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DEVELOPMENT OF FACILITIES FOR SHIPBOARD
CHEMICAL CLEANING OF BOILERS

Final Evaluation Report
NDTL Project P-360
SROJ7-08-04, Task 0614
30 November 1962
by
S. GREENBERG

NAVAL BOILER AND TURBINE LABORATORY
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ABSTRACT

Several descalants that can be safely handled by non-technical ships' personnel were evaluated for chemical cleaning of shipboard boilers. The selected descalant must be a non-toxic, water-soluble solid formulation and its solutions possess scale removing properties similar to inhibited hydrochloric acid and at the same time be non-corrosive to boiler steels. Wyandotte Chemicals Corporation, under contract with the Bureau of Ships, conducted bench-scale evaluations on scaled boiler tube sections using various formulations. The Laboratory continually monitored the application of the Wyandotte-suggested procedures to full scale boiler cleaning trials. Based on these tests, a chemical cleaning procedure was developed that is suitable for shipboard use. The selected descalant formulation consists of 89% sulfamic acid, 6% citric acid and 5% diethylthiourea. A 20% solution of this descalant approaches the strength and scale-dissolving characteristics of 10% inhibited hydrochloric acid and at the same time offer excellent corrosion protection to boiler steels, except Croloy 16-1 desuperheater alloy. Although further investigation is required to resolve some minor corrosion and storage stability problems, the solid descalant formulation meets the above requirements and is recommended for shipboard chemical cleaning of boilers.

SUMMARY PAGE

The Problem

To develop a chemical cleaning procedure for the removal of boiler water-side deposits that can be safely carried out by non-technical ships' personnel. The descalant used shall be a non-toxic, water-soluble, one-package solid formulation that will not undergo degradation under normal shipboard storage conditions. In addition, will 10% or 20% solutions of the selected formula be capable of solubilizing deposits to the same degree as 10% hydrochloric acid and do these solutions offer corrosion protection to boiler steels?

Findings

A chemical cleaning procedure was developed by Wyandotte Chemicals Corporation for use by shipboard non-technical personnel. The selected descalant formulation consists of 89% sulfamic acid, 6% citric acid and 5% diethylthiourea and meets the above requirements for safety in handling, scale solubility and corrosion protection. Results of full scale shipboard boiler cleaning trials, conducted under Laboratory supervision, showed that the Wyandotte procedure is suitable for shipboard use and that the selected descalant formulation is superior to any other solid descaling compound evaluated to-date. Based on laboratory bench-scale evaluations, it was also shown that, in most cases, the solid descalant was equally effective in removing waterside deposits from boiler tube sections as inhibited hydrochloric acid. The selected descalant could also be safely applied to carbon steel, chrome-nickel steel and 15-5 superheater metal. However, the solid formulation as well as the hydrochloric acid were extremely corrosive to Croloy 16-1 desuperheater metal. The descalant formulation also exhibited degradation when stored under adverse conditions.

Recommendations

It is recommended that the solid descalant formulation be adopted for shipboard use and that the current BUREAU Instruction 9310.29 of 5 February 1956

be revised accordingly. The material shall not be used on 16-1 desuperheaters. Further studies are needed to resolve some of the corrosion and storage stability problems.

ADMINISTRATIVE INFORMATION

The project to develop facilities for shipboard chemical cleaning of boilers was initially authorized by BUSHIPS letter ALL/NS-041-001(342)J19 (64096) Ser 342-69 of 15 February 1957.

The cost of the project was chargeable to Allotment 30007/RDN 57.71. The Navy Index Number was NS-041-001.

The evaluation was conducted intermittently from 1957 to 1962 since, in addition to the development of shipboard chemical cleaning facilities, the project entailed monitoring of the application of selected full-scale boiler cleaning procedures based on successful bench-scale evaluations conducted by Wyandotte Chemicals Corporation. These additional evaluations were conducted by the Laboratory under Subproject SRO07-08-04, Task 0614.

References:

- (a) Trial of Boiler Chemical Descaling Procedure Developed by Wyandotte Chemicals Corporation; final evaluation report of NBTL Project P-357(NS-041-001) : 18 Sep 1957
- (b) Instructions for Chemical Cleaning of Boilers by Ship's Force - Enclosure (1) of NBTL ltr Code 750J19(P-360) of 8 Aug 1957
- (c) Chemical Cleaning of Naval Boilers, Information for - Enclosure (1) of NBTL ltr Code 752J19(P-360) of 29 May 1958
- (d) Chemical Descaling of Waterside Deposits in Boilers Aboard USS BEATTY (DD-756) - Enclosure (1) of NBTL ltr report Code 752 A9(P-360) of 15 Jul 1958
- (e) Chemical Descaling of Waterside Deposits in Boilers Aboard USS CADMUS (AR-14) - Enclosure (1) of NBTL ltr report Code 752 A9(P-360) of 17 Sep 1958
- (f) Boiling Out of PLG-6 Boiler, NBTL report Code 752 S51(S-270) of 31 Oct 1958

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(g) Chemical Descaling of USS CAPERS (AR-14) Boilers, Additional Information Concerning, NBTL ltr report Code 752 (P-360) of 10 Nov 1958

(h) Electrometric Procedure for the Assaying of the Manganese Descalant CR-3909-C; report of NBTL Project P-360(NS-041-001), Code 752/22(P-360) of 5 Jan 1959

(i) Chemical Descaling of Waterside Surfaces in Fire Tube Auxiliary Boilers Aboard the USS FEARLESS (MSO-442); report of NBTL Project P-360(NS-041-001), Code 752/4(P-360) of 1 Apr 1959

(j) Chemical Descaling Results of USS VULCAN (AR-5) Boiler Tubes; SONECON report of 18 Jun 1959 - Record of Conversation of 26 Jun 1959

(k) Chemical Descaling of USS VULCAN (AR-5) Boiler Tubes; Additional Information Concerning, NBTL Project P-360 (SR007-08-04), Code 752/10330(P-360) of 17 Aug 1959

(l) Chemical Descaling of Waterside Deposits in Boilers Aboard USS VULCAN Enclosure (1) of NBTL (Chemistry Branch, Code 752) Bi-Monthly Progress Report of 9 Oct 1959

(m) Removal of Waterside Deposits from USS MASSEY (DD-778) Boiler Tube; Report of NBTL Project P-360(SR007-G3-04), Code 752/10330(P-360) of 8 Dec 1959

(n) Chemical Cleaning of Oil Contaminated Boiler Waterside Surfaces; report of NBTL Project P-360, Code 764/10330(P-360) of 22 Mar 1960

(o) Chemical Descaling of the Boilers Aboard USS HARWOOD (EXE-861) - Enclosure (1) of NBTL ltr report Code 764/10330(P-360) of 10 May 1960

(p) Chemical Descaling of the USS TAUSIG (DD-746) Boilers; Information Concerning (NBTL Project P-360) - Enclosure (1) of NBTL ltr report Code 764/10330(P-360) - of 20 Jun 1960

(q) Effects of Various Treatments on After-Rusting Resulting from Chemical Cleaning; report of NBTL Project P-360 of 17 Aug 1960

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(r) Extent of Hydrogen Evolution During Chemical Descaling of Boilers with Inhibited Sulfamic Acid; report of NBTL Project P-360(R007-08-04, Subtask 0614) of 16 May 1961

(s) NBTL ltr report to Wyandotte Chemicals Corporation (with copies to BUSHIPS), Code 2764/10330(P-360) of 18 Jul 1961

(t) NBTL ltr report to Wyandotte Chemicals Corporation (with copies to BUSHIPS), Code 2764/10330(P-360) of 13 Nov 1961

(u) NBTL Chemistry Branch (Code 2764) Bi-Monthly Progress Reports of Aug 1959 through Jul 1962

REPORT OF INVESTIGATION

INTRODUCTION

A chemical descaling procedure suitable for shipboard use is needed for the removal of deposits from waterside surfaces of naval boilers. The method shall be sufficiently simple and safe so that it can be easily handled by non-technical shipboard personnel. In addition, the descalant shall be a solid formulation that is water-soluble, non-volatile, non-toxic, non-hazardous during storage and handling and chemically stable when stored aboard ship. The descalant formulation, when in solution, shall possess a scale-solubilizing capacity comparable to that of mineral acids and at the same time offer maximum corrosion protection to boiler metals, including those of superheaters in high pressure boilers.

