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INVESTIGATION OF BLACK SPOTS AND OTHER BLEMISHES INSIDE SMALL STAINLESS STEEL PRESSURE VESSELS

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INVESTIGATION OF BLACK SPOTS AND OTHER BLEMISHES INSIDE SMALL STAINLESS STEEL PRESSURE VESSELS

C. R. Heiple, J. H. Doyle, and P. Burgardt

ABSTRACT

Black spots and other blemishes were found on the inside surface of small stainless steel pressure vessels by borescope inspection. Most of the black spots originated from pyrolysis of lint contaminating the interior surface of these parts prior to welding. The lint originated from cotton gloves used to handle parts and from cotton gauze used to clean the parts. Pyrolysis of other hydrocarbons can also create black spots.

INTRODUCTION

Borecope inspection of several types of small stainless steel pressure vessels was recently initiated to verify cleanliness and inspect the weld underhead. These inspections revealed surface blemishes on a significant fraction of otherwise acceptable units. The blemishes most commonly appear as black spots with a diameter of 1 mm or less. Occasionally, various other blemishes are found. The black spots are generally near the GTA girth welds on the parts. Observation of these blemishes prompted concern for either the presence of loose or potentially loose particles in the units or that possibly the spots could be chemically reactive sites, which could react with material subsequently placed into the units. Thus, presence of these blemishes was initially made a cause for rejection of the units.

This investigation was undertaken to determine the nature of the blemishes to assess their effect (if any) on the functioning of the units. In addition, the study attempted to determine the origin of the blemishes with the intention that appropriate processing changes could be made to reduce or eliminate the blemishes.

EXPERIMENTAL PROCEDURE

The first step was to verify that the blemishes were real, i.e., that they were not artifacts of the borescope

inspection. This was accomplished by inspecting several rejected parts with a borescope, marking the approximate locations of the blemishes (usually black spots) on the outside of the parts, noting the appearance of the blemishes, sectioning the parts, and confirming that blemishes of similar appearance could be found in the indicated locations. In all cases, this effort was successful, demonstrating that the blemishes (usually black spots) are seldom, if ever, inspection artifacts. This does not preclude the possibility that inspection artifacts may occasionally occur.

The study of the nature of the black spots was conducted primarily with a Phi 660 Scanning Auger Multiprobe. Certain other blemishes were examined with a Surface Science SX-100 ESCA spectrometer. The Auger examinations suggested that one class of black spots resulted from pyrolysis (during welding) of lint contaminating the inside of the units. Various test welds were therefore performed on material intentionally contaminated with lint and other substances to verify that black spots similar to those on production parts could be produced intentionally.

It was suggested that useful information on black spots and other blemishes might be obtained by baking out the parts and analyzing the gasses produced during bakeout. Four parts, both with and without black spots observable during borescope inspection, were evacuated to about 10^{-7} torr and heated slowly to 480 °C; then the gasses produced were analyzed with a residual gas mass spectrometer.

RESULTS AND DISCUSSION

Observations on Type A Assemblies

First Unit

This assembly consists of two parts. Only one (the smaller part) is borescope inspectable; it can be

inspected at the subassembly stage, prior to attachment of the larger part. The first unit was rejected after borescope inspection because of two prominent black spots in the smaller part. Approximate locations of these spots were marked on the outside, and the part was sectioned with a hacksaw. This procedure minimizes surface contamination during sectioning since no cutting fluids or coolants are used; the cutting chips are relatively large; and they are easily identified. The black spots were easily visible in their predicted locations after sectioning.

An optical photograph of the first black spot is shown in Figure 1. Note that it consists of three parts: a central black dot, a curved white track (subsequently referred to herein as a worm track), and a surrounding black ring. (These features are shown more clearly in Figure 2, except that the central black dot is rendered white by an artifact of the lighting.) Viewed at unit magnification, the feature appears as a black spot with a barely discernible white line in the center.

The central dot and most of the worm track are shown in a scanning secondary electron micrograph in Figure 3. The fact that the worm track appears white and the central dot appears black in the secondary electron image (as they do optically) is fortuitous. The black dot is clearly sitting on top of the worm track, which must have formed first.

Surface composition of the black spot is mapped in Figures 4 and 5. Concentration of carbon (Figure 4) and oxygen (Figure 5) at any position is proportional to the brightness (dark equals low concentration). The central black dot is nearly pure carbon, and the surrounding black ring is rich in carbon.

