



## Standard Practice for Preparing Sulfur Prints for Macrostructural Examination<sup>1</sup>

This standard is issued under the fixed designation E 1180; 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.

<sup>ε1</sup> NOTE—Editorial changes were made throughout in October 2003.

### 1. Scope

1.1 This practice provides information required to prepare sulfur prints (also referred to as Baumann Prints) of most ferrous alloys to reveal the distribution of sulfide inclusions.

1.2 The sulfur print reveals the distribution of sulfides in steels with bulk sulfur contents between about 0.010 and 0.40 weight percent.

1.3 Certain steels contain complex sulfides that do not respond to the test solutions, for example, steels containing titanium sulfides or chromium sulfides.

1.4 The sulfur print test is a qualitative test. The density of the print image should not be used to assess the sulfur content of a steel. Under carefully controlled conditions, it is possible to compare print image intensities if the images are formed only by manganese sulfides.

1.5 The sulfur print image will reveal details of the solidification pattern or metal flow from hot or cold working on appropriately chosen and prepared test specimens.

1.6 This practice does not address acceptance criteria based on the use of the method.

1.7 *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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section 9.

### 2. Referenced Documents

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

E 3 Methods of Preparation of Metallographic Specimens

E 7 Terminology Relating to Metallography

E 340 Test Method for Macroetching Metals and Alloys

E 381 Method of Macroetch Testing Steel Bars, Billets, Blooms, and Forgings  
E 407 Test Methods for Microetching Metals and Alloys

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, see Terminology E 7.

### 4. Summary of Practice

4.1 The sulfur print provides a means for macroscopic evaluation of the sulfur distribution in steels and cast irons by contact printing using photographic paper soaked in an aqueous acid solution, for example, sulfuric acid, citric acid, or acetic acid.

NOTE 1—No longer are there available emulsion coated half weight fiber based papers suitable for sulfur printing. Emulsion coated single weight fiber base paper is not readily available. Emulsion coated double weight fiber base paper is available, and is preferable to emulsion coated single weight resin coated paper.

4.2 The test specimen is usually a disk or rectangular section, such as used in macroetch evaluations, cut from an as-cast or wrought specimen with either a transverse or longitudinal orientation. The specimen is freshly ground smooth and cleaned to remove cutting oils, scale, abrasives, or other contaminants. The specimen should be at room temperature when sulfur printed.

4.3 A sheet of photographic paper with (usually) a matte surface finish of appropriate size is soaked in the dilute aqueous acid solution, any excess liquid removed, and the emulsion side of the paper is placed on the ground surface of the specimen. After a suitable time, the paper is removed, washed in water, fixed, washed again in water, and dried as flat as possible.

4.4 The distribution of sulfur in the specimen is revealed as a mirror image on the photographic paper as darkly colored areas of silver sulfide embedded in the emulsion.

<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 Selection and Preparation of Samples.

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

## 5. Significance and Use

5.1 The sulfur print reveals the distribution of sulfur as sulfide inclusions in the specimen. The sulfur print complements macroetch methods by providing an additional procedure for evaluating the homogeneity of a steel product.

5.2 Sulfur prints of as-cast specimens generally reveal the solidification pattern and may be used to assess the nature of deoxidation, that is, rimming action versus killed steel sulfur distributions.

5.3 Sulfur prints will reveal segregation patterns, including refilled cracks, and may reveal certain physical irregularities, for example, porosity or cracking.

5.4 The nature of metal flow, such as in various forging operations, can be revealed using sulfur prints of specimens cut parallel to the metal flow direction.

5.5 The sulfur print method is suitable for process control, research and development studies, failure analysis, and for material acceptance purposes.

5.6 The intensity of the sulfur print is influenced by the concentration of sulfur in the steel, the chemical composition of the sulfide inclusions, the aggressiveness of the aqueous acid solution, and the duration of the contact printing between the acid soaked emulsion coated paper and the ground surface of the specimen (this time is the order of seconds rather than minutes). Very low sulfur content steels will produce too faint an image to be useful for macrostructural evaluations. Selection of appropriate printing practices including selection of type of emulsion coated media, acid type and strength, will yield satisfactory prints. Very faint images in the sulfur print can be made more visible by scanning the sulfur print into a PC, and using a photo editor to increase the color saturation. Steels with compositions that produce predominantly titanium or chromium sulfides will not produce useful images.

## 6. Interferences

6.1 The specimen must be properly cleaned, otherwise dark spots will be produced which may be incorrectly interpreted as a gross sulfide segregate.

6.2 Hydrogen sulfide gas is produced while the paper is in contact with the specimen. The hydrogen sulfide is readily absorbed by the wet emulsion. The hydrogen sulfide reacts with the silver halides in the emulsion to lay down insoluble silver sulfide. If the specimen contains pores or cracks, hydrogen sulfide gas may become entrapped in these openings and may produce a brown color on the paper which may be incorrectly interpreted as a gross sulfide segregate.

6.3 If air is entrapped between the contacting paper and specimen, and is not removed, a white spot may be produced on the print. Air entrapment must be quickly removed by the use of a rubber squeegee or roller to move bubbles to the edge of the specimen.