The Wyndotte Chemicals Corporation, under BUSHIPS contract, has been evaluating various materials and procedures that would meet the above requirements. The investigation included bench-scale studies in such areas as: waterside deposit solubility, metal corrosion protection, metal passivation, prevention of copper plating, descalant storage stability, safety to operating personnel, optimum control conditions and the development of analytical procedures to be included in the specification for the procurement of the selected descalant formulations. The Laboratory's mission was to apply the successful bench-scale findings to full scale boiler descaling evaluations on Laboratory and shipboard boilers.

A chemical procedure proposed by Wyndotte was given a full scale trial on the Laboratory Guest boiler. Results of this evaluation, reported by reference (a), showed complete removal of the waterside deposits and satisfactory metal passivation on the carbon steel boiler surfaces. Although the procedure was not fully perfected, particularly in the area of corrosion protection for chrome-moly steels, there was sufficient information available to plan for development of facilities for shipboard chemical cleaning of boilers. The Laboratory

was therefore authorized to proceed with the preparation of the following facilities for a shipboard evaluation:

Suitable mixing tanks for preparation of solutions. These tanks should be either collapsible or easily disassembled for storage.

Chemical resistant pumps and hose

Protective clothing

Necessary steam, air and nitrogen lines to the chemical mixing tanks and boiler.

Detailed instructions covering the procedure described in reference (a), including boiler and cleaning equipment piping arrangement, so that the method can be easily followed by ship's operating personnel.

In addition, the Laboratory was authorized to continually monitor all improved boiler descaling procedures, developed by Wyandotte Chemicals Corporation with respect to boiler metal corrosion protection, copper plating, scale dissolution, optimum control conditions and application of selected methods to full scale boiler cleaning evaluations aboard ship. As part of this program, the Laboratory also participated in the verification and technical appraisal of the analytical methods contained in the Wyandotte-proposed specifications for the procurement of the selected descalant formulations.

DESCRIPTION OF MATERIALS

Chemicals

The following Wyandotte-proposed descalant formulations were evaluated:

Constituent	WYANDOTTE DESIGNATED FORMULATIONS			
	CR-3909-C (percent)	CR-5923 (percent)	CR-7064-B (percent)	3.17.1 (percent)
Sodium bisulfate	91	89	-	-
Sulfamic acid, WAC*	-	-	-	89
Sulfamic acid, WOAC*	-	-	89	-
Citric acid, monohydrate	6	6	6	-
Citric acid, anhydrous	-	-	-	6
Armour RD-2508-P**	3	-	-	-
Diethylthiourea(DETU)	-	5	5	-
Pennacne E inhibitor***	-	-	-	5

* WAC - with anticaking agent (microfine silica). WOAC - without anticaking agent.

** A liquid inhibitor added separately.

*** A blend of about 97% diethylthiourea and about 3% microfine silica.

The passivating formulation, Wyandotte designation CR-3875-B, consisted of the following on a dry basis:

<u>Constituent</u>	<u>Percent</u>
Sodium nitrite	50
Monosodium hydrogen phosphate	25
Disodium hydrogen phosphate	25

Equipment

Collapsible rubber-coated nylon mixing tanks (nominal capacity - 3000 gallons).

Stainless steel chemical mixing tanks (nominal capacity - 2400 gallons).

Stainless steel chemical mixing tanks (nominal capacity - 80 gallons).

Neutralizing tanks.

Acid resistant pumps.

Acid resistant hose.

Steam hose.

Safety equipment.

METHODS AND RESULTS

Preparation of Shipboard Chemical Cleaning Facilities

Two collapsible rubber-coated nylon mixing tanks, an acid resistant pump and necessary hose were purchased by BUSHIPS and shipped to the Laboratory for evaluation. Since these tanks were normally used for storage of potable water, it was necessary to determine whether the tanks were reliable for handling hot acidic and caustic solutions. Several specimens cut from the patches provided with this equipment were exposed to 20% solutions by weight of Wyandotte descalant formulation CR-3909-C and held at 185 F for 4 hours. Other specimens were treated with hot 5% solutions of caustic soda to simulate acid neutralization conditions. Hot chemical solutions were also poured over confined areas of the

bottom of the tanks and after several hours examined for material degradation. All tests showed that there was no degradation of the material and the tanks could be safely used for handling the chemicals. However, it was noted that wherever slight damage to the rubber coating occurred, thus exposing the nylon fabric, degradation would take place. Since damage to the coating was always a possibility, patching trials were also conducted in accordance with the manufacturer's instructions and using the repair kit provided with the equipment. Results showed that the tanks were easily repairable in case of damage. After filling the tanks with water and hooking up the hose and pump and recirculating the water, it was found that, with proper care, the system was suitable for use during shipboard boiler chemical cleaning operations.

Moreover, the tanks could be cleaned, and collapsed into a relatively small package and stored aboard a tender or other ship.

Based on this trial, the tanks and other cleaning equipment were crated and shipped to COMDESLANT for the forthcoming boiler descaling trial aboard the USS MILLER (DD-535). A detailed chemical descaling procedure similar to that used during reference (a) was forwarded to COMDESLANT, with copies to BUSHIPS, by reference (b). This information also included methods for tank erection, tank repair, preparation of the boiler and equipment for cleaning and necessary safety precautions.

Boiler Descaling Trial Aboard USS MILLER (DD-535)

The No. 3 boiler was chemically cleaned on 10 September 1957 by the ship's engineering personnel, assisted by repair personnel from the USS YOSEMITE (AD-19). Before closing the boiler, several RA, RB and RC row tubes were plugged for subsequent removal to compare with removed adjacent tubes (not plugged) for comparison and appraisal of the cleaning operation. Test specimens of carbon steel, carbon-moly and chrome-moly were also suspended in the steam drum for additional metal corrosion information. The boiler piping hook-up method and the

chemical cleaning procedure used were in accordance with the instructions of reference (b) with the exception that the hot water in the boiler, used for preheating the boiler, was pumped into one of the mixing tanks to dissolve the solid descalant chemicals. After the nitrite-phosphate passivating treatment, the boiler was opened for inspection. Preliminary inspection of the steam and water drums and tube ends from each drum showed that the descaling operation was successful. However, after removal and splitting of the plugged (not exposed to the descalant solutions) and the adjacent unplugged (exposed to descalant solutions) boiler tubes, it was found that not all of the waterside deposits, particularly those toward the side of the fire, were removed from some of the tubes. Further examination at the Laboratory revealed that the plugged RA screen row tubes were heavily scaled and would be expected to offer resistance to complete descaling after four hours of treatment. For example: the RA-7 screen tube that was not exposed to the descaling treatment had a scale thickness of 1/16" on the side toward the fire and was badly pitted; the adjacent RA-6 tube, exposed to the descaling treatment, was clean on the side away from the fire but had considerable deposits on the other half of the tube and considerable after-rusting. Comparison of the RB-8 screen tube (plugged) with the RB-9 (unplugged) tube showed satisfactory descaling results. Similar comparisons of the one inch tubes (plugged and unplugged) also showed satisfactory descaling results except for sporadic redeposited but loosened deposits. Where no loose deposits were evident, the waterside metal surfaces were steel grey and well passivated. It was also evident that any loose deposits coating the steel surfaces rejected the nitrite-phosphate passivating treatment. It was estimated that about 80 to 90% of the boiler's deposits were removed by this descaling procedure.

Chemical analyses of the deposits from two adjacent (plugged and unplugged) screen tubes are presented below:

<u>Constituent</u>	<u>Expressed As:</u>	<u>RA-7 (plugged)</u> <u>(Percent)</u>	<u>RA-6 (unplugged)</u> <u>(Percent)</u>
Iron	Fe ₂ O ₃	43.5	20.2
Copper	CuO	21.6	38.9
Calcium	CaO	9.9	7.8
Magnesium	MgO	8.6	2.4
Phosphate	P ₂ O ₅	12.4	5.6
Silica	SiO ₂	2.5	13.5
Zinc	ZnO	3.4	1.8
Sulfate	SO ₃	None	7.8

Results of the analyses indicate the following:

Based on the premise that the adjacent tubes had about the same amounts of deposit with similar chemical composition, it is reasonable to conclude that the 20% by weight CR-3909-C descalant solution selectively dissolved and/or removed considerably more iron, magnesium, phosphate, zinc and to a lesser extent calcium than copper and silica.

