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SULFEX PROCESS:

DEPASSIVATION OF STAINLESS STEEL

T. A. Gens

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ORNL-2785

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

SULFEX PROCESS: DEPASSIVATION OF STAINLESS STEEL

T. A. Gens

DATE ISSUED

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ABSTRACT

The time required to break the passivation of films on 304 stainless steel produced by 1 hr treatment in refluxing 15.8 M HNO_3-0.025 M Cr(III) decreased as the sulfuric acid concentration increased and increased greatly when nitric acid was added to the sulfuric acid. The films resisted refluxing 6 M H_2SO_4 for 7 min, 6 M H_2SO_4-0.001 M HNO_3 for 2 hr, and 6 M H_2SO_4-0.01 M HNO_3 for several days. In refluxing 12 M H_2SO_4 the films dissolved in about 10 sec with up to 0.001 M HNO_3 in the solution, but 0.5 hr was required with 0.01 M HNO_3. The addition of 0.1 M HCOOH to refluxing sulfuric acid solution effectively destroyed as much as 0.01 M HNO_3. Films on stainless steel specimens in contact with platinum resisted refluxing 6 M H_2SO_4 for several hours. Films on bundles of 304 stainless steel tubes brazed together with Nicrobraze-50 dissolved instantly in refluxing 6 M H_2SO_4.

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1.0 INTRODUCTION

This work was performed to discover the causes of, and methods of preventing, passivation of stainless steels in the Sulfex process. In the Sulfex process, sulfuric acid is used to dissolve nuclear fuels containing stainless steel or to remove stainless steel cladding.[1,2] The formation on metallic materials, especially stainless steels, of an oxygen-rich film which resists sulfuric acid dissolution is a well-known phenomenon.[3,4] In recent tests of the Sulfex flowsheet with fuel irradiated in a water-cooled reactor, stainless steel passivation in 6 M H_2SO_4 was a serious problem. This report describes experiments carried out with specimens of 304 stainless steel passivated in the laboratory by treatment with chromium-nitric acid solutions. Breaking the passivation by raising the temperature and by increasing the sulfuric acid concentration, the passivation effect of nitrate ion in the sulfuric acid, and the destruction of nitrate ion with formic acid were studied. The effect of the Nicrobraze-50 in the Consolidated Edison fuel on passivation of 304 stainless steel was also investigated.

Further work will be needed to determine if the laboratory-produced passive films are as resistant to sulfuric acid as the films produced in water-cooled reactors and to study the increase in passivation produced by contact with platinum.

Discussions with G. H. Cartledge, J. C. Griess, and E. S. Snavely of Oak Ridge National Laboratory and N. Hackerman of the University of Texas were very helpful in this work.

The laboratory work was performed competently by G. E. Woodall.

2.0 DEPASSIVATION EXPERIMENTS

2.1 Effect of Temperature and Sulfuric Acid Concentration

The depassivation time of laboratory-passivated stainless steel specimens (Section 3.0) decreased rapidly as the concentration of refluxing sulfuric acid used for dissolution increased (Fig. 1). Both temperature and sulfuric acid concentration appear to be of major importance in decreasing depassivation times. At a constant temperature ($97.5 \pm 0.5^{\circ}C$) and at the boiling point, the depassivation time of laboratory-passivated specimens in 10 M H_2SO_4 was about one-fourth and one-twentieth, respectively, of the depassivation time in 5 M H_2SO_4 (Fig. 2). Over the 5-10 M concentration range, the sulfuric acid boiling point increased from about 105 to 148°C. Increasing the molarity of the sulfuric acid from 8.3 to 9.3 also produced only a small decrease (less than 30%) in depassivation time at $88.0 \pm 0.5^{\circ}C$ (Fig. 2). It may not be necessary to increase the concentration of sulfuric acid if other methods of raising the temperature are used to depassivate stainless steel.