The second black spot was similar visually, but it had two worm tracks, no central black dot, and the black ring was more diffuse. Further examination of the unit revealed two additional small black spots with all three features and 10 additional worm tracks lacking a central dot or significant surrounding black rings.

Proposed Mechanism for Black Spot Formation

The observations and measurements described above led to the following mechanism, proposed as the source of black spots. Lint on the part surface is

heated as the weld pool approaches. As the lint is heated, carbon is evolved, which protects the steel surface underneath from further oxidation. The lint may also offer some mechanical protection from oxidation. The worm track is then a clean trace on the steel surface, contrasting with the surrounding area darkened by additional oxidation from heat during welding. Upon further heating, the lint shrivels into a ball and continues to boil off carbon rapidly. As the area cools with passage of the weld pool, vaporized carbon condenses as a ring around the dot of pyrolyzed carbon.

It is likely that a black spot with all three features (central black dot, worm track, and black ring) can be found only in a fairly narrow range of time-temperature cycles. Furthermore, the lint must stay in place and not fall off during the heating cycle. Thus, as observed, the most common feature is expected to be worm tracks without a central dot or significant black ring. In addition, the full black spots are expected to lie in a narrower distance band away from the weld edge than the partial black spots. This expectation was confirmed experimentally. In this unit, the 10 worm tracks were found 0.10 to 0.26 in. from the edge of the weld underhead, while the three full black spots lay 0.15 to 0.18 in. from the underhead.

Verification of the Black Spot Formation Mechanism

Initial verification of the proposed mechanism was provided by test welds on plates intentionally contaminated with lint. The lint was provided by shaking cotton gloves of the same type used to handle the parts in production. These gloves produced an essentially inexhaustible supply of lint. Welding was carried out in an inert glovebox. The lint was on top of the plate; so even with the GTA torch shielding gas turned off, gas flow created by the arc was sufficient to blow the lint away. (This does not occur when welding parts, because the contamination is on the underhead side of the weld.) The lint was therefore wet with acetone, which prevented it from blowing away.

This procedure produced numerous worm tracks identical to those in production parts. An example is shown in Figure 6. There were also several partial

black spots created, consisting of a black dot and surrounding ring (Figure 7), but missing the worm track.

The most direct verification of the proposed mechanism was discovery of a segment of what appeared to be pyrolyzed lint and its accompanying worm track on the large part's interior surface. The segment was black when viewed optically. A scanning secondary electron image of the segment is shown in Figure 8. A white track could be seen optically under the segment. As is apparent from Figure 8, attachment of the segment to the part was tenuous at best. It was lost during further sectioning of the part intended to provide a sample containing the segment for Auger analysis. However, the worm track was now easily visible (Figure 9). (Note that the conditions for secondary electron emission rendered the track dark in this case, but it was white optically.)

First Unit, Large Part

In addition to the pyrolyzed lint segment and its accompanying track described above, there were several other worm tracks inside this part. They were identical in appearance to tracks in the small part of this unit. A small piece of weld spatter (Figure 10) was also located. Apparently, it came from the electron beam weld on top of the unit.

There were, in addition, several partial black spots more typical in appearance to those on other assemblies than the small part of Type A assemblies. These partial spots look like dots made with a pencil, lack a worm track, and are featureless up to several times optical magnification. At higher magnification, a central particle and surrounding ring can be seen (Figure 11). For the partial spot shown in Figure 11, the central particle is nearly pure carbon, and the ring is high in carbon--as expected (Figure 12). The surprising observation was high fluorine concentrations in the ring (Figure 13). The fluorine observation is partially an artifact of the instrument. Under the conditions used, the instrument is six times more sensitive to fluorine than carbon; that is, the size of the fluorine peak (thus the concentration map brightness) will be six times larger for fluorine than for carbon, with the same surface concentration of each.

Fluorine was also detected on the surface of a second unit during the examination described in the following subsection. This sample was subsequently examined in the ESCA to quantify the fluorine surface concentration. The surface fluorine concentration well away from the black spot for the as-received condition was about 7%. After the surface was etched 30 seconds to remove surface carbon contamination, the fluorine surface concentration was nearly 25%. Origin of the high surface concentration of fluorine in this unit is uncertain, but it does not appear to be related to the black spots. Fluorine was not detected on surfaces of any other units examined.