The presence of sulfate ion in the RA-6 screen tube unremoved deposit is probably due to the sodium bisulfate in the descaling solution that soaked the deposit.

Subsequent analysis of the "spent" acid descalant showed the following:

Percent acid consumption (based on the original strength) - 18%

Soluble copper - 14 ppm

Suspended copper (undissolved) - 53 ppm

Soluble iron, expressed as Fe₂O₃ - 9.1 lbs./100 gallons of "spent" solution.

Total soluble iron, expressed as Fe₂O₃, removed from the boiler - 228 lbs.

Total suspended iron (undissolved), expressed as Fe₂O₃, removed from the boiler - 8 lbs.

These results further confirm the above observation that more iron was solubilized by the descalant than copper. The fact that the original deposit contained less than 50% iron as Fe₂O₃, it is also presumed that considerably more scaled deposits were removed by this cleaning procedure than the 236 lbs. of total iron

shown above.

Further examination of descaled but rusty split boiler tubes where the thin layers of deposit were originally presumed to be caused by scale re-deposition and/or after-rusting was later shown to be caused by copper plating. When the "rusty" tube surfaces were treated with a copper removing agent, consisting of a dilute ammonium hydroxide solution and containing small amounts of sodium chlorate, potassium bromate and ammonium carbonate, clean tube surfaces were obtained. Needless to say, the copper removing solution turned deep blue, indicating the presence of large amounts of copper deposition. The copper plating problem was known to exist during chemical cleaning of waterside surfaces when the deposits are high in copper content and no copper removing or complexing agent is used. The corrosion inhibitor RD-2508-P, although offering excellent corrosion protection to carbon steel, does not possess inhibiting properties against copper plating. Removal of copper, in the amounts shown above, could only be accomplished by either an external ammonium hydroxide treatment in the presence of oxidizing media or by suitable copper complexing agents contained in the descaling formulation. After treatment of the descaled split tube sections with ammonia, a number of "rusty" tube surfaces looked clean and therefore, after a second appraisal of the shipboard cleaning trial, it was concluded that the trial was satisfactory except for the copper plating problem that will be discussed later in this report. No copper plating problem was encountered during the Laboratory full scale cleaning trial on the Quest boiler (reference (a)), using the same CR-3909-C descalant, because relatively small amounts of copper were present in the waterside deposits.

The previously weighed and measured corrosion test specimens suspended in the steam drum were removed and cleaned with the ammonia-oxidant solution to

remove the copper plating. After drying and reweighing, the corrosion losses were determined. The corrosion rates of these steels expressed as lbs./ft²/hr. are given below:

Type	Loss*
Carbon steel	0.0011
Carbon-moly steel	0.0055
2 1/2% Chrome- 1% moly steel	0.0150

* Average values of duplicate determinations

These corrosion values were in fair agreement with those normally obtained in laboratory beaker tests when similar test specimens were exposed to 20% by weight of CR-3909-C descaler solutions containing corrosive additives normally found in "spent" descalants. However, the corrosion losses of the chrome-moly steel were only about half of those obtained during the Guest boiler descaling trial (reference (a)). These losses were still considered prohibitive and, therefore, this formulation was only acceptable for cleaning the generating bank of a boiler.

At a subsequent meeting with Bureau and Wyandotte Chemicals Corporation personnel, based on the results obtained, the following items were resolved:

Since only 18% of the original acid strength was consumed after the four-hour soaking period, the operation shall be extended to a seven-hour soaking period.

Formulation CR-3909-C shall not be used on carbon-moly and chrome-moly steels.

The ammonia-oxidant copper removing procedure, although effective for removing copper from boiler waterside deposits, shall not be used on shipboard installations due to the potential hazard involved. Other inhibitors, capable of preventing copper deposition, shall be evaluated and blended into the formulation.

The information contained in reference (b) and that obtained from the boiler descaling trial aboard the USS MILLER (DD-535) was used for the preparation by BUSHIPS of the chemical cleaning procedure under Method II of Appendix B of Enclosure (1) of BUSHIPS Instruction 9510.29 Ser 551B-70 of 5 February 1958. The only exception was the extension of the soaking period from four hours to seven hours with intermittent solvent recirculation.

Technical Assistance on Chemical Cleaning of Naval Boilers

Following the USS MILLER boiler descaling trial, the Laboratory conducted training sessions for COMDESLANT personnel, who in turn would supervise the descaling operations on ships under their command. Instruction was offered on piping-up details, acid strength control during the soaking period and the colorimetric determination of soluble iron in the used solutions. In addition, since frequent operations were anticipated, COMDESLANT desired to set up a more permanent chemical mixing facility than the rubber tanks. Moreover, during chemically cleaning of the USS BEATTY boilers No. 1 and No. 2, the rubber-coated nylon mixing tanks sprung leaks and patching proved unsuccessful. The Laboratory furnished this command with details for construction of a stainless steel mixing tank (nominal capacity - 2400 gallons) comparable to that used at the Laboratory. A procedure for the colorimetric determination of total iron was developed and details forwarded. This method also contained maximum limits for iron content (a maximum of 1.2%) as a control for possible reuse of "spent" descalant solutions. This information was forwarded by reference (c).

Boiler Descaling Trial Aboard USS BEATTY (DD-756)

Boilers No. 3 and 4 were descaled by the ship's force on 6-7 May 1958 under the supervision of Laboratory personnel. Inspection of the boiler watersides prior to descaling showed them to be heavily scaled. The piping-up procedure

and descaling method used were in accordance with BUSHIPS Instruction 9510.29 of 5 February 1958. The acid consumption rate and iron pick-up were determined periodically. Boiler No. 4 was the first to be treated with the strong descalant. After about 7 hours, the CR-3909-C solution concentration dropped from 19.0% to 15.1%. Since the iron pick-up did not exceed the maximum limit of 1.2% as Fe (a maximum figure fixed by the Laboratory based on past experience), it was decided to reuse the "spent" solution on the No. 3 boiler. The descalant concentration on this boiler dropped from 15.1% to 10.6%. Boilers No. 1 and 2, although found to be in fair condition, were scheduled for cleaning. However, they were not cleaned due to failures of the rubber-coated mixing tanks. The total amount of iron removed from the No. 3 boiler was 208 lbs. as Fe_2O_3 and that from the No. 4 boiler was 254 lbs. as Fe_2O_3 .

Inspection of plugged (not chemically cleaned) and adjacent unplugged (chemically cleaned) "A" row screen tubes revealed that they were about 90% clean. Considerable pitting was noted on the cleaned tubes. Results of the cleaning trial were generally satisfactory. This information was forwarded to BUSHIPS by reference (d).

Boiler Descaling Trial Aboard USS CADMUS (AR-14)

Boilers No. 1 and 2 were descaled by ship's force on 23-24 August 1958 under the supervision of Laboratory personnel. Both boilers were considered heavily scaled, although No. 1 boiler had 75% of its tubes renewed. The procedure employed was in accordance with BUSHIPS Instruction 9510.29 of 5 February 1958. A 22% solution by weight of CR-3909-C was pumped into the No. 1 boiler and after seven hours of soaking and alternate circulation the concentration dropped to 17.7%. Since the total iron content did not exceed the 1.2% maximum limit, the solution was reused on Boiler No. 2. After some dilution of the "spent" descalant due to heavy rain, the solution strength in the boiler dropped from

16.8% to 11.4%. The total iron pick-up during this trial was rather low where only 102 lbs. of iron as Fe_2O_3 was removed from the No. 1 boiler and only 89 lbs. from the No. 2 boiler. An evaluation was also made of the use of pH test paper as a means for shipboard control of acid depletion rate. Although satisfactory results were obtained at the Laboratory when compared with readings on a Beckman pH meter, the results obtained during this trial were subject to question and the idea was abandoned.

Inspection of the boilers made it appear at first that the cleaning operation was successful. However, inspection of plugged and unplugged split screen row tubes showed only about 80% scale removal, presumed to be due to the heavy deposits originally on the tubes. Consideration was therefore given to re-cleaning of the No. 2 boiler. This information was reported by reference (e).

