

Common etchants for Irons and Steels

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*Etchants for revealing macrostructures in iron and steel**

Etching reagent	To reveal	Composition	Remarks
Hydrochloric acid	Segregation, porosity, cracks, depth of hardened zones in tool steels	50 mL H ₂ O, 50 mL HCl	Temperature: 71–82°C (160–180 °F). Time: 1–60 min, depending on type of steel and type of structure to be developed.
Mixed acids	Welds, segregation, cracks, and hardened zones	50 mL H ₂ O, 38 mL HCl, 12 mL H ₂ SO ₄	Temperature: 93°C (200°F), Time: 15–45 s, or Temperature: 22°C (72°F), Time: 2–4 hours
Ammonium persulfate (Rawdon)	Welds	90 mL H ₂ O 10 mL (NH ₄) ₂ S ₂ O ₈	Surface should be rubbed with absorbent cotton during etching. Time: etched to desired contrast
Nitric acid	Same as hydrochloric acid	75 mL H ₂ O 25 mL HNO ₃	Use cold on large surfaces that cannot be conveniently heated
Oberhoffer's reagent	Develops dendritic pattern in steel. Iron enriched areas are darkened.	500 mL H ₂ O 30 g FeCl ₃ 0.5 g SnCl ₃ 1 g CuCl ₂ 500 mL ethyl alcohol 500 mL H ₂ O	Use at room temperature. Immerse about 20 s.
Kalling's reagent	Develops dendritic pattern in steel; attacks ferritic and martensitic stainless steels. Ferrite darkened; martensite darker; austenite light	33 mL H ₂ O 1.5 g CuCl ₂ 33 mL methyl alcohol 33 mL HCl	Etch to desired contrast
Humfrey's reagent	Develops dendritic segregation	500 mL H ₂ O 25 mL HCl 60 g Cu (NH ₃) ₄ Cl ₂	Slight abrasion of surface after etching is recommended.
Bell's reagent (electrolytic)	Welds in stainless steel	40 mL H ₂ O 60 mL H ₂ NO ₃	Stainless steel cathode 5 V Time: to desired contrast.
Watertown arsenal	For carbon and stainless steels, general structure	50 mL H ₂ O 12 mL H ₂ SO ₄ 38 mL HCl	Temperature: 71–82 °C (160–180 °F) Time: 10–60 min Used with cut or ground surfaces.
Dilute aqua regia	For high-alloy steels, Fe-Co high-temperature alloys	25 mL H ₂ O 25 ml HNO ₃ 50 mL HCl	Time: 10–15 min at room temperature
Pearcy and co-workers	Maraging steel macrostructure	60 mL lactic acid 20 mL HNO ₃ 10 mL HCl	Use at room temperature
Burg and Weiss	Nitriding steels macrostructure	85 mL H ₂ O 15 mL ammonium persulfate	Temperature: 71 °C (160 °F) Time: 10 min
Marbles reagent	General etch for austenitic stainless steel	50 mL H ₂ O 10 g CuSO ₄ 50 mL HCl	Solution can be heated
Miller and Houston	Welds and general macrostructure of austenitic stainless steel	90 mL H ₂ O 10 g CrO ₃	Use electrolytically with polished surface. Platinum or stainless steel cathode. Temperature: 16–38 °C (60–100 °F) 6 V Time: 2–7 min

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This datasheet is taken from the new 350-page ASM book *Metallographer's Guide: Practices and Procedures for Irons and Steels*. The table of contents and a sample chapter may be viewed at www.asminternational.org. It may be ordered online, or call customer service at 800/336-5152. Cost to ASM members is \$152.

Etchants for revealing macrostructures in iron and steel*, continued

Etching reagent	To reveal	Composition	Remarks
Loria (nitrosulfuric acid etch)	As-cast structure and grain size in cast steels	20 mL H ₂ O 20 mL HNO ₃ 10 mL H ₂ SO ₄	Use at room temperature
Nielsen	Stress-corrosion cracks in austenitic stainless steel	95 mL methyl alcohol 5 mL bromine	Temperature: room Time: approx. 1 h crack pattern vividly revealed

*Before using any chemicals, materials safety data sheets (MSDS) should be reviewed.