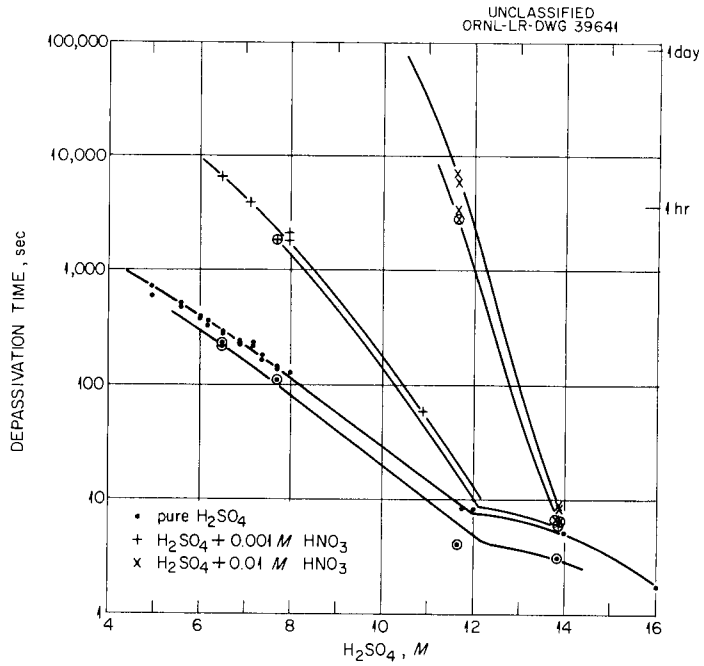

Fig. 1. Depassivation time of 304 stainless steel in refluxing sulfuric acid. Passivation treatment: 1 hr in refluxing 15.8 M HNO_3-0.025 M or 0.25 M Cr(III) (circled points refer to 0.25 M.)

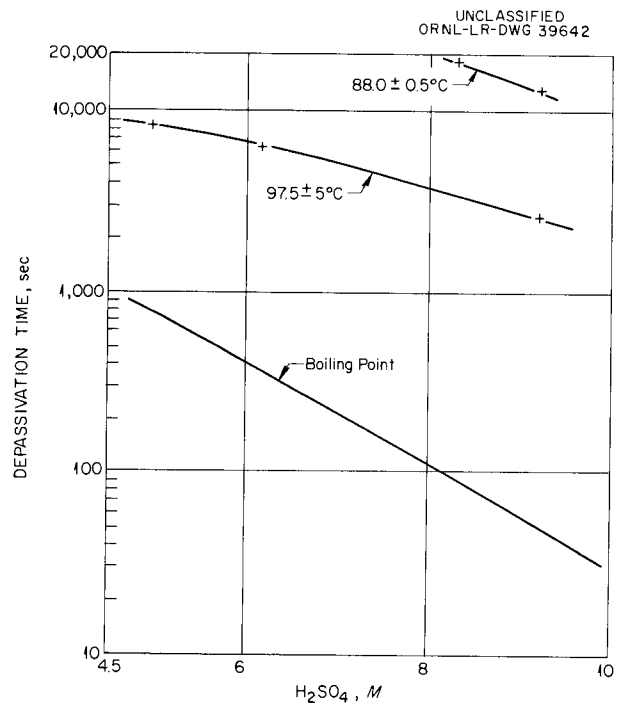

Fig. 2. Comparison of depassivation times of 304 stainless steel in sulfuric acid at the boiling point, at 97.5 ± 0.5°C, and at 88.5 ± 0.5°C. Passivation treatment: 1 hr in refluxing 15.8 M HNO_3-0.025 M Cr(III).

2.2 Effect of Nitric Acid

Addition of as little as 0.001 M HNO_3 to 5-9 M H_2SO_4 increased the depassivation time more than ten times and 0.01 M HNO_3 caused a much greater increase in depassivation time (Fig. 1). Specimens passivated in either 15.8 M HNO_3-0.025 M Cr(III) or 15.8 M HNO_3-0.25 M Cr(III) behaved similarly, with the latter specimens being depassivated slightly faster in all cases. In hot-cell work, the standard test for passivation has involved placing the stainless steel specimen in refluxing 6 M H_2SO_4 for 1 hr. The addition of as little as 0.0005 M HNO_3 to the refluxing 6 M H_2SO_4 caused the laboratory specimens, that were passive to refluxing 6 M H_2SO_4 for 7 min, to be passive for 1 hr (Fig. 3). This curve was obtained by interpolating and extrapolating the data of Figure 1. Since nitric acid is used in part of the Sulfex process as applied to fuels with oxide cores,[2] it is probable that some nitric acid, unless destroyed chemically, will always be present in the sulfuric acid.