Further tests were requested by BUSHIPS to account for the low iron content in the "spent" descalant solutions, while the acid consumption was relatively high. It was therefore decided to determine the nature of the deposit on a split boiler tube section, removed prior to the descaling trial, that was submitted for analysis. Examination of the tube showed that the deposit was composed of two distinct layers. The top layer was a soft, reddish brown powdery deposit easily removable by brushing. The lower uniform layer made up the major part of the deposit and was 1/16" thick. This layer was not removable by wire brushing and was very hard and tenacious and would be difficult to remove with the bisulfate formulation. Results of the analyses indicated that the lower dense layer, which comprised the major part of the deposit, contained only 15.33% of iron, expressed as Fe_2O_3 . The principal component of the deposit was zinc (55.65% as ZnO) followed by phosphate (12.78% as P_2O_5) with lesser amounts of other waterside scale constituents. It was of interest to note that the copper content was quite low (0.55% as CuO). The upper soft layer contained

more iron and less zinc. This explained the reason for the low iron pick-up by the descaling solution and the relatively high acid consumption. Since only a small portion of the deposit consisted of iron, it was conceivable that only 102 lbs. and 89 lbs. expressed as Fe_2O_3 , were removed from boiler No. 1 and 2 respectively. It is also safe to assume, based on the low iron content in the major portion of the deposit, that at least three hundred lbs. of scale were removed from each boiler. This type of hard deposit would not be readily removable by the CR-3909-C descalant formulation or, for that matter, by a 10% inhibited hydrochloric acid solution.

Results of the analyses of the waterside deposits also showed that the iron pick-up test used during descaling operations is not significant enough as a criterion for the completion of a boiler descaling process, particularly where the baked-on sludge is low in iron. It was therefore recommended that the iron test be dropped. The acid-base titration procedure is the simplest means for predicting the completion of the operation when an average amount of soft scale is present in the boiler. Under extreme conditions, as found on these tubes, a 16-hour soaking period would have been more effective to remove all of the deposits. Similar deposits, treated at the Laboratory, usually require 16 hours of treatment for complete scale removal.

The results of the analyses of the descaling solutions after successive hourly recirculations and the analyses of the deposits were reported by reference (g).

Electrometric Procedure for the Assaying of the CR-3909-C Descalant Formulation

A proposed military specification for the procurement of a Navy solid descalant compound similar in composition to the CR-3909-C formulation was prepared by Wyandotte. Included in the specification was a proposed procedure for the assaying of the solid form compound for total acidity, bisulfate acidity

and citric acid. The method, developed by Wyndotte, was electrometric, whereby the composition of the sodium bisulfate - citric acid mixture could be determined in a single titration. This procedure was less time-consuming than the conventional gravimetric methods of analysis for citric acid by the pentabromacetone method, for sulfate by the barium sulfate method and for total acidity by the standard acid-base titration method. The electrometric procedure consisted of titrating the descalant sample with tetramethyl ammonium hydroxide (TMAH) in isopropanol. Two inflection points are obtained in this titration from which the percentage total acidity, bisulfate acidity, citric acid and sodium bisulfate can be calculated. Sharp end points are produced at each inflection, provided the proposed schedule for the addition of the small increments of TMAH is closely followed.

The Laboratory was requested to verify this analytical procedure and offer a technical appraisal as to the accuracy and reproducibility of the method and pertinent comments. Three separate batches of the solid portion of the Wyndotte descalant formulation CR-3909-C were used for this analytical study where 12 aliquot samples (four from each batch) were prepared. Results for total acidity, bisulfate acidity and citric acid showed excellent reproducibility and in good agreement between the average values obtained at the Laboratory and those of Wyndotte. The composition limits listed in the proposed specification for the Navy descalant (CR-3909-C) were 37.5 to 41.2% for total acidity as H_2SO_4 , 33.0 to 37.0 for bisulfate acidity as H_2SO_4 , and 6.2 $\pm$ 1.0% for citric acid. The average results obtained at the Laboratory were 39.5% total acidity, 34.9% bisulfate acidity and 6.6% citric acid, or about half-way between the proposed specification limits.

The Laboratory therefore recommended that the proposed analytical procedure be considered acceptable as part of the specification requirement for the

procurement of Navy Boiler Descalant Compound (CR-3909-C). A report on the analytical investigation was forwarded by reference (h).

Descaling Trial on Fire Tube Auxiliary Boiler Aboard the USS FEARLESS (ASO-442)

Wyandotte Chemicals Corporation, based on their bench-scale corrosion data on a number of non-ferrous alloys and including silicon-bronze, reported that the descalant formulation CR-3909-C can be safely used on silicon-bronze fire tube boiler waterside surfaces without the need of a corrosion inhibitor. In addition, since no after-rusting on these surfaces takes place, the nitrite-phosphate treatment step can be eliminated. In order to fully evaluate this procedure, a silicon-bronze fire tube auxiliary boiler was descaled on 24 February 1959 by ship's personnel under supervision of Bureau and Laboratory representatives. Before this operation, six previously weighed and measured silicon-bronze test specimens were hung in the boiler to compare corrosion values during boiler descaling with those obtained at Wyandotte. A fire tube carbon steel auxiliary boiler was also descaled. The silicon-bronze boiler received the 20% by weight of uninhibited solid descalant (CR-3909-C) treatment followed by a mild acid-rinse (pH-2) and a water rinse. The carbon steel auxiliary boiler received the regular inhibited descaling treatment, including the pH-2 rinse and the nitrite-phosphate application, as required by BUSHIPS Instruction 9510.29 of 5 February 1958. In addition, air displacement of solutions was used on the silicon-bronze boiler, while nitrogen gas displacement was applied on the carbon steel boiler. Both boilers were treated for seven hours with the strong descalants.

A post-cleaning inspection of the waterside surfaces of both boilers revealed that the descaling operation was successful. However, tube No. 23 in the carbon steel boiler had developed a leak during the operation and required plugging. Tubes No. 3 and 23 were subsequently removed and shipped to the Laboratory. Inspection of the watersides revealed much corrosion and pitting,

with pit penetrations of 50 to 100% on tube No. 23 and 50 to 60% on tube No. 3. The cause of this trouble was directly attributed to the use of untreated water in the boiler.

The silicon-bronze test specimens hung in the boiler were removed, cleaned, dried, weighed and metal loss calculated. Results showed only negligible corrosion losses even in the absence of a corrosion inhibitor and without a nitrite-phosphate passivating treatment.

An analysis of the original waterside scale found in the silicon-bronze boiler showed the principal constituents to be calcium, magnesium, copper, silica and iron. Analyses of the spent descalants from both boilers were also made.

Based on the negligible corrosion losses obtained on the silicon-bronze specimens, the Laboratory recommended that the uninhibited formulation CR-3909-C can be safely used for descaling of silicon-bronze boilers. It was also recommended that the ship should adopt a water treatment program in order to minimize the corrosion and pitting in the carbon steel boiler. This information - reported by reference (1).

Boiler Descaling Trial Aboard USS VULCAN (AR-5)

Since copper plating was shown to be a serious problem, particularly during the USS MILLER (DD-535) descaling trial where the copper content in the waterside deposits was high, Wyandotte evaluated a number of sulfur-bearing corrosion inhibitors that looked promising in preventing copper plating on cleaned boiler waterside surfaces. Diethylthiourea inhibitor (DETU) showed to be the most suitable agent for blending into the solid portion of the CR-3909-C descalant formulation with respect to prevention of copper plating and the absence of objectionable evolution of sulfide gases, so characteristic of other sulfur-bearing inhibitors. In addition, this inhibitor (DETU) offered excellent

corrosion protection to stainless and chrome-moly steels and their bi-metallic junctions, while inhibitor RD-250E-P, contained in the CR-3909-C formulation, exhibited very poor protective characteristics for chrome-moly steels. Use of the DETU inhibitor would therefore offer a bonus feature during chemical descaling of superheaters on 600 psi boilers, where $1\frac{1}{2}$ chrome or $2\frac{1}{2}$ chrome is found in the superheaters and on 1200 psi boilers, where the headers are $1\frac{1}{2}$ or $2\frac{1}{2}$ chrome, with $1\frac{1}{2}$ or $2\frac{1}{2}$ chrome tubes, followed by 18-8 stainless in the last pass of the superheaters. In the 1200 psi boiler systems, where bi-metallic welds join the chrome-moly steels with the 18-8 stainless steels, chemical cleaning of the superheaters would be safe when DETU is used. A new descalant was therefore formulated, containing sodium bisulfate, citric acid and diethylthiourea, Wyandotte designation CR-5923. Since past boiler descaling trials showed that the bisulfate-citric acid mixture was effective on boilers that contained relatively small amounts of waterside deposits and was not totally effective on dense, hard and tenacious deposits, it was decided to select a ship known to have heavily scaled boilers for the next boiler descaling trial.