Second Unit

The second unit was one of the parts subjected to vacuum bakeout and gas analysis. (See the subsection describing fourth unit observations.) The second unit had a prominent black spot prior to bakeout. It was reinspected after bakeout, and the spot remained. Location of the spot was noted, and the part was sectioned. A prominent black spot (complete with worm track, central dot, and ring) was in the indicated location. A scanning secondary electron image of the spot is shown in Figure 14. The central dot is all carbon, and the ring is high in carbon (Figure 15).

Third Unit

The third unit was also one of those subjected to vacuum bakeout and gas analysis. (See the following subsection describing fourth unit observations.) In addition to a prominent black spot, borescope examination revealed several blemishes not typical of other units. The blemishes were golden brown rather than black and angular rather than round. The blemishes and black spot appeared visually to be unchanged by the vacuum bakeout.

The unit was sectioned, and the angular blemishes were examined with the Scanning Auger Multiprobe. Part of one such blemish is shown in Figure 16. The blemish is high in chromium and manganese and somewhat elevated in carbon (Figure 17). Other blemishes in this unit were similar. The blemishes appear to be a thicker surface oxide. Their origin is at present unknown.

Fourth Unit

As discussed previously, black spots without the typical lint morphology (worm track, central dot, and ring) are occasionally found in all assemblies. These spots represent a small fraction of the total blemishes, which are mostly of the lint type.

After the initial part of this study, the design agency (Sandia National Laboratory, Livermore) determined that black spots arising from lint pyrolysis would not interfere with proper functioning of the unit and were therefore not cause for rejection. Since the origin of black spots without lint morphology is at present uncertain and their nature consequently less well-defined, the presence of these spots remained a cause for rejection.

Measurements were therefore made of additional black spots, not typical of lint, to better characterize these spots. Three spots without lint characteristics were examined from the fourth unit. The first was a prominent black spot with no ring or worm track (Figure 18). The spot is almost entirely carbon with a trace of potassium (Figure 19). This composition measurement was made in the Scanning Auger Microprobe using its ability to perform X-ray analysis as well as Auger electron analysis. Results using Auger analysis are consistent with those from X-ray analysis.

The spot shown in Figure 18 was subsequently cleaned in liquid carbon dioxide and reexamined. The spot was essentially unaffected by the cleaning treatment, which is consistent with its being a pyrolyzed hydrocarbon.

The second spot examined was similar to the first, but it was smaller and appeared thicker visually (Figure 20). This spot was also mostly carbon, with minor sodium, potassium, and manganese contamination (Figure 21).

The third spot was even smaller and differed from the first in that it was surrounded by a white ring (Figure 22). It was also primarily carbon but contained sodium, aluminum, silicon, sulfur, potassium, and calcium (Figure 23). Presumably, the hydrocarbon particle pyrolyzed to form this black spot was contaminated with dirt.

Gas Analysis During Vacuum Bakeout

In all cases, the total amount of gas evolved during vacuum bakeout was very small--substantially less than if the parts had contained one fingerprint. There was no consistent relation between the quantity or composition of evolved gas and the presence or absence of blemishes on the parts.

It should be noted that some black flakes were found in the parts after bakeout. These flakes were identified by a scanning electron microscope as copper oxide. While initially alarming, they represented an artifact, entering the parts during disassembly of the vacuum fittings following bakeout.

Other Assemblies

Assemblies of three types were examined. They are similar in design, and the blemishes appear to be common to all three. Observations on these assemblies are therefore considered together.

As indicated previously, the typical rejectable blemish in these assemblies is a partial black spot (central particle and surrounding ring without a worm track), which appears in the borescope as a featureless black dot, much like a pencil dot. An example is shown in Figure 24. Three such spots were sectioned early in this investigation and sent to an outside laboratory for ESCA analysis. The spot from the first unit was mostly carbon. (It should be noted that this unit had been cleaned with nitric acid prior to analysis.) Spots on the second and third units were identified as manganese or iron/manganese oxides.

The spots on the first and second units were rerun on the Scanning Auger Multiprobe. (This instrument had not been delivered to Rocky Flats when the spots were originally analyzed.) A scanning secondary electron image of the partial black spot on the first unit is shown in Figure 25. A portion of the central black dot is shown at higher magnification in Figure 26. The central black dot is all carbon, and the surrounding ring is high in carbon (Figure 27). This result is consistent with the ESCA analysis.