Formic acid is very effective in destroying nitrate in refluxing sulfuric acid. When as little as 0.1 M was introduced in refluxing 8 M H_2SO_4, the depassivating time, with as much as 0.01 M HNO_3 present, was reduced nearly to the depassivating time in nitrate-free 8 M H_2SO_4 (Fig. 4). The uppermost point in Figure 4 was obtained by extrapolation of data in Figure 1. The other points were determined experimentally. Purging with an inert gas should cause even better nitrate destruction by decreasing the amount of nitrogen dioxide reabsorbed by water in the condenser.

2.3 Effect of Contact with Other Metals

Contact with nonpassive iron-base alloys destroys passivation instantly. However, laboratory-passivated stainless steel specimens, which were ordinarily depassivated in 300-400 sec (Fig. 1), remained passive for periods of one to several hours in refluxing 6 M H_2SO_4 when the specimens contacted a piece of platinum metal.

2.4 Depassivation of Brazed 304 Stainless Steel Tubes

Individual prototype Consolidated Edison fuel pins irradiated in water-cooled reactors have shown passivation behavior resembling that of the specimens prepared in this work. However, in the actual Consolidated Edison fuel assembly, the 304 stainless steel tubes will probably be brazed together with Nicrobraze-50 or a similar brazing alloy. The passivation behavior of Nicrobraze-50 is not the same as that of 304 stainless steel. Dissolution started within 3-5 sec when bundles of 304 stainless steel tubes, brazed together with Nicrobraze-50 and subjected to the passivation treatment described in Section 3.0, were immersed in refluxing 6 M H_2SO_4. In one test, 304 stainless steel specimens with no Nicrobraze were passivated simultaneously with the brazed tubes. The specimens with no Nicrobraze required a depassivation period (>300 sec) equal to that of previous studies in refluxing 6 M H_2SO_4 (Fig. 1). These results indicate that passivation will not be a problem in Sulfex dissolution of Consolidated Edison fuel. Spherical 2-g samples of Nicrobraze-50 pretreated the same way lost weight at the rate of 4.6 $mg/cm^2 \cdot min$ for the first 10 min, 1.0 $mg/cm^2 \cdot min$ for the next 10 min, and 0.16 $mg/cm^2 \cdot min$ for the next 16 hr in refluxing 6 M H_2SO_4.