During the forthcoming trial, it was also desired to study the effect of using "spent", but reformed descalant solution on the corrosion of boiler steels.

Boilers No. 1 and 2 were descaled by ship's force on 3-4 June 1959 under the supervision of BUSHIPS and Laboratory personnel. Boiler watersides inspection prior to the descaling operation could not be made because the boilers were closed up by ship's personnel before the arrival of Laboratory representatives. Before closing the boiler, several boiler tubes were plugged for subsequent removal and comparison with adjacent removed unplugged tubes in order to determine the efficacy of the cleaning operation. Also, previously supplied corrosion test specimens representative of all types of boiler steels and including bi-metallic welds of $2\frac{1}{2}$ chrome and 321 stainless steel, were suspended in the steam

drums of both boilers. This was done in order to compare the corrosion losses obtained on these specimens with the fresh descalant to be used on the No. 1 boiler and the partially spent solutions, refortified with additional descalant and inhibitor to be used on the No. 2 boiler. These specimens were exposed to saturated water vapor for about 24 hours before exposure to the descaling and passivating treatments. The piping up procedure and descaling method used were in accordance with BUSHIPS Instruction 9510.29 of 5 February 1958 except that the new descaling formulation CR-5923 was employed. However, due to operating difficulties, particularly with leaking fittings on the rubber-coated nylon tanks and inadvertent dilution, the initial acid concentrations were below the desired 20% strengths. After seven hours of soaking in boiler No. 1, part of the "spent" solution was used to fill boiler No. 2 after first injecting 800 gallons of 17.9% by weight of fresh CR-5923 descalant solution into this boiler. During this trial, the procedure for external dissolution of diethylthiourea in bulk form was also evaluated. This was successfully accomplished by applying steam to the inhibitor in a separate container and adding the molten mass to the large tank containing the dissolved descalant. Hourly solvent samples were taken from the steam drum and port and starboard water drums and descalant concentrations determined.

Inspection of the boilers at the conclusion of the trial showed that the descaling operation was unsuccessful. Split, plugged tubes (not exposed to the descaling treatment) from both boilers showed extremely heavy and tenacious deposits. Some of the split, adjacent unplugged tubes (exposed to the treatment) also showed heavy, tenacious deposits that were not removable by wire brushing. A number of split tube sections were shipped to the Laboratory for further examination. The deposits, before descaling varied in appearance and thickness, with some deposits exceeding 0.030" in depth. A row B-12 tube from boiler No. 1, after descaling and wire brushing, had a dark brown glazed

deposit ranging from 0.015" to 0.025" thick. This deposit could only be removed by crimping of the tube in a vise.

Several samples of deposit, removed from the boiler tubes before and after descaling, were analyzed by wet chemical techniques, by X-Ray spectrographic methods and identified by X-Ray diffraction. Results showed a predominance of copper and zinc on all samples. A good bit of the copper was present in metallic form. The iron content and the other typical sludge deposits were low.

Visual examination of the corrosion specimens, removed from the steam drums, showed no evidence of corrosion, pitting or copper plating and was indicative of the effectiveness of the DETU as an inhibitor and an agent for preventing copper plating, in spite of the high copper concentration in the boiler deposits. The corrosion data, supplied by Wyandotte, on six boiler steels and one bi-metallic weld junction showed low and acceptable metal loss values in the presence of the corrosive contaminants present in the boiler sludge. In addition, the corrosion losses were of the same magnitude in either boiler, namely, using the fresh CR-5923 descalant in No. 1 boiler or the re-rtified "spent" acid solution in No. 2 boiler.

Results of this trial showed that the CR-5923 formulation was not effective in the removal of the heavy, hard and tenacious baked-on sludge deposits present in the USS VULCAN boilers. This was also confirmed by laboratory tests which showed that similarly scaled tube samples, when exposed to a 20% by weight of CR-5923 solution and maintained for seven hours at 185 F, were only partially descaled (60%). Treatment of similarly scaled tube sections from these boilers with inhibited 10% hydrochloric acid solutions at 170 F completely removed the deposits within two hours. It follows that this type of deposit should have been treated with either hydrochloric acid or a solid descalant that possesses greater scale solubilizing properties than sodium bisulfate. This information was reported by reference (1).

Additional descaling evaluations were conducted on split, scaled USS VULCAN boiler tube sections using 10% inhibited hydrochloric acid solutions and 16% CR-5923 solutions (concentration used during the boiler descaling trial). Since a high silica content was first suspected, 1% of ammonium bifluoride was added to some of the solutions. Results of these evaluations showed that the tube sections were completely descaled by the hydrochloric acid in one half to three hours, while only 70 to 80% of the deposits were removed from similar tube sections after seven hours of treatment with the CR-5923 formulation. Addition of ammonium bifluoride had no effect on either of the solutions. All of the HCl descaled surfaces showed considerable copper plating. The CR-5923 and DETU-inhibited steel surfaces also indicated slight copper plating. Since this inhibitor was known to prevent copper plating, further study was suggested to establish whether the copper was a result of plating even in the presence of DETU or was initially present before the descaling treatment. This information was reported by reference (j).

Additional tests were conducted to establish whether DETU prevents copper plating and to further compare the descaling ability of the CR-5923 formulation with that of inhibited hydrochloric acid when applied to USS VULCAN split boiler tube sections. New steel specimens were exposed to 20% solutions of CR-5923, CR-3909-C and 10% HCl solutions, inhibited with Rodine 213 and also with DETU. The specimens were immersed in 100 ml. of the indicated solutions, each containing 625 ppm of anhydrous cupric sulfate, and treated under static conditions for 7 hours. Results showed that all the DETU-inhibited solutions completely prevented copper plating. Formulation CR-3909-C, inhibited with RD-2508-P and the hydrochloric acid solutions, inhibited with Rodine 213 indicated slight copper plating after five minutes of exposure to those solutions. Heavy copper plating was noted after exposure for one hour. Split, scaled USS VULCAN boiler tube sections were treated with 20% CR-5923 solutions and similar sections with 10% HCl solutions, inhibited with Rodine 213. The specimens were immersed in

100 ml. of the indicated solutions and held at 165 F and 170 F respectively at static conditions. The percentage of scale removal was estimated each hour. Results showed that the specimens treated with hydrochloric acid were descaled in less than two hours, while those exposed to the CR-5923 formulation were incompletely descaled (60 to 90% removal) after seven hours of treatment. The remainder of the deposits was soft and was readily removed by wire brushing. The HCl-treated tube sections were copper plated, while the CR-5923-treated sections exhibited presence of high copper, it was presumed that the copper was not a result of plating but rather due to the presence of high copper (25 to 50%) in the unremoved portions of the deposits.

The results of the above tests indicated that diethylthiourea inhibitor completely prevented copper plating even in hydrochloric acid solutions. The superiority of the hydrochloric acid descalant over the CR-5923 formulation in removing the hard, tenacious deposits from USS VULCAN split tube sections, as reported by references (j) and (i), was further confirmed by these tests. In addition, the 20% CR-5923 solution strength did not notably improve scale removal over the 10% solution used during the USS VULCAN boiler descaling trial. This information was reported by reference (k).

Removal of Waterside Deposits from USS MASSEY (DD-778) Boiler Tube

Since considerable difficulty was experienced in removing various hard and tenacious boiler waterside deposits from tube surfaces when solutions of sodium bisulfate - citric acid formulations were used, further laboratory tests were conducted to compare the scale removing ability of the CR-5923 descalant with inhibited hydrochloric acid. The deposit on an RA row tube was 0.009 to 0.013" thick and was hard enough not to be removable by wire brushing or chiseling. One tube specimen was exposed to the CR-5923 descaling treatment and held at

165 F for seven hours, while another was treated with a 10% hydrochloric acid solution and maintained at 170 F. Inspection of the treated samples revealed the following:

Only about 30% of the deposit was removed by the CR-5923 formulation. The remainder of the hard, baked-on sludge was not removable by wire brushing.

There was no copper plating on the cleaned surfaces nor on the cut edges of the specimen. This further confirmed that DAFU, contained in the CR-5923 formulation, offered adequate protection against copper plating.

The deposit was completely removed by the hydrochloric acid after 30 minutes of exposure time.