6.4 Image blurring may result from movement of the paper during contact.

6.5 Specimens with low sulfur contents are often pre-etched before printing to expose more sulfides and enhance the image. If the pre-etchant contains sulfate ions (for example, a stainless steel specimen etched with Marble's reagent), the print will be

lightly colored, even if sulfides are not present in the steel. Such etchants should not be used for this purpose.

6.6 If chromium replaces some of the manganese in the sulfide inclusions, the print intensity for a given sulfur level will be reduced. An image will not be obtained, irrespective of the sulfur content, if titanium or chromium sulfides are present.

## 7. Apparatus

7.1 *Lighting*—If the chosen photographic paper when exposed to the existing room light for 15 min changes from white to light blue and then clears back to white when processed in the sequence of solutions, there is no need to turn off the existing white lighting, and work under amber bulb lighting; never expose the paper to sunlight.

7.2 *Shallow Container*, such as a photographic tray, is required to contain the dilute aqueous acid solution. The container must be large enough to soak the emulsion coated paper without wrinkling.

7.3 *Timing Device*, such as used in a photographic dark-room, is helpful for timing the contact printing time, and the washing and fixing periods.

7.4 *Tank*, of suitable size with cool flowing water, is required for washing the print.

7.5 *Tank, or Covered Tray*, to hold the fixing agent and the print; two can be used sequentially for faster fixing when using emulsion coated double weight fiber based paper.

7.6 *Drying*—Heated drum dryers are no longer made. Heated drying cabinets are available for fiber base prints laid horizontally on a screen. Resin coated papers can be dried with an infra red dryer very quickly. Clothes lines and cork peg boards will also work but the prints do not dry perfectly flat.

## 8. Reagents and Materials

8.1 Photographic enlarging paper with a matte finish and a fiber base is preferred. Sharper images are produced by the use of glossy photographic printing paper. Due to the smooth surface finish, it is difficult to prevent blurring of the image. Resin-coated paper when used with small area specimens can produce satisfactory results; as the area gets larger it becomes more difficult to have the paper conform to the specimen surface, because the paper base is coated with a thin layer of polyethylene which does not absorb any water and become sufficiently limp, as with fiber base paper. Photographic paper is available in cut sheets and rolls of various widths. Cut sheets are ideal if the specimen size matches the sheet size. Roll dispensed paper can be fed from a "safe" box and cut as needed. The paper sheet should be 12 to 20 mm ( $\frac{1}{2}$  to  $\frac{3}{4}$  in.) larger than the specimen around the perimeter of the specimen. If the overhang of the paper is too great then the paper will not lie tight to the edge of the specimen.

8.2 Technical or reagent grade acids, sulfuric acid, acetic acid, citric acid, etc., are used to make the solution in which the paper is soaked prior to contact printing; typical concentrations of acid are 2 to 10 % sulfuric acid, 10 to 15 % acetic acid, and 10 to 15 % citric acid.

8.3 A commercial photographic fixing solution (a liquid rapid fixer) is used to fix the sulfur print image after contact printing and washing. The fixer should be tested periodically to ensure that it is still active; set aside a print in the sunlight and

if the appearance changes then the fixer is deleted and should be replaced. Used fixer contains silver and should be disposed of in concordance with local regulations. There is not enough silver to justify having the silver recovered from the used fixer.

## 9. Hazards

9.1 Sulfuric acid,  $H_2SO_4$ , is a highly corrosive, dangerously reactive, strong oxidizing agent. It reacts with water releasing substantial heat. Add sulfuric acid very slowly to the water with constant stirring. Contact with concentrated sulfuric acid must be avoided. The dilute solution used to soak the prints is not particularly dangerous but exposure to it should be minimized and hands should be washed after any contact. The use of rubber gloves should be considered. Use tongs to handle the paper in the soaking solution. The other acids recommended for sensitizing the paper are less aggressive than sulfuric acid, however, appropriate care should be taken in mixing and handling.

## 10. Sampling and Specimens

10.1 Samples are generally selected in the same manner and extent as for macroetching, as described in Methods E 3, E 340, and E 381. Specimens are frequently prepared to represent the entire transverse cross section, in addition, depending on the purpose of the examination; the longitudinal plane may be selected, and while it is usually vertical, it may be horizontal, when required, for example, checking near the edge of a slab.

10.2 The number, orientation, and location of specimens may be subject to producer-purchaser agreement.

10.3 Specimens should be cut in a region away from any effects from hot shearing or burning; unlike macroetching, the sulfur print appearance is not affected by being within the heat affected zone (HAZ) which results from torch cutting.

10.4 Specimens can be thin enough for ease of handling, generally 12 to 25 mm (0.5 to 1 in.) thick, but may thicker, especially if being prepared on only one side for electrolytical macroetching after sulfur printing (40 to 50 mm (1.6 to 2.0 in.) thick). The surface to be contact printed should be freshly ground until smooth, and carefully cleaned. Edges should be free of flash, burrs, or scale.

10.5 Very smooth surfaces, such as produced by polishing, will promote slippage between the paper and disk resulting in blurred images.