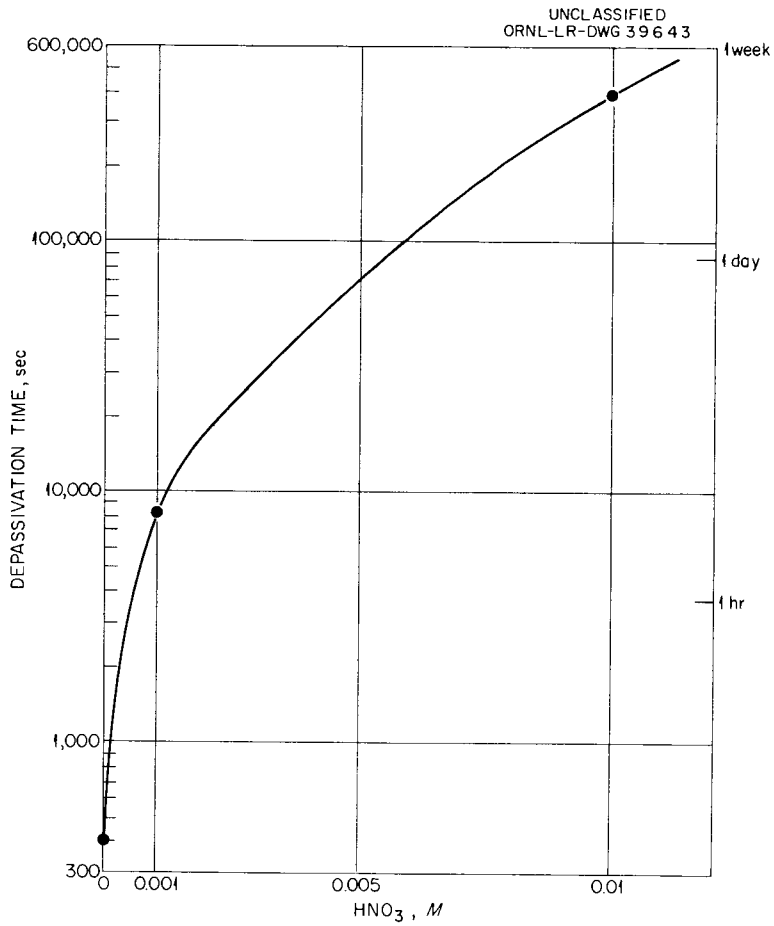

Fig. 3. Depassivation time of 304 stainless steel in refluxing 6 M H_2SO_4-HNO_3. Passivation treatment: 1 hr in refluxing 15.8 M HNO_3-0.025 M Cr(III).

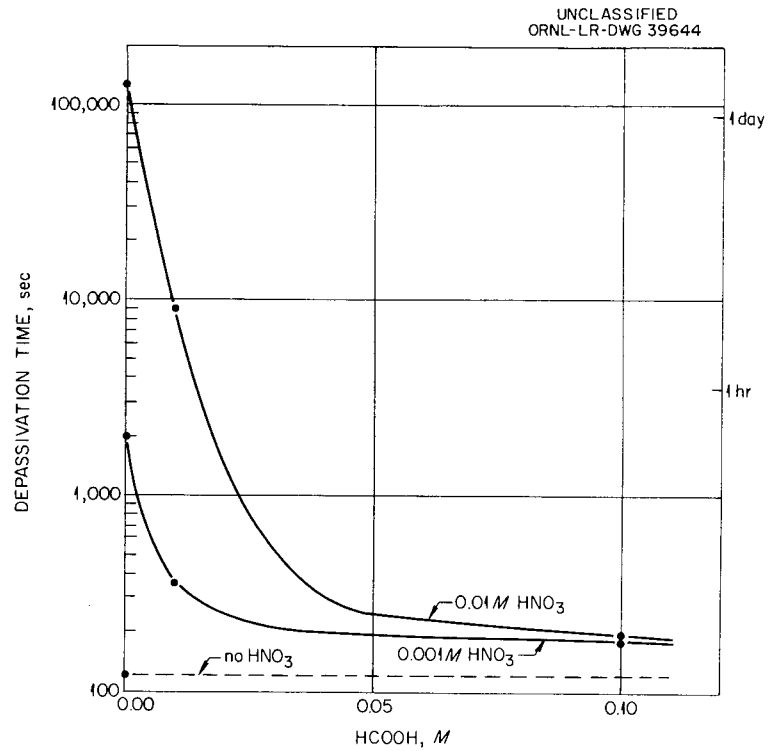

Fig. 4. Depassivation time of 304 stainless steel in refluxing 8 M H_2SO_4-HCOOH-0.001 M and 0.01 M HNO_3. Passivation treatment: 1 hr in refluxing 15.8 M HNO_3-0.025 M Cr(III).

Untreated samples gained weight the first 20 min, and, surprisingly, dissolved at a slower rate, 0.07 $mg/cm^2 \cdot min$, than treated samples for the next 16 hr.

The specimens of 304 stainless steel used in depassivation studies were cut from a sheet with a shear press before passivation by the technique described in Section 3.0. These specimens required slightly longer to be depassivated and the results showed less scatter than with hand-cut specimens. All sulfuric acid solutions were prepared by dilution from a single container. Molarities were determined to the second decimal place by titration with 0.1000 N NaOH. All specimens used in determining a single curve were passivated in a single batch.