A bright, metallic copper plate was visible on the metal surface and particularly on the cut edges of the specimen. This was due to the use of Redine 213 inhibitor in the hydrochloric acid solution which does not possess copper plating inhibiting characteristics.

A qualitative identification of the loosened deposit, obtained by crimping a section of the original sealed tube, showed it to consist of iron, phosphate,

per, zinc, nickel and other waterside scale components. The main constituents were iron and phosphate, indicating a baked-on sludge. This was another instance of a stubborn waterside deposit not removable by the CR-5923 formulation while easily solubilized and/or removed by a 10% hydrochloric acid solution, used as the standard decalcant throughout these evaluations. It follows that a more effective solid decalcant formulation is needed to be capable of solubilizing and/or removing a variety of boiler waterside deposits found on heat transfer surfaces. This information was reported by reference (m).

Boiler Descaling Trial /board USS HAWOOD (DDK-361)

Boilers No. 1 and 2 were descaled on 24-25 April 1960 by ship's fitter and COMDESLANT personnel under the supervision of Laboratory representatives. Before

closing up the boilers, one RA row tube was plugged (not cleaned) and the adjacent tube wire brushed and plugged (not cleaned) on each boiler in order to compare the condition of the original tube (plugged) with the wire-brushed tube and that of another adjacent tube that was exposed to the decalcant solution. The procedure used was in accordance with BUSF's instruction 9510.29 of 5 February 1958, employing the CR-300-0 decalcant solution except that two stainless steel tanks (nominal capacity - 2600 gallons) were utilized in place of the rubber-coated nylon tanks. Although the boilers were tested hydrostatically prior to the descaling trial, boiler No. 1 developed a leak around the manhole cover of the steam drum which made it necessary to dump the solution after four hours of soaking and alternate circulation and boiler No. 2 developed an uncontrollable leak around the cover of the sidewall header which made it necessary to dump the solution after two hours and 40 minutes of treatment. Both boilers received the pH-2 solution rinse followed by the nitrite-phosphate passivating rinse. Inspection of the boilers and the removed tubes revealed the following:

Boiler No. 1 appeared clean looking down from the steam drum with a lot of loosened debris on the drum internals. The three previously identified screen tubes were removed and split. A loose, gray residual deposit remained on the tube that was exposed to the decalcant, but this was easily removed by wire brushing. Once the tube was brushed, bare metal was revealed. Crimping of this tube produced no further scale. The tube that was plugged (not chemically cleaned) and the tube that was wire brushed and plugged contained considerable amounts of scale. It was noted that wire brushing only polished the hard scale but did not remove it. However, it was recommended that the boiler be mechanically cleaned since the loosened deposits after decalcant were removable by this method.

Boiler No. 2 when viewed from the steam drum appeared clean. However, when three split tubes, similar to those removed from No. 1 boiler, were examined,

Incomplete scale removal was noted. This was to be expected because the descaling solution remained in the boiler only two hours and 40 minutes instead of the specified seven hours. It was recommended that this boiler be retreated at a later date after the manhole and handhole gaskets were replaced prior to cleaning to avoid recurrence of solvent leakage.

It was also recommended that the cleaned boilers be blown down frequently to facilitate removal of any loose residual deposits. Blowdown was to continue until the boiler water was clear. A report of this trial was forwarded by reference (c).

Boiler Descaling Trial Aboard USS TAUSIG (DD-746)

Based on the above boiler descaling trials and Laboratory bench-scale evaluations, it was evident that the sodium bisulfate - citric acid formulations were only effective as scale removing agents on some types of waterside deposits, but ineffective on others, such as those present in the USS VULCAN, USS CADMUS and USS MASSEY and other hard, tenacious deposits. In addition, whenever hard and tenacious deposits were being removed, the solid formulations never approached the descaling characteristics of a 10% solution of inhibited hydrochloric acid.

As a result, Wyandotte Chemicals was requested to evaluate other solid descalant formulations that would meet shipboard descaling needs and at the same time possess better scale solubilizing properties than the bisulfate - citric formulations. Of the formulations tried on USS VULCAN and other difficult to remove deposits, sulfamic acid in combination with citric acid was the most promising descalant and compared favorably with the scale-dissolving properties of a 10% hydrochloric acid solution. During these evaluations, it was also established that treatment of split USS VULCAN tube specimens was not a fair test for the evaluation of descaling characteristics of the various solutions because lifting of deposits at the cut edges was noted. For more realistic conditions, whole (3 to 4" long), sealed boiler tube sections were filled with the indicated

solutions and maintained at specified temperatures. The tubes were then split and examined. Results showed that although the hydrochloric acid treatment was slightly better than the sulfamic acid, the latter formulation was far superior to the CR-5923 formula as a descalant.

Subsequent Laboratory descaling evaluations on scaled USS VULCAN and other whole tube specimens produced the same results as above, namely, that sulfamic-citric acid was far superior to bisulfate - citric, but slightly inferior to hydrochloric acid. Although the mineral acid was generally slightly superior to the sulfamic - citric mixture, better descaling results were obtained in some instances with the solid formulation on several whole, scaled tube sections removed from other boilers. Another phase of this evaluation consisted of scale solubility studies, where weighed amounts of finely divided (200 mesh) waterside scale samples were exposed to various acid treatments. Results were generally the same as those obtained on scaled tube sections and in agreement with results obtained by Wyndotte that none of the solid descalants evaluated equalled the boiler scale solubilizing properties of hydrochloric acid. However, the sulfamic-citric acid formulation was superior to all other solid descalant combinations.

Another distinct advantage of the sulfamic acid descalant over the bisulfate formulation is that the reaction products are more water soluble. This was particularly evident when calcium-bearing waterside scales were exposed to the various solutions. Sodium bisulfate treatment of these deposits showed poor solubilities due to formation of calcium sulfate reaction products. Although the sulfamic-citric acid solution caused a gradual decrease in solubility of the calcium-containing compounds with an increase in solution concentration and temperature (150 to 185 F), presumably due to partial hydrolysis of the sulfamic acid to ammonium bisulfate, the extent of scale solubility was considerably greater than with the sodium bisulfate solution. Needless to say, under these conditions the hydrochloric acid was by far the best solvent. This information was reported

periodically by reference (u).

Although some difficulty was experienced with the DETU-inhibited sulfamic acid formula in completely preventing the deposition of copper, a 20% by weight descalant solution, consisting of 17.8% sulfamic acid, 1.2% citric acid and 1.0% DETU (Wyandotte designation CR-7064-B) was selected for use in the forthcoming boiler descaling trial aboard the USS TAUSSIG.

On 18-19 May 1960, boilers No. 3 and 4 were chemically cleaned with the 20% CR-7064-B solution by USS TAUSSIG personnel under the supervision of Wyandotte Chemicals Corporation, BUSHIPS and Laboratory representatives. Before closing up the boilers, two A-row tubes were plugged for future comparison with adjacent unplugged tubes in order to appraise the cleaning efficacy of this operation. Boiler tube test specimens, ranging from carbon steel to 18-8 stainless, were suspended in the steam drums in order to compare the results of corrosion losses under actual service conditions with those previously obtained during laboratory bench-scale tests, using the same descaling conditions. Instead of using a large mixing tank equal or greater than the boilers' capacity, a small stainless steel tank (80 gallon capacity) was used to mix the descalant. This was accomplished by recirculating the hot water from the preheated boiler through the mixing tank to which the solid descalant chemicals were gradually added. The continuous recirculation, aided by a steam line at the bottom of the tank, dissolved the chemicals and returned the solution to the boiler. Sufficient descalant was added to yield a 20% solution. It required about 2½ to 3 hours to mix and circulate the solution in each boiler. Soaking continued for 7½ hours with intermittent recirculation. The average temperature was at 175 F. The strength of the "spent" solutions in each boiler was 15.9%. After dumping the "spent" solutions, the boilers received a mild (pH-2) rinse and a passivating rinse as set forth in BUSHIPS Instruction 9510.29 of 5 February 1958,

except that sulfamic - citric was used in preparing the pH-2 rinse solution.

Examination of the drum surfaces revealed satisfactory descaling.

However, when RA row tubes were removed and split, it was noted that some scale remained on both straight and bent sections on the side toward the fire. An adjacent plugged tube that did not receive the chemical treatment was heavily scaled. It was estimated that about 85% of the original deposit was removed.

