



Designation: E407 – 23

# Standard Practice for Microetching Metals and Alloys<sup>1</sup>

This standard is issued under the fixed designation E407; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the U.S. Department of Defense.*

## 1. Scope

1.1 This practice covers chemical solutions and procedures to be used in etching metals and alloys for microscopic examination. Safety precautions and miscellaneous information are also included.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific cautionary statements, see 6.1 and Table 2.

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

E7 Terminology Relating to Metallography

E2014 Guide on Metallographic Laboratory Safety

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definition of terms used in this standard, see Terminology E7.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *tint etch*—an immersion etchant that produces color contrast, often selective to a particular constituent in the microstructure, due to a thin oxide, sulfide, molybdate, chromate or elemental selenium film on the polished surface that

reveals the structure due to variations in light interference effects as a function of the film thickness (also called a “stain etch”).

3.2.2 *vapor-deposition interference layer method*— a technique for producing enhanced contrast between microstructural constituents, usually in color, by thin films formed by vacuum deposition of a dielectric compound (such as ZnTe, ZnSe, TiO<sub>2</sub>, ZnS or ZnO) with a known index of refraction, generally due to light interference effects (also known as the “Pepperhoff method”).

## 4. Summary of Practice

4.1 Table 1 is an alphabetical listing of the metals (including rare earths) and their alloys for which etching information is available. For each metal and alloy, one or more etchant numbers and their corresponding use is indicated. Alloys are listed as a group or series when one or more etchants are common to the group or series. Specific alloys are listed only when necessary. When more than one etchant number is given for a particular use, they are usually given in order of preference. The numbers of electrolytic etchants are *italicized* to differentiate them from non-electrolytic etchants.

4.2 Table 2 is a numerical listing of all the etchants referenced in Table 1 and includes the composition and general procedure to be followed for each etchant.

4.3 To use the tables, look up the metal or alloy of interest in Table 1 and note the etchant numbers corresponding to the results desired. The etchant composition and procedure is then located in Table 2, corresponding to the etchant number.

4.4 If the common name of an etchant is known (Marble’s, Vilella’s, etc.), and it is desired to know the composition, Table 3 contains an alphabetical listing of etchant names, each coded with a number corresponding to the etchant composition given in Table 2.

## 5. Significance and Use

5.1 This practice lists recommended methods and solutions for the etching of specimens for metallographic examination. Solutions are listed that highlight the phases and constituents present in most major alloy systems.

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee E04 on Metallography and is the direct responsibility of Subcommittee E04.01 on Specimen Preparation.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard’s Document Summary page on the ASTM website.

## 6. Safety Precautions

6.1 Before using or mixing any chemicals, all product labels and pertinent Safety Data Sheets (SDS) should be read and understood concerning all of the hazards and safety precautions to be observed. Users should be aware of the type of hazards involved in the use of all chemicals used, including those hazards that are immediate, long-term, visible, invisible, and with or without odors. See Guide E2014 on Metallographic Laboratory Safety for additional information on; Chemical Safety, Electrolytic Polishing/Etching and Laboratory Ventilation/Fume Hoods.

6.1.1 Consult the product labels and SDSs for recommendations concerning proper protective clothing.

6.1.2 All chemicals are potentially dangerous. All persons using any etchants should be thoroughly familiar with all of the chemicals involved and the proper procedure for handling, mixing, and disposing of each chemical, as well as any combinations of those chemicals. This includes being familiar with the federal, state, and local regulations governing the handling, storage, and disposal of these chemical etchants.

6.2 Some basic suggestions for the handling and disposing of etchants and their ingredients are as follows:

6.2.1 When pouring, mixing, or etching, always use the proper protective equipment, (glasses, gloves, apron, etc.) and it is strongly recommended to always work under a certified and tested fume hood. This is imperative with etchants that give off noxious fumes or vapors that may accumulate or become explosive. In particular, note that solutions containing perchloric acid must be used in an exclusive hood equipped with a wash down feature to avoid accumulation of explosive perchlorates. See Guide E2014 on Metallographic Laboratory Safety for additional information on safety precautions for electrolytes containing perchloric acid.