10.6 Surface preparation (see Methods E 3, E 340 and E 381) should not produce excessive cold work at the test surface that can close up voids and cracks.

## 11. Procedure

11.1 Soak the photographic paper in the selected aqueous acid solution. The strength of the solution will depend upon the acid selected, the sulfur content of the steel and the desired printing time (the reaction is very rapid). AISI 10XX steels with sulfur contents between 0.015 wt % and 0.035 wt % are typically printed using a 2 % sulfuric acid solution. AISI 11XX series steels are more successfully printed with a 15 % citric acid solution. Steels with low sulfur contents (under 0.010 wt %) may be printed using 5 to 10 % sulfuric acid solutions.

When large size prints are desired, a longer working time may be required, necessitating a weaker acid solution.

11.2 Soak the paper in the solution for 1 to 5 min. A 3-min soak time is commonly used. Periods in excess of 5 min may cause swelling of the emulsion. The tendency of the paper to curl must be removed and the paper must become very limp.

11.3 After soaking the required time, remove the paper from the solution and allow excess solution to drip off the paper into the bath. To minimize paper movement during printing, it may be advisable to place the paper on a glass plate and remove excess liquid with a rubber roller or squeegee.

11.4 When the paper surface is relatively dry, lay the paper, emulsion side down, on the clean, ground surface of the specimen.

11.5 Any air bubbles between the test piece and paper must be carefully moved off to the edge of the sample using a roller, squeegee, sponge, or paper towel soaked in the aqueous sulfuric acid solution. This must be done carefully so that the paper does not move.

11.6 The emulsion side of the paper is kept in contact with the ground surface of the test piece for 30 s to 10 min, depending on the acid selected, the concentration of the acid solution, and the sulfur content of the steel.

11.7 When comparing test results for relatively similar specimens, it is best to standardize the selection of acid and the concentration of the bath, the soak time, and the contact time.

11.8 After the required contact time, peel off the print carefully from the disk. Avoid excessive handling of the print before washing, fixing, washing, and drying.

11.9 Wash the print in clear running water for about 15 min.

11.10 Fix the print in the photographic fixing solution for 15 to 20 min, or as long as it takes to complete the fixing.

11.11 Wash the print in clear running water for about 30 min, or as long as it takes to get all the fixer out of the paper. (Use of a fixer clearing agent, according to its instructions, permits use of a shorter wash time.) (Use of two trays of fixer solution will ensure that the second tray is not depleted; this is an important point if using double weight fiber base paper.)

11.12 Dry the print using an appropriate method for the paper used.

11.13 All of the above steps can be conducted under ordinary room illumination. Avoid strong sunlight, however. The unused paper stock should have minimal exposure to light. All solutions and washes should be at room temperature.

NOTE 2— If the precaution concerning excessive light exposure is not followed, a bluish or purplish tint will appear on the paper after printing and development.

11.14 In most cases, only one sulfur print can be made without regrinding the surface. For steels with high sulfur contents (above 0.100 weight % sulfur), the first print is generally very dark and a second print may give better results. For steels with ordinary sulfur contents, a second print can generally be made if the ground surface is superficially macroetched at room temperature (not deep etched with hot acid etchants, or even with cold dilute acid as with electrolytic macroetching). A room temperature macroetch with 10 % aqueous nitric acid, or a general purpose microetchant (see Methods E 407), may be used.

11.15 For steels with low sulfur contents (less than 0.010 wt. % S), the initial print quality is usually enhanced if the disk surface is first superficially macroetched as described in 11.14.

11.16 A specimen that has been sulfur printed can be immediately macroetched with no further preparation. The same is not true in the reverse situation where aggressive macroetching has been done ahead of sulfur printing.

## 12. Interpretation of Results

12.1 The presence of sulfides is revealed on the print by the brown coloration produced by silver sulfide,  $\text{Ag}_2\text{S}$ . This coloration is produced wherever manganese sulfide, or more generally,  $(\text{Mn}, \text{Fe})\text{S}$ , is present in contact with the treated paper.

12.2 The greater the sulfur content of the steel, the darker the image under controlled test conditions, except as noted in 6.6.

12.3 Localized sulfur segregation is revealed on the print as a concentration of darker spots. Dark spots may also be formed at cracks or holes (as discussed in 6.2) or due to improper cleaning (as discussed in 6.1).

12.4 White spots are usually due to entrapped air between the paper and the disk (see 6.3).

12.5 Comparison of the sulfur print with the aggressive macroetch should be made, keeping in mind that the segregation coefficient for sulfur is higher than for carbon. Refilled cracks can contain both sulfides and carbides, and not necessarily both.

## 13. Report

13.1 The test report should include the actual sulfur print(s), or a photographic reproduction, depending on the circumstances. The orientation of the sulfur print relative to the specimen should be shown on the sulfur print.

13.2 The report should include the complete identity of the sample(s) tested and the chemical analysis of the specimen or its parent sample, if known.

13.3 The report should state the sulfur print variables used, acid selected, and concentration of the acid solution.

## 14. Keywords

14.1 Baumann print; ferrous alloys; macrostructural examination; photographic paper; specimen preparation; sulfur print

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