3.0 PREPARATION OF PASSIVE FILMS

The films produced on stainless steels may be colorless and ultrathin (30-60 Å), colored (300-500 Å), or oxide scale (>500 Å).[3] The thin, colorless films are probably the most resistant to sulfuric acid dissolution and are probably the type now being found on fuel irradiated in water-cooled reactors. Thin colorless films were produced rapidly on 304 stainless steel by contact with refluxing chromium-nitric acid solutions. Rhodin has also produced thin films on 304 stainless steel by a 30-min treatment in 5% HNO_3-0.5% $K_2Cr_2O_7$ at 60°C.[3] After testing various chromium-nitric acid solutions, 1 hr in refluxing 15.8 M HNO_3-0.025 M Cr(III) was chosen as the standard passivation treatment. The azeotropic nitric acid was chosen for convenience and not because it produces the greatest passivation (see Section 3.2). The time required for depassivation in refluxing sulfuric acid was measured with a stopwatch to test and compare the effectiveness of various passivation treatments. The instant the protective film is penetrated, dissolution of the stainless steel starts and spreads very rapidly over the entire surface, releasing large volumes of gas which are easily detected.

3.1 Effect of Cr(III) and Cr(VI) Concentration

Hand-cut 304 stainless steel specimens were placed in refluxing 15.8 M HNO_3 containing Cr(III), Cr(VI), or mixed Cr(III) and Cr(VI) for 10 min. The chromium concentrations which produced the film most resistant to refluxing 6.15 M H_2SO_4 were 0.025 M Cr(III) and 0.001 M Cr(VI) (Fig. 5). A 10-min treatment in pure boiling 15.8 M HNO_3 produced specimens nearly as passive, about 150 sec being required for depassivation. Specimens placed in pure boiling water for 10 min were depassivated in 3 sec.

When the passivation produced by 1 hr in the boiling 15.8 M HNO_3-0.025 Cr(III) solution was compared to that of a similar solution to which 0.001 M Cr(VI) was added (Fig. 6), any differences in depassivation time in refluxing 6 M H_2SO_4 were less than the scatter. The passivation reached a maximum in about 30 min. A small amount of Cr(VI) mixed with Cr(III) apparently aids passivation, but sufficient Cr(VI) is probably produced by reaction between nitric acid and Cr(III) that no Cr(VI) need be added along with the Cr(III).

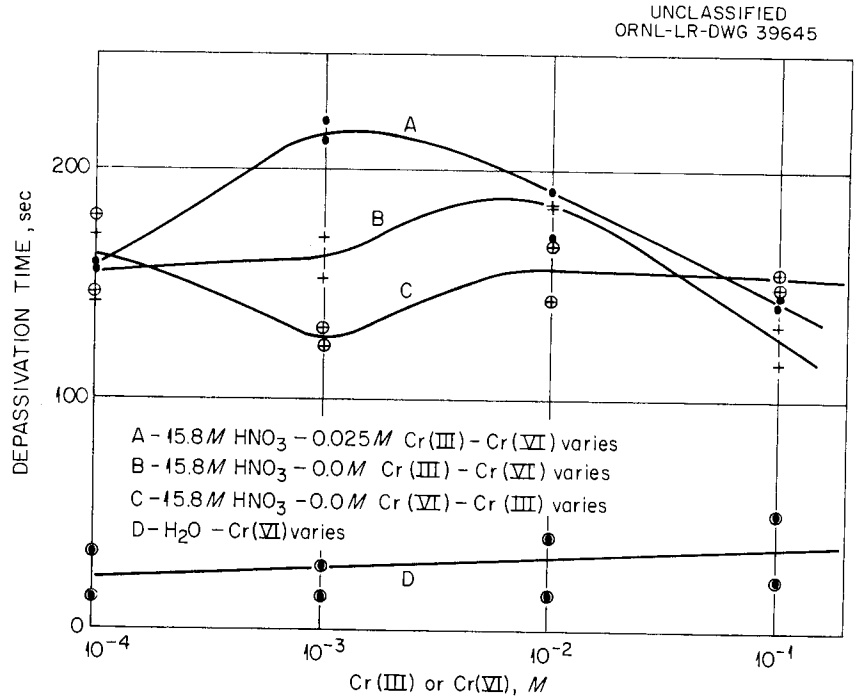

Fig. 5. Depassivation time of 304 stainless steel in refluxing 6.15 M H_2SO_4 as a function of Cr(VI) or Cr(III) concentration in the refluxing 15.8 M HNO_3 passivating solution and in boiling water. Passivation treatment: 10 min at boiling point.