6.2.2 No single type of glove will protect against all possible hazards. Therefore, a glove must be carefully selected and used to ensure that it will provide the needed protection for the specific etchant being used. In some instances it may be necessary to wear more than one pair of gloves to provide proper protection. Information describing the appropriate glove may be obtained by consulting the SDS for the chemical being used. If that does not provide enough detailed information, contact the chemical manufacturer directly. Additionally, one can contact the glove manufacturer or, if available, consult the manufacturers glove chart. If the chemical is not listed or if chemical mixtures are being used, contact the glove manufacturer for a recommendation.

6.2.3 Use proper devices (glass or plastic) for weighing, mixing, containing, and storage of solutions. A number of etchants generate fumes or vapors and should only be stored in properly vented containers. Storage of fuming etchants in sealed or non-vented containers may create an explosion hazard.

6.2.4 When mixing etchants, always add reagents to the solvent unless specific instructions indicate otherwise.

6.2.5 When etching, always avoid direct physical contact with the etchant and specimen; use devices such as tongs to hold the specimen (and tufts of cotton, if used).

6.2.6 Methanol is a cumulative poison hazard. Where ethanol or methanol, or both are listed as alternates, ethanol is the preferred solvent. Methanol should be used in a properly designed chemical fume hood.

6.2.7 When working with HF always be sure to wear the appropriate gloves, eye protection and apron. Buying HF at the lowest useable concentration will significantly reduce risk. Additionally, it is recommended that a calcium gluconate cream or other appropriate HF neutralizing agent be available for use if direct skin contact of the etchant occurs.

6.2.8 The EPA states that human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure. Therefore, when working with Cr(VI) compounds such as  $K_2Cr_2O_7$  and  $CrO_3$  always use a certified and tested fume hood. Additional information can be obtained at the EPA website<sup>3</sup>.

6.2.9 For safety in transportation, picric acid is distributed by the manufacturer wet with greater than 30% water. Care must be taken to keep it moist because dry picric acid is shock sensitive and highly explosive especially when it is combined with metals such as copper, lead, zinc, and iron. It will also react with alkaline materials including plaster and concrete to form explosive compounds. It should be purchased in small quantities suitable for use in six to twelve months and checked periodically for lack of hydration. Distilled water may be added to maintain hydration, It must only be stored in plastic or glass bottles with nonmetallic lids. If dried particles are noted on or near the lid, submerge the bottle in water to re-hydrate them before opening. It is recommended that any bottle of picric acid that appears dry or is of unknown vintage not be opened and that proper emergency personnel be notified.

6.2.10 Wipe up or flush any and all spills, no matter how minute in nature.

6.2.11 Properly dispose of all solutions that are not identified by composition and concentration.

6.2.12 Store, handle and dispose of chemicals according to the manufacturer's recommendations. Observe printed cautions on reagent bottles.

6.2.13 Information pertaining to the toxicity, hazards, and working precautions of the chemicals, solvents, acids, bases, etc. being used (such as safety data sheets, SDS) should be available for rapid consultation. A selection of useful books on this subject is given in Refs. (1-11)<sup>4</sup>.

6.2.14 Facilities that routinely use chemical etchants should have an employee safety training program to insure the employees have the knowledge to properly handle chemical etchants.

6.2.15 When working with etchants always know where the nearest safety shower, eye-wash station, and emergency telephone are located. These facilities should be close enough to the chemical working area to be effective.

<sup>3</sup> [https://iris.epa.gov/ChemicalLanding/&substance\\_nmbr=144](https://iris.epa.gov/ChemicalLanding/&substance_nmbr=144)

<sup>4</sup> The **boldface** numbers in parentheses refer to the list of references at the end of this standard.

## 7. Miscellaneous Information

7.1 If you know the trade name of an alloy and need to know the composition to facilitate the use of Table 1, refer to a compilation such as Ref (12).