Analyses of the original boiler waterside deposits, conducted at the Laboratory, revealed that the major constituents were iron, zinc, copper and calcium compounds. Analyses of "spent" solution from No. 4 boiler showed that there were 235 lbs. of scale, expressed as R_2O_3 . Since the original deposit only contained 19.7% as Fe_2O_3 , it was concluded that the total amount of removed scale was considerably greater than 235 lbs.

Further Laboratory descaling tests on USS TAUSSIG split RA row tube sections, using various descalants showed that complete descaling was accomplished with hydrochloric acid and sulfamic acid based formulations. Only negligible amounts of scale were removed by the CR-5923 bisulfate - citric formulation. No copper plating was noted on the specimens that were exposed to hydrochloric acid, inhibited with DETU. Slight copper plating was noted on the samples treated with DETU-inhibited sulfamic acid and heavy copper plating where no DETU was used. Similar descaling tests were conducted on USS YELLOWSTONE (AD-27) split tube specimens where the scale thickness ranged from 0.022 to 0.042". On these samples, only the hydrochloric acid completely removed the scale and none of the solid formulations were effective as descalants. However, the CR-7064-B formulation was considerably superior to the CR-5923 descalant. Unfortunately, the lack of scale thickness uniformity made this evaluation rather difficult.

The boiler tube specimens that were suspended in the steam drum during the descaling operation on the USS TAUSSIG were removed and the metal corrosion

rates determined at the Laboratory. Results showed that low and acceptable corrosion values were obtained on low carbon, medium carbon, carbon-moly, Croloy 1 $\frac{1}{2}$ and Croloy 2 $\frac{1}{2}$ steels. Negligible corrosion values were obtained on 18-8 stainless steel. No copper plating was found on any of the specimens. These data were in fair agreement with bench scale laboratory corrosion tests and with those obtained by Wyandotte Chemicals Corporation. Although hydrochloric acid is still somewhat the better descalant, it cannot be used to clean superheaters on high pressure boilers. The present formulation CR-7064-B can be used with safety on 18-8 desuperheaters should cleaning of these systems become necessary. This information was reported by reference (p).

Effects of Various Treatments on After-Rusting Resulting from Chemical Cleaning

Since a proprietary descalant, containing sulfamic acid, and a proprietary neutralizing compound were previously used by USS TAUSIG personnel to clean boilers No. 1 and 2 and other ships would be likely to employ the same chemicals, it was desired to study the merits of this neutralizing compound when compared to the passivating treatment CR-3875-B that was used during the above boiler descaling trials. Examination of the proprietary neutralizer revealed that it consisted of sodium carbonate, known to produce considerable after-rusting on acid treated metal surfaces. The Laboratory, therefore, conducted a number of tests to determine the effects of the various rinsing and passivating treatments on after-rusting resulting from chemical cleaning.

Six inch long, scaled A-row USS MASSEY boiler tubes were used in the Laboratory investigation. Each tube was treated as a "boiler" in a manner similar to a full scale boiler descaling trial. The tubes were filled with the indicated descaling, rinsing and passivating solutions through the bottom and displaced with nitrogen gas from the top. Filling and draining time was also controlled to simulate an actual boiler operation. Results were as follows:

Considerable after-rusting took place when either sodium carbonate or the proprietary neutralizer were employed after the descaling step regardless of the acid used.

No after-rusting resulted when the tubes were treated with DETU-inhibited sulfamic acid (both 5.5% and 20% by weight), followed by a mild acid rinse (pH-2) and by passivating with the nitrite-phosphate formulation CR-3875-B.

After-rusting also took place when the proprietary sulfamic acid formulation was used even when the tube was exposed to a mild acid rinse and followed by a nitrite-phosphate passivation in lieu of proprietary neutralizer. Since the waterside deposits on the USS MASSEY tubes were high in copper and the proprietary descalant did not contain an inhibitor that would prevent copper plating, the copper deposited on the metal surface and rejected passivation. This phenomenon did not occur when DETU-inhibited sulfamic was used.

Based on these results, the Laboratory recommended that sodium carbonate or the proprietary neutralizer not be used for neutralizing purposes following chemical cleaning of boilers. Furthermore, since the proprietary sulfamic acid descalant did not prevent copper plating and also caused after-rusting due to incomplete passivation, it was not recommended for use as a descalant. A report on boiler metal after-rusting was forwarded by reference (q).

Extent of Hydrogen Evolution During Chemical Descaling of Boilers with Inhibited Sulfamic Acid

During chemical cleaning of boiler watersides with inhibited sulfamic acid, CRUDESPEC employs a small stainless steel tank (similar to that used on the USS TAUSSIG descaling trial) for continuously dissolving and mixing the solid descalant formulation. During this operation, this tank (40 gallon capacity) has been located dockside. In order to simplify and reduce the piping hook-up

to a minimum, CRUDESAPAC was considering relocating the mixing tank in the fireroom near the boilers being cleaned. Since it is known that some hydrogen evolution takes place with inhibited hydrochloric acid, the Laboratory was requested to obtain information on the extent of hydrogen evolution around the small tank when an inhibited sulfamic acid solution is used. Based on the relatively low metal loss in inhibited sulfamic acid solutions, very little gas evolution would be expected. However, before permitting the mixing tank to be located in the fireroom, Laboratory tests should be conducted.

Bench-scale evaluations as well as a full scale boiler test were conducted at the Laboratory. The bench-scale tests were made on scaled 6" lengths of 2" boiler tubes. These tubes were partially filled with the descaling solutions and the vents closed to prevent escape of hydrogen. The full scale evaluation was conducted in conjunction with the cleaning of the superheater on the CVA-63 test boiler. The descalants used in the bench-scale tests were 10% solutions of inhibited hydrochloric acid, DETU-inhibited sulfamic acid and DETU-inhibited bisulfate formulations. The descalant used during the full scale boiler test was a 10% solution by weight of the CR-7064-B formulation. The small stainless steel mixing tank, similar to that used at CRUDESAPAC, was employed during this operation. A cone-shaped lid with a petcock on top was fabricated and attached to the tank to entrap and measure the hydrogen gas evolved. A Mine Safety Appliance Hydrogen Explosimeter was used to determine the percentage explosivity.

Results on the scaled boiler tube sections, when the vents were opened, showed presence of explosive hydrogen in both the hydrochloric acid and solid descalant filled tubes. Results on the full scale test also showed presence of explosive hydrogen gas on top of the mixing tank whenever the solution was recirculated through the superheater and the tank. Since the CVA-63 superheater is composed of chrome-moly and stainless steel, very little corrosion due to the

inhibited sulfamic acid takes place and hence, very little hydrogen evolution. During the chemical cleaning of the saturated side of a boiler, consisting of carbon steel, considerably greater quantities of hydrogen gas will be evolved during recirculation of the inhibited sulfamic acid solution. This is based on laboratory results where, although low and acceptable corrosion values are obtained on carbon steel, practically negligible corrosion values are obtained on stainless steel.

In view of the explosive mixtures of hydrogen gas found around the mixing tank during descalant recirculation, the Laboratory recommended that CRUDESPAC be instructed not to locate the mixing tank in the fireroom during chemical descaling of boiler watersides. It was also emphasized that the command strictly adhere to the safety precautions set forth in BUSHIPS Instruction 9510.29 of 5 February 1958. A report of this investigation was forwarded by reference (r).

Inter-Laboratory Analytical Studies

Based on the results of the boiler descaling trial aboard the USS TAUSSIG, Wyandotte's progress reports and the Laboratory's reports (references (p), (q)

(u)), it was evident that some problems, such as, complete inhibition against copper plating, reuse of "spent" solutions, use of lower acid concentrations and metal passivation after hydrostatic tests, have yet to be resolved. However, although additional work toward improving the descalant formulation CR-7064-B would continue, the Bureau indicated that it was satisfied with its performance and wished to place the formulation into the Navy stock system. Wyandotte was therefore requested to prepare an interim specification for the existing sulfamic - citric - DETU formulation. This specification should contain suitable analytical methods for the determination of sulfamic acid, citric acid and diethylthiourea in the presence of each other because it is desired that the finalized compound be stocked as a one-package formulation.

In connection with the writing of the specification, Wyandotte was to consider the storage problem of the compound under shipboard conditions, and if necessary, include an anti-caking agent. If the latter is used, an analytical method for its determination should also be included in the specification.

