & scale removal
**The CAIROX® Process for Metal Surface Cleaning Features and Benefits:**

Incorporated into your wire, rod or parts cleaning line, the CAIROX process for smut and scale removal will provide the following features and benefits:

- Removes Stubborn Smut and Scales: including annealing and acid smuts.
- Improves Quality: shorter acid pickling contact times produce a smoother, cleaner wire, rod or part.
- Improves Plating and Drawing: cleaner surfaces increase die life and reduce rejects.
- Improves Processing: The CAIROX process makes wire, rods or parts easier to coat or fabricate.

**How is it used:**

Smut and scale typically consist of lower oxides of metallic substances or reduced carbonaceous soot produced by previous processes. Smut and scale are oxidized or conditioned by the CAIROX/caustic bath, so that subsequent acid pickling will quickly and completely remove the oxidized substances from the rod or wire.

A mild steel tank with a heating device to raise the temperature of the CAIROX bath to 190-205 °F (88-96 °C) is installed in the cleaning line, usually ahead of the acid pickle tanks. This is followed by a water rinse to remove excess CAIROX solution, and then followed with a short acid pickle. A cleaning cycle is set up to allow a minimum of 10 minutes in the CAIROX/caustic bath prior to rinsing and acid pickling. In many stainless steel and tool steel cleaning lines, a combination of nitric and hydrofluoric acid is used for pickling. For extremely difficult-to-remove scale, the acid pickle may precede the CAIROX/caustic bath. As the CAIROX solution oxidizes the scale and smut, a sludge containing manganese dioxide and other insoluble metallic oxides will form in the tank. This sludge must be removed on a regular basis, since it can seriously hamper the effectiveness of the cleaning operation. There are three important parameters in the operation of the CAIROX/caustic bath.

1. **Concentration**
   CAIROX concentration must be maintained between 2-5%, caustic concentration should be maintained between 6-10% and must not exceed 12%.

2. **Temperature**
   Temperature must be maintained between 190-205 °F (88-96 °C). Higher temperatures result in abnormally high consumption of permanganate and caustic. Lower temperatures result in longer cleaning times or poor cleaning.

3. **Time**
   Time must be determined. Smut may be easily removed in minutes, while scale may take longer. Operating experience will best determine the proper cleaning conditions for each type of rod, wire, or part.

**Typical CAIROX Method Cleaning Line**

Wire to be cleaned is first soaked in a hot CAIROX/caustic bath . . .

Then the wire is rinsed of excess solution in a water bath . . .

Then the wire receives a shortened acid pickle . . .

After a final rinse or acid dip, the wire is free of smut and scale.
Removal of Annealing Smut:

Organic materials, such as fats or the organic constituents of drawing lubricants (stearate, soap), left on the surface of carbon and alloy steel wires during manufacture, are completely oxidized and removed by CAIROX potassium permanganate. These substances are particularly difficult to remove without permanganate when the organic constituents have been “cracked” to acid-insoluble products by annealing. In protective atmosphere annealing, drawing lubricants of an organic nature are mainly carbonized into carbon residues. Protective gases containing carbon, e.g. carbon monoxide, carbon dioxide, methane, propane etc. may themselves be subject to cracking during heat treatment and lead to carbon residues.

The finely-distributed carbon deposit on the wire surface gives a black appearance and is difficult to remove by mechanical methods. It is also insoluble in pickling acids and can only be removed incompletely by over-pickling (removing the metal or metal oxide layer below).

The practical advantages of the CAIROX process are as follows:

• A clean, residue-free surface with complete degreasing.

• Considerable reduction of pickling time and therefore:
  - avoidance of overpickling (attack on the metal base) allowing a good finish.
  - avoidance of pickling residues, particularly with sulfuric acid.
  - reduction of hydrogen embrittlement and general reduction of surface damage due to excessive pickling times.

• Notable improvement in die life due to clean, purely metallic surfaces.

High alloy steels in particular are sometimes susceptible to the formation of extremely hard metal carbides under the conditions of the annealing process. These metal carbides can quickly destroy dies and the wire surface.