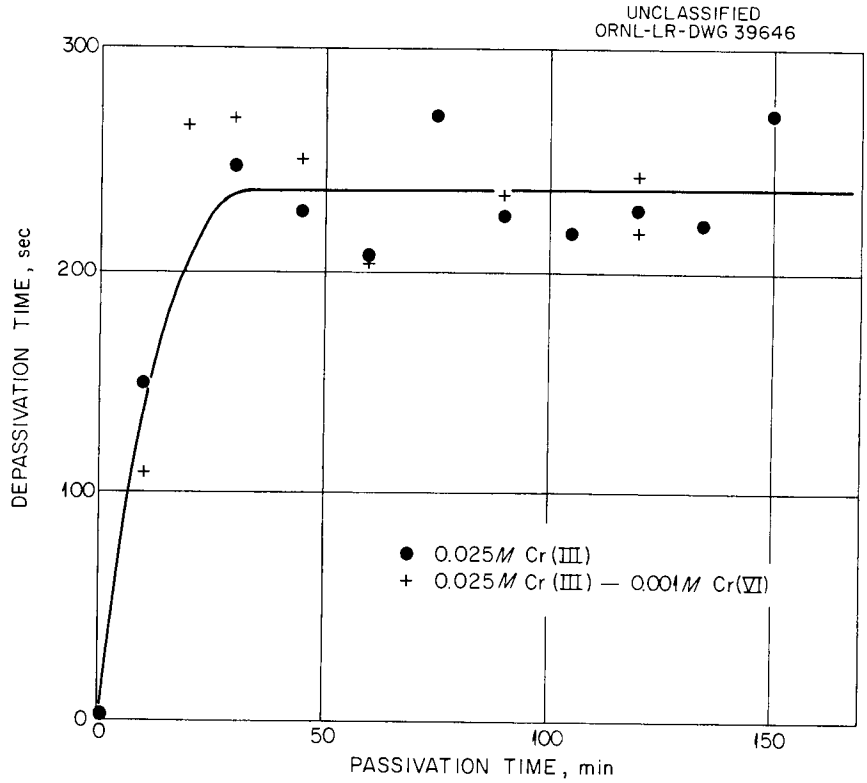

Fig. 6. Depassivation time of 304 stainless steel in refluxing 6.15 M H_2SO_4 as a function of passivation time in refluxing 15.8 M HNO_3-Cr(III) or mixed Cr(VI) and Cr(III).

3.2 Effect of Nitric Acid Concentration

Several specimens were passivated 1 hr in refluxing solutions of various nitric acid molarity-0.025 M Cr(III). Depassivation times in refluxing 6.16 M H_2SO_4 (Fig. 7) indicated that 10 M HNO_3 produces the best passivation. The specimens were hand-cut 304 stainless steel.

3.3 Effect of Temperature

The passivation achieved by a 1-hr treatment is very dependent on the temperature of the solution. Depassivation time in refluxing 6.15 M H_2SO_4 varied from 6-7 sec with passivation at 58°C in 15.8 M HNO_3-0.025 M Cr(III) to nearly 400 sec when the solution was at the boiling point (Fig. 8). The specimens were hand-cut 304 stainless steel.

