

PHORGOTTEN PHENOMENA

# Rouging— A Discoloration of Stainless Steel Surfaces

RICHARD A. CORBETT, *Corrosion Testing Laboratories, Inc.*

**R**ouging is a thin film—usually reddish-brown or gold in color—of iron oxide ( $\text{Fe}_2\text{O}_3$ ) or hydroxide [ $\text{Fe}(\text{OH})_3$ ], typically on stainless steels (SS). The contrast between the film and shiny metal accentuates this aesthetics problem. The rouge film typically wipes off easily with a light cloth (Figure 1), but it reforms while the process fluid is in contact with the SS. This problem is most common in the pharmaceutical industry on the interior surfaces of high-purity water (water for injection) distillation units, storage tanks, distribution systems (piping, valves, pump housings, fittings, etc.), and process vessels.

As stated, rouge is  $\text{Fe}_2\text{O}_3$  (rust), but the film may contain not only iron but also chromium and nickel compounds in various forms, and hence the film may vary in color and tenacity (Figure 2). Rouging occurs more often on type 304/304L SS (UNS S30400/S30403) than on type 316/316L (UNS S31600/

S31603), and less on electropolished surfaces than mechanically polished surfaces. Particles of rust can become dislodged and be dispersed throughout a piping distribution system, often collecting on in-line filters.

SS is “stainless” because the alloy forms a thin, protective, tenacious, transparent oxide film that protects it against destructive corrosive species in aqueous solutions. This film is composed of chromium oxide, and is said to make the steel “passive” against corrosion. The exact nature of this film remains debatable. In fact, its exact structure and nature may vary depending on a number of variables.

It is known that the film forms very rapidly in most environments that are not actively reducing. Exposure to moist air provides this passivation within a matter of minutes, and the film thickens with time. Exposure to oxidizing acids, particularly nitric acid ( $\text{HNO}_3$ ), only speeds up the process. Therefore, the treatments described as “passivation” are actually cleaning procedures—passivation of clean, uncontaminated SS occurs spontaneously, and no chemical treatment is needed to facilitate it.

The passive layer on the surface of SS can be broken down by the interaction of ultrapure water, which is devoid of ionic species and leads to rouging or rust blooms. The water’s ionic pull is strong enough to strip the protective chromium oxide off the steel surface. This causes the SS to re-passivate by forming another layer of oxide film, which incorporates the rouge and causes discoloration. During the brief re-passivation period, a thin layer of the SS dissolves, or corrodes.

The major elements in SS are iron, chromium, and nickel. The chromium and nickel ions are soluble and go into the bulk solution. The iron, however, precipitates above a pH of 3 as  $\text{Fe}(\text{OH})_3$ , that readily oxidizes to  $\text{Fe}_2\text{O}_3$ , which is red (rouge) in color. If this progresses uniformly across the surface of the steel and the de-passivation/re-passiva-

**FIGURE 1**

Rouge wipes easily off the SS substrate but will reform.

**FIGURE 2**

Rouging comes in many colors and degrees of tenacity.

tion process is cycled many times, the surface of the SS takes on a light-gold to dark-brown appearance depending on the ionic state of the various oxide layers and their depth (Figure 3).

Another process, which is more damaging, is the creation and propagation of pits. Nonmetallic inclusions such as sulfides and oxides inherently result from alloy production. They are dispersed throughout the metal and are highly susceptible to attack by aggressive environments. These inclusions typically dissolve in a particular

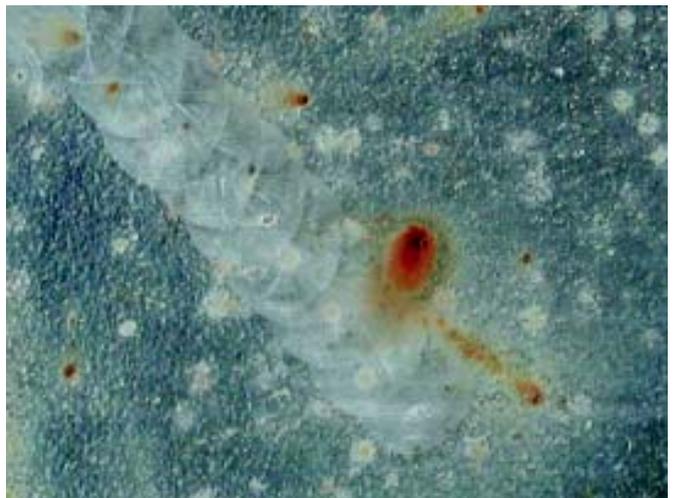
solution or environment and leave behind a microvoid. This void becomes an occluded cell where solution chemistry can differ from the bulk solution. If the SS does not readily repassivate, then corrosion attack within the void can propagate. The corrosion products within the now-formed pit spill out onto the bulk metal surface, producing localized rouging or rust blooms (Figure 4). After a pit initiates, it may propagate and progress until through-wall penetration occurs. Alternatively, if the pit

heals, the activity ceases and no propagation occurs. However, the red product remains to indicate that something has occurred.

SS pitting is known to occur in chloride-containing environments such as those frequently encountered in the pharmaceutical and chemical process industries. It has been found that, for a particular SS in a particular chloride environment, there is a specific temperature above which certain SS begin to corrode immediately and below which corrosion does not begin for an

**FIGURE 3**

After repeated cycles, a clean SS surface can take on a multicolored appearance.

**FIGURE 4**

Rouging or rust blooms identify pit sites.

indefinite time. This temperature is called the critical pitting temperature (CPT). Although corrosion begins immediately when the SS is exposed above the CPT (as measured by potentiostatic monitoring [ASTM G150<sup>1</sup>]), it generally takes from 24 to 720 h of exposure for pitting to develop to the extent that pit sites are visible—as typified by localized roughing, even at 20X magnification aided by surface-scratching techniques. Therefore, in many instances in cyclic service or batch production, SS is briefly (i.e., 1 to several h) exposed to conditions above the CPT. Although corrosion damage is accumulated, intense maintenance and cleaning practices may extend the service life of such equipment. However, anything that extends the period of exposure

above the CPT—whether larger equipment or an unrelated deviation in process schedule—can lead to severe corrosion damage in a single cycle in batch operation.

## Reference

1. ASTM G150, "Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels," Annual Book of ASTM Standards (West Conshohocken, PA: ASTM, 1997).

**Richard A. Corbett** is a Principal Corrosion Scientist at Corrosion Testing Laboratories, Inc., 60 Blue Hen Drive, Newark, DE 19713-3406. He has been working in the fields of corrosion and materials engineering, materials problem solving, and failure analysis of products and structures for more than 25 years. He received a NACE Distinguished Service Award and is a Fellow of the Institute of Corrosion, a NACE Corrosion and Cathodic Protection Specialist, and a 28-year NACE member. *MP*