Removal of Acid Smut:

Steel pickled in sulfuric acid is generally not completely bright, but covered with a dark, stubborn deposit. The black deposit consists of ferrous salts and undissolved alloying elements such as C, Si, P, S, Cu, Ni and As. The deposit must be cleaned off if a subsequent surface coating is to be applied. Water rinsing is generally not successful, as the pickling residue adheres too strongly. Inconvenient mechanical methods such as sand or gravel scrubbing or hard brushing are sometimes used to remove this acid smut. A brief acid pickle, followed by a CAIROX/caustic treatment and then a short-term acid dipping gives a residue-free wire surface.

The CAIROX Process versus Salt Bath Treatment:

The CAIROX process is often preferred to salt bath treatment when processing Monel 400 and 500, titanium containing nickel alloys, pure nickel steels with low content of other alloying elements, Inconel 600 and Incoloy alloys. The reasons are: 1) unlike salt baths, no staining is left, 2) high temperature salt baths can lead to structure damage, and 3) the highly insoluble titanium nitride in the scale is removed. A pickling pretreatment in nitric-hydrofluoric acid may be given. A sulfuric acid pickling is typically used after the permanganate dip. Contact Carus for more information regarding quality metal surface cleaning and enhanced smut & scale removal with CAIROX.

Alloy Wire Case Study:

An American firm uses alloy carbon steels and structural steels to produce wire for the manufacture of screws:

The cleaning method is:
1. Removal of mill scale by hot (80 °C) inhibited sulfuric acid pickle (30 min. dip).
2. After rinsing, the wire is lime coated and given a single draft reduction in calcium stearate.
3. Anneal in protective atmosphere.
4. 30-min. in CAIROX/caustic (5% CAIROX and 10% NaOH) at 95 °C in a 15 m³ bath.
5. Water rinse, followed by second 10-min. sulfuric acid pickle.
6. Final water rinse, followed by lime coating, drawing to required size and surface plating treatment.

The plant reports producing better quality wires using only 600 grams CAIROX per ton of steel. A reduction of pickling time from 1 hour to 10 minutes was noted as an additional benefit.

CARUS CHEMICAL COMPANY
Tool Steels:

The CAIROX process can be applied to cold working tool steels, hot working tool steels, and high speed steels.

The following cleaning treatment is given:

1. Hot rolled and annealed rod is given a 20 min. treatment in an oxidizing salt bath.
2. After rinsing (cooling), a 20 min. hot pickle in 15% inhibited sulfuric acid, where pickling deposits are formed.
3. Without rinsing, the coils are dipped in a CAIROX/caustic solution for 20 min. at 95 °C.
4. Short term dipping (several seconds) in sulfuric acid and subsequent lime coating and drawing to required size.

The advantages of the CAIROX process include:

- Complete removal of pickling deposits.
- Significant improvement in die life by removal of very hard deposits of a carbide nature.
- Improved surface quality, due to an absence of carbide deposits and consequent surface damage in drawing.

Welding Wire Process:

CAIROX solutions have been used for welding wire cleaning with the following process:

1. Hot rolled wire is dipped 30 min. in CAIROX/caustic solution (95 °C).
2. High pressure rinse, then 30 min. pickling in hot inhibited sulfuric acid.
3. Water rinse, then 3-5 min. dip in non-inhibited HCl (40 °C)
4. After final rinse, the wire is usually coppered or borax coated before drawing. Wire is drawn from 5.6 mm to 1.5 mm in 8 dies.

The consumption of permanganate was found to be a maximum of 1 kg CAIROX/ton steel.

Advantages reported include:

- Complete removal of rolling scale
- Reduction of pickling time in sulfuric acid by half and hydrochloric by 15 min., thereby avoiding:
  - holing by acid attack
  - pickling residues
  - hydrogen embrittlement and giving
  - a better surface finish
- Doubling of die life

Technical Service Assistance:

Carus Chemical Company has perfected techniques for using CAIROX potassium permanganate to condition smut and scale. We're prepared to share these techniques with you.

If you have a cleaning problem, call Carus for a cleaning evaluation, or complete the metal surface cleaning fax-back form. We will give you a recommended cleaning procedure to help solve your cleaning problem. If you're satisfied with the results, we'll be glad to work with you to incorporate the CAIROX/caustic bath in your cleaning line.

We can demonstrate the use of instruments necessary for proper chemical control that is essential for good bath performance. We can also assist you with any technical problems you may encounter. If necessary, our technical service staff can visit your plant to work with you.

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