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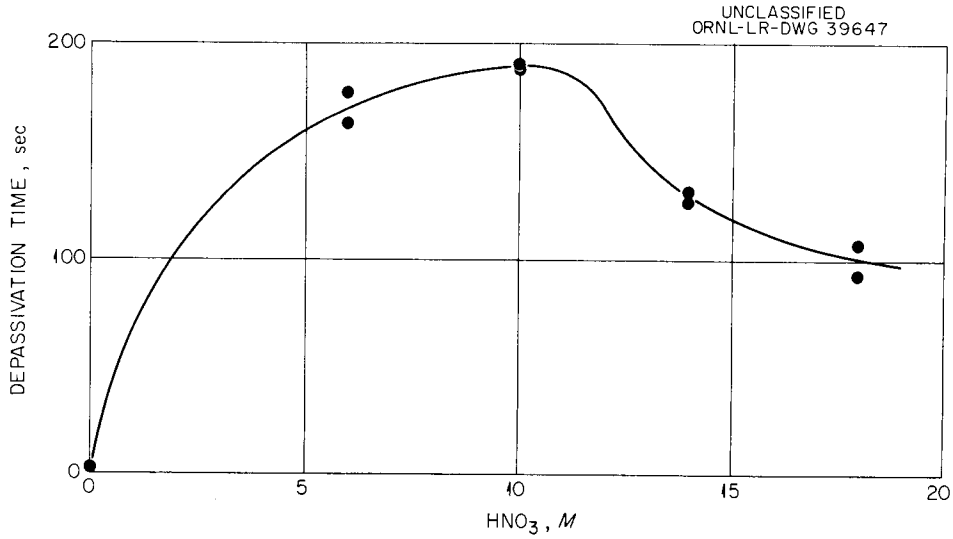

Fig. 7. Depassivation time of 304 stainless steel in refluxing 6.16 M H_2SO_4 as a function of nitric acid concentration used in 1-hr passivation treatment in refluxing 0.025 M $Cr(NO_3)_3$-HNO_3.

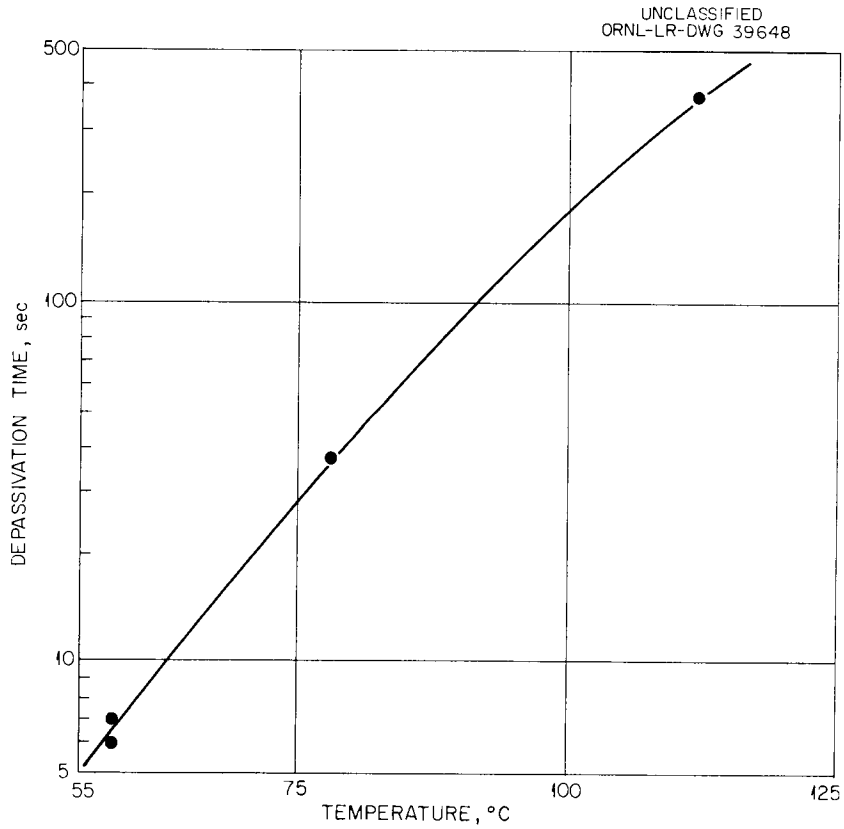

Fig. 8. Depassivation time of 304 stainless steel in refluxing 6.15 M H_2SO_4 as a function of temperature used in 1 hr passivation in 15.8 M HNO_3-0.025 M Cr(III).

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