Etchants for revealing phases and constituents in ferrous materials

Etching reagent	Composition	Remarks
Ferrite grain boundaries: Nital	1 to 5 mL HNO ₃ (nitric acid) 99 to 95 mL ethyl	The authors recommend a 2% solution; usually samples are etched 10 to 20 s with a gentle agitation and the polished surface facing upward to reveal the ferrite grain boundaries. To reveal all the grain boundaries, the last polishing step should be with silicon dioxide for at least 60 s, and the sample should then be etched shortly after polishing before a passive layer forms to prevent an even etch. If the sample is to be examined in the as-polished condition, it should be repolished for 10 to 15 s with silicon dioxide prior to etching. Note: A nital etch is not recommended for etching pearlite, because it does not etch evenly.
Ferrite grain boundaries: Marshall's reagent	Stock solution A 100 mL H ₂ O 8 g oxalic acid 5 mL H ₂ SO ₄ (sulfuric acid) Stock solution B H ₂ O ₂ (30%) (hydrogen peroxide)	Excellent etchant to show both equiaxed and cold-worked micro-structures. Mix stock solution A to equal parts of solution B just prior to etching. Place the polished face of the sample on its side during immersing in the etchant to prevent or minimize pitting. If the sample does not react to the reagent, add 1 mL hydrofluoric acid to 100 mL of solution. If a haze covers the surface, remove by placing the sample in a 3% aqueous disodium ethylenediamine tetraacetate EDTA solution. Place the sample and solution in an ultrasonic cleaner for several minutes. Flush the sample with water, then alcohol, then dry.
Ferrite grain boundaries: Beraha's	100 mL H ₂ O 10 g Na ₂ S ₂ O ₃ (potassium thiosulfate) 3 g K ₂ S ₂ O ₅	Pre-etch for 3 s with 2% nital. Etch in Beraha's reagent with the polished side of the sample face up for 45 s; do not agitate. Rinse with water, flush with alcohol, and dry. If the sample is over- or under-etched, remove etchant by polishing with 0.3 aluminum oxide for 15 s, followed by silicon dioxide for 45 s, and re-etch.
Pearlite structure: 4% picral	96 mL ethyl alcohol 4 g picric acid 5 drops 17% zephiran (benzalkonium chloride, Sanofi-Synthelabo Inc.) per 75 mL solution	Picral is one of few etchants that improves with use. A common practice is to age the etchant by placing piece of a ground steel into the solution until the etchant turns a dark green. This technique makes the etching time constant, usually 20 s for pearlite or Fe ₃ C carbides. The etchant can be saved for future use. Samples with more than 0.5% Cr, add 5 drops of hydrochloric acid per 100 mL of solution.
Pearlite structure: Marshall's reagent	Stock solution A 100 mL H ₂ O 8 g oxalic acid 5 mL H ₂ SO ₄ Stock solution B H ₂ O ₂ (30%)	Excellent etchant to outline pearlite colony boundaries.
Pearlite structure: Alkaline sodium picrate	100 mL H ₂ O, 25 g NaOH, 2 g picric acid	Bring the solution to a low boil; do not boil dry. Etching time: 5–10 min. The solution will attack Bakelite mounts; thermosetting epoxy mounts are recommended. The solution will color cementite but will not color carbides with high (10%) Cr content. The solution will also attack sulfides and delineate grain boundaries in steels that have been cooled slowly.
Pearlite structure: Klemm's reagent	50 mL H ₂ O Na ₂ S ₂ O ₃ enough for saturation 1 g K ₂ S ₂ O ₅	Tint etches pearlite. Etching time: 40–120 s. Etch in Klemm's reagent with the polished side of the sample face up, do not agitate. Ferrite appears black-brown, but carbides, nitrides, and phosphides remain white. Phosphorus distribution can be detected more sensitively than with phosphorus reagents based on copper salts.