The spot on the second unit is shown in Figure 28. It appears that the central black carbon dot responsible

for the feature has been knocked off, leaving the high carbon ring and traces of carbon on the surface where the carbon dot originally lay (Figure 29). The shadow of the black dot is high in iron, for reasons presently obscure. We propose that the spot on the second unit is the same as on the first, but with the central black dot knocked off. If the central dot were quite small, it could not be detected visually. The Scanning Auger Multiprobe results are not consistent with the spot being an iron/manganese oxide.

Observations of a fourth unit support the thesis that the spot on the second unit shown by the Scanning Auger Multiprobe is the same as on the first, but with the black dot knocked off. Two black spots were observed in this unit by borescope, one on the cap and the other on the side, but the location was not marked on the outside by the Inspection group. After sectioning, no spot could be found on the side. It presumably fell off and was lost during sectioning. The spot on the cap survived when the part was cut to a shape suitable for Auger analysis, but the central dot was blown away while removing cutting chips from the surface with a low-velocity gas jet. (Reference to Figure 11, taken subsequently, indicates that the attachment of these particles may be quite fragile.)

The shadow of the dot is shown in the secondary scanning electron image in Figure 30, and composition maps are shown in Figure 31. The results on the fourth unit, where the spot was known to have been blown away, are similar to those on the second unit, where the spot is postulated to have been knocked off.

Additional confirmation of the nature of partial black spots is provided by observations on a blemish from another assembly. The partial black spot was found by borescope examination. A scanning secondary electron micrograph of the partial black spot is shown in Figure 32, with the central black dot at higher magnification in Figure 33. The ring is almost nonexistent. The central dot is nearly all carbon (Figure 34).

Twenty-four units were followed through the production process in an effort to determine when surface blemishes were forming inside the units. Three of these were sectioned and submitted for ESCA analysis. Each of the first two had a large (1/4-

inch diameter) black ring on the bottom. These parts were cut to a suitable shape for ESCA analysis. When cutting chips were blown from the first unit, the black ring was blown away also. The second unit was treated more gently, and the black ring was identified as manganese oxide. Manganese apparently vaporized during welding and condensed on the relatively cold bottom surface of the part. Such a layer would not be very adherent, consistent with observation. The third unit had a large stain, about 1/8 inch in diameter. The stain was non-conductive, and only carbon could be detected with the ESCA. It was partially pyrolyzed, and it is apparently an oil.

Joining Intentionally Contaminated Assemblies

Assemblies were intentionally contaminated with white crystals from the Nitradd cleaning tank and bits of foam from the trays used to move and store parts. The assemblies were then welded together. Many stains and blemishes were produced, but none were similar to black spots (without lint characteristics) on production parts.

CONCLUSIONS

The complete black spot blemishes (worm track, black ring, and central black dot) originate from the pyrolysis of lint contaminating the interior surface of these parts prior to welding. One source of lint is the cotton gloves used to handle the parts. Another is the cotton gauze used to clean the parts.

Under proper conditions, pyrolysis of lint can also produce partial black spots, i.e., those missing worm tracks. (See Figure 7.) However, pyrolysis of other contaminants can also produce partial black spots that are indistinguishable by a borescope from partial spots caused by lint pyrolysis. The contaminant producing these black spots without lint characteristics has not been conclusively identified. Attempts to produce these spots intentionally have not been successful. However, their composition indicates that they almost certainly arise from pyrolysis of hydrocarbons, with plastic a likely source for at least some spots. If the plastic particle (or other hydrocarbon) is dirty, then the resultant black spot is also contaminated with

elements such as silicon, aluminum, sodium, and potassium.

After it was known that black spots originated from pyrolysis of lint, it was possible to determine that their presence would not impact proper functioning of the units. Units having black spots with lint characteristics were therefore acceptable. Occasional units had black spots without lint characteristics, and these parts continued to be rejected.

Several changes were made in the production process to reduce the incidence of black spots. For example, cotton gauze used for cleaning was replaced with a lint-free material. The parts were kept covered as much as possible between processing steps to reduce

incidental contamination, and there was a higher awareness by production personnel of the need to keep parts clean. These changes appeared to reduce the number of black spots substantially.

This study was undertaken near the end of Type A Assembly production. These were the units of most concern because they could not be recleaned after welding if black spots were found. However, because of the small number of parts produced after implementing production changes, reliable statistical information is unavailable on the extent of black spot reduction produced by these changes. The major benefit of this study was that a substantial number of assemblies were accepted because the spots proved to be harmless.