7.2 Reagent grade chemicals shall be used for all etchants. Unless otherwise indicated, it is intended that all reagents conform to specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. Other grades, such as United States Pharmacopeia (USP), may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without detrimental effect.

7.2.1 Unless otherwise indicated, references to water shall be understood to mean distilled water. Experience has shown that the quality of tap water varies significantly and can adversely affect some etchants.

7.3 Methanol is usually available only as absolute methanol. When using this alcohol it is imperative that approximately 5 volume % of water is added whenever an etchant composition calls for 95 % methanol. Some of these etchants will not work at all if water is not present.

7.4 For conversion of small liquid measurements, there are approximately 20 drops/mL.

7.5 Etching should be carried out on a freshly polished specimen.

7.6 Gentle agitation of the specimen or solution during immersion etching will result in a more uniform etch.

7.7 The etching times given are only suggested starting ranges and not absolute limits.

7.8 In electrolytic etching, direct current (DC) is implied unless indicated otherwise. AC for alternating current.

7.9 A good economical source of direct current for small scale electrolytic etching is the standard 6V lantern battery.

7.10 In electrolytic etching, the specimen is the anode unless indicated otherwise.

7.11 Do not overlook the possibility of multiple etching with more than one solution in order to fully develop the structure of the specimen.

7.12 Microscope objectives can be ruined by exposure to acid fumes from etchant residue inadvertently left on the specimen. This problem is very common when the specimen or mounting media contain porosity and when the mounting material (such as Bakelite) does not bond tightly to the specimen resulting in seepage along the edges of the specimen. In all cases, extreme care should be taken to remove all traces

of the etchant by thorough washing and complete drying of the specimen before placing it on the microscope stage.

7.13 Tint etchants (13, 14-16) are always used by immersion, never by swabbing, as this would inhibit film formation. An extremely high quality of polish is required as tint etchants will reveal remaining polishing damage even if it is not visible with bright field illumination. After polishing, the surface must be carefully cleaned. Use a polyethylene beaker to contain the etchant if it contains fluorine ions (for example, etchants containing ammonium bifluoride,  $\text{NH}_4\text{FHF}$ ). The specimen is placed in the solution using tongs, polished face up. Gently agitate the solution while observing the polished surface. After coloration begins, allow the solution to settle and remain motionless. Remove the specimen from the etchant when the surface is colored violet, rinse and dry. A light pre-etch with a general-purpose chemical etchant may lead to sharper delineation of the structure after tint etching.

7.14 Specimens should be carefully cleaned before use of a vapor-deposition interference film (“Pepperhoff”) method (13, 14-17). A light pre-etch, or a slight amount of polishing relief, may lead to sharper delineation of the constituents after vapor deposition. The deposition is conducted inside a vacuum evaporator of the type used to prepare replicas for electron microscopy. One or several small lumps of a suitable dielectric compound with the desired index of refraction is heated under a vacuum until it evaporates. A vacuum level of 1.3 to 0.013 Pa ( $10^{-3}$  to  $10^{-5}$  mm Hg) is adequate and the polished surface should be about 10–15 cm beneath the device that holds the dielectric compound. Slowly evaporate the lumps and observe the surface of the specimen. It may be helpful to place the specimen on a small piece of white paper. As the film thickness increases, the surface (and the paper) will become colored with the color sequence changing in the order yellow, green, red, purple, violet, blue, silvery blue. Stop the evaporation when the color is purple to violet, although in some cases, thinner films with green or red colors have produced good results.

7.15 The ASM Handbook Metallography and Microstructure (18) provides additional advice on etching solutions and techniques for various alloys.

## 8. Precision and Bias

8.1 It is not possible to specify the precision or bias of this practice since quantitative measurements are not made.

## 9. Keywords

9.1 etch; etchant; interference method; metallography; metals; micro-etch; microscope; microstructure; Pepperhoff method; tint etch