ILLUSTRATIONS

(Figures 1 through 34)

FIGURE 1. Optical Photograph of a Complete Black Spot (bottom) and Worm Track on Assembly A, Unit 1. 35X

FIGURE 2. Optical Photograph of a Complete Black Spot (right) and Worm Track on Assembly A, Unit 1. The Central Dot in the Black Spot is Black; the White Appearance is a Lighting Artifact. 32X

FIGURE 3. Scanning Secondary Electron Micrograph of the Central Dot and Worm Track Shown in Figure 2

FIGURE 4. Scanning Auger Carbon Map of the Black Dot Shown in Figure 2. Carbon concentration is proportional to brightness.

FIGURE 5. Scanning Auger Oxygen Map of the Black Dot Shown in Figure 2. Oxygen concentration is proportional to brightness.

FIGURE 6. Optical Photograph of a Worm Track Produced by Welding a Plate Intentionally Contaminated with Lint. 32X

FIGURE 7. Optical Photograph of a Partial Black Spot Produced by Welding a Plate Intentionally Contaminated with Lint. 32X

FIGURE 8. Scanning Secondary Electron Micrograph of a Piece of Pyrolyzed Lint on the Interior Surface of the Large Part of Assembly A. Unit 1. Note the worm track under the lint.

FIGURE 9. Scanning Secondary Electron Micrograph of the Worm Track Remaining After Pyrolyzed Lint (Figure 8) Fell from the Surface

FIGURE 10. Scanning Secondary Electron Micrograph of a Small Piece of Weld Spatter on the Large Part of Assembly A, Unit 1

(a) Central Dot and Surrounding Ring

(b) Detail of Central Dot

FIGURE 11. Scanning Secondary Electron Micrograph of a Partial Black Spot on the Large Part of Assembly A, Unit 1

FIGURE 12. Scanning Auger Carbon Map of the Partial Black Spot Shown in Figure 11

FIGURE 13. Scanning Auger Fluorine Map of the Partial Black Spot Shown in Figure 11

FIGURE 14. Scanning Secondary Electron Micrograph of a Black Spot on Assembly A, Unit 2

FIGURE 15. Scanning Auger Composition Maps for C, O, Cr, and F from the Black Spot Shown in Figure 14

FIGURE 16. Scanning Secondary Electron Micrograph of a Blemish on Assembly A, Unit 3

FIGURE 17. Scanning Auger Composition Maps for C, O, Cr, and Mn from the Blemish Shown in Figure 16

FIGURE 18. Scanning Secondary Electron Micrograph of a Large Partial Black Spot on Assembly A, Unit 4

FIGURE 19. X-ray Spectrum from the Large Partial Black Spot Shown in Figure 18

FIGURE 20. Scanning Secondary Electron Micrograph of a Small Partial Black Spot on Assembly A, Unit 4

FIGURE 21. X-ray Spectrum from the Small Partial Black Spot Shown in Figure 20

FIGURE 22. Scanning Secondary Electron Micrograph of a Small Partial Black Spot with Surrounding Ring, Assembly A, Unit 4

FIGURE 23. X-ray Spectrum from a Small Partial Black Spot Shown in Figure 22

FIGURE 24. Optical Photograph of a Typical Partial Black Spot on Other Assemblies

FIGURE 25. Scanning Secondary Electron Micrograph of the Partial Black Spot Shown in Figure 24

FIGURE 26. Scanning Secondary Electron Micrograph of a Portion of the Central Black Dot Shown in Figure 25

FIGURE 27. Scanning Auger Composition Maps for C, O, Fe, and Cr from the Partial Black Spot Shown in Figure 25

(a) Optical Photograph, 35X

(b) Scanning Secondary Electron Micrograph

FIGURE 28. Partial Black Spot on Another Unit

FIGURE 29. Scanning Auger Composition Maps for C, O, Fe, and Cr from the Partial Black Spot Shown in Figure 28

FIGURE 30. Scanning Secondary Electron Micrograph of the Shadow of a Blown-off Partial Black Spot on a Fourth Uni.

FIGURE 31. Scanning Auger Composition Maps for C, O, Fe, and Ni from the Shadow of the Blown-off Partial Black Spot Shown in Figure 30

FIGURE 32. Scanning Secondary Electron Micrograph of a Partial Black Spot on Another Assembly

FIGURE 33. Scanning Secondary Electron Micrograph of a Portion of the Central Black Dot Shown in Figure 32

FIGURE 34. Scanning Auger Composition Map for C and Fe from the Partial Black Spot Shown in Figure 32

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