On 10 March 1961, BUSHIPS and Laboratory representatives visited Wyandotte Chemicals Corporation to review the progress made on the study of storage characteristics of the combinations of various grades of sulfamic acid, citric acid, when stored in contact with and without DETU, under various conditions and to discuss details pertaining to the proposed interim specification for the Navy Boiler Scale Removing Compound. Wyandotte presented a summary on the storage characteristics of 23 mixtures. The data listed the various components of each mixture and included storage properties as to degree of caking, flow, dustiness and chemical reaction phenomena, such as discoloration and resultant odor. A laboratory demonstration of the storage properties of these mixtures after prolonged storage time was witnessed so that the optimum free-flowing and dust-free one-package formulation could be selected. Formulation 3.17.1, consisting of 89.0% of crystalline sulfamic acid, 6.0% of anhydrous citric acid and 5.0% of Penzone E inhibitor was selected as the best formulation based on its storage characteristics. The inhibitor contained 96.6% of crystalline diethylthiourea and 3.4% of microfine silica, used as an anti-caking agent. Based on the 5% Penzone E inhibitor concentration, the silica contribution was 0.17% and that of diethylthiourea 4.83%. Since the crystalline sulfamic acid contributed an additional 0.06% of microfine silica (added by the manufacturer), the total silica content in the 3.17.1 formulation was 0.23%. Although formulation 3.24.1, consisting of 88.7% of crystalline sulfamic acid, 6.0% of anhydrous citric acid, 5.0% of DETU and 0.3% Quso F-20 (microfine silica), exhibited slightly better flowing characteristics than the 3.17.1 mixture, it was not considered acceptable because its total silica content was higher (0.36%) and produced considerable

dusting that was irritating to the eyes and nose due to carryover of fine particles of the sulfamic acid. Since Penoxone E is a proprietary inhibitor, it was agreed to specify an inhibitor mixture consisting of about 4.85% crystalline DETU and 0.15% of microfine silica where the combination would be blended with the acid constituents in one package. The interim specification details were also discussed and maximum and minimum limits of each constituent were resolved.

Upon receipt of the Wyandotte-proposed interim specification of 7 March 1961 for the procurement of the "Boiler Scale Removing Compound", the Laboratory was requested by BUSHIPS to participate in the inter-laboratory evaluation of the analytical procedures contained in the specification. This included analyses on a referee sample CR-10572, submitted by Wyandotte, for sulfamic acid, citric acid, diethylthiourea and silica. It was also requested that these analyses be conducted by two analysts on two separate days completing four determinations each day, totaling a minimum of sixteen determinations for each constituent in the referee descalant sample. Results, including comments and suggestions, were to be submitted to Wyandotte. The information was to be used for a statistical study to determine the validity of the proposed analytical methods contained in the specification. The analytical methods called for the determination of sulfamic acid by potentiometric titration with a standard sodium nitrite solution; for the determination of DETU by ultra-violet absorption; for citric acid by difference after subtracting the sulfamic acid acidity, the ammonium bisulfate acidity and the interference due to DETU from the total acidity that is obtained by titration with a standard sodium hydroxide solution. The determination for silica was the standard laboratory procedure. Although the Laboratory followed the details of the proposed procedure, it was found necessary to make certain changes in the potentiometric titration for sulfamate ion and in the calculations for citric acid by difference to obtain meaningful results. The procedure for arriving

at the end point with reasonable accuracy in the potentiometric titration for sulfamate ion was simplified so that the titration could be completed within 20 minutes instead of several hours. This procedure was verified by running a number of samples containing known amounts of sulfamic acid with and without DETU. In the proposed method for the determination of the citric acid content, the latter is obtained from the total acidity titration with a standard sodium hydroxide solution after correction for acidity due to sulfamic acid, ammonium bisulfate (a product of hydrolysis of sulfamic acid) and the interference due to DETU. When the proposed equation is applied, the calculated citric acid value is low and incorrect. This is due to the fact that there is no interference from the DETU in the acid-base titration for total acidity. A number of synthetic samples with and without DETU were prepared and analyzed to establish the absence of DETU interference in the total acidity titration. It was therefore recommended that the proposed correction for DETU interference be deleted from the procedure and the equation for calculating the citric acid content modified.

Other comments included concurrence with Wyandotte that DETU interferes with the sodium nitrite potentiometric titration for sulfamic acid, requiring an empirical correction factor for the inhibitor. It was also agreed that no ammonium bisulfate acidity was detected during these analyses, requiring no correction in the citric acid calculation. However, it was suggested that the proposed correction remain in the equation should hydrolysis of sulfamic acid occur.

The results of the inter-laboratory evaluation of the analytical methods, including pertinent comments and suggestions were forwarded by reference (s).

A project conference was held at BUSHIPS on 14 September 1961 to review the results of the inter-laboratory evaluation of the analytical procedures contained in the proposed interim specification for the "Boiler Scale Removing Compound". At that time, Wyandotte reported that the results obtained by the

Laboratory and reported by reference (a) were in close agreement with the actual values of the prepared referee sample. In general, Wyandotte concurred with the Laboratory's suggestions and the proposed modifications of the specification as contained in reference (a). Since the presence of diethylthiourea inhibitor in the formulation offered interference during the potentiometric titration for sulfamic acid and required an empirical correction in the calculation, extraction and removal of the inhibitor from the aliquot portion being analyzed for sulfamic acid would eliminate the need for an empirical factor correction and further simplify the titration method. Wyandotte reported that methylene chloride (dichloromethane) proved to be an effective extractant for the DETU, thereby eliminating the need for the correction and thus reducing the potentiometric titration for sulfamate ion to stoichiometric relations. It was therefore decided to conduct a second inter-laboratory evaluation of the analytical methods in the interim specification. A carefully blended new referee sample CR-10594, conforming to the formulation 3.17.1, was given to the Laboratory representative to conduct the additional work. Results of these analytical studies were to be submitted to Wyandotte Chemicals Corporation for statistical study and comparison with the data obtained during the first inter-laboratory evaluation. Since the citric acid content is not analyzed, but taken by difference after subtracting the sulfamate and ammonium bisulfate acidity from the total acidity, thus causing all of the cumulative experimental errors to appear in the citric acid results, it was also decided that the specification limit for citric acid be modified as dictated by the results from the forthcoming inter-laboratory method evaluation. It was also agreed that a requirement for a direct quantitative procedure or at least a qualitative test for citric acid would be desirable for inclusion in the modified specification.

After receipt of the proposed modified interim specification of 4 October 1961, containing the revised analytical procedures based on the results of the inter-laboratory evaluations, the Laboratory repeated the analytical work reported by reference (c) on the new referee desiccant sample CR-10594. The results of the second inter-laboratory method evaluation were forwarded to Wyandotte with the following comments:

Extraction of the DETU with methylene chloride has simplified and definitely improved the method for the potentiometric titration for sulfamic acid. However, slight interference from DETU was noted, presumably due to the incomplete extraction of the inhibitor. This was later confirmed by additional tests where samples of sulfamic acid with and without DETU were analyzed by this procedure.

Methylene chloride does not interfere with the sodium nitrite titration.

The titration for total acidity proceeded with ease. No correction for ammonium bisulfate was necessary.

Although visual observation of the sample indicated some segregation of the DETU, the results for DETU content, obtained by two analysts, were fairly reproducible.

Strict adherence to the cleaning procedure of the silica optical cells is necessary to obtain meaningful spectrophotometric readings for DETU content.

The analytical procedures contained in the modified specification have been simplified and improved considerably and should present no difficulty to analysts of other Navy and commercial laboratories who may be required to conduct these tests.

This information was reported by reference (t). Other details of the results obtained during the inter-laboratory evaluations of the analytical procedures, and including Wyandotte's concurrence with the Laboratory's comments and proposed changes to the revised specification, were reported periodically by reference (u).

Since the citric acid content in the 3.17.1 detergent formulation is obtained by difference, with no confirmatory test for this reagent, it was desirable to find a suitable procedure for the direct determination of the citric acid content. A method for citric acid, adapted from AOAC, Official Methods of Analysis, 9th Edition (1960), where the acid is converted to pentabromoacetone, was suggested by Wyandotte. Since their preliminary results looked promising, it was desirable that the Laboratory also participate in this evaluation. Should this procedure prove valid, it would be incorporated into the new specification.

Results of preliminary Laboratory tests showed that extremely high and erratic results for citric acid content were obtained using the pentabromoacetone precipitation method on the referee sample CR-10594. It appeared that either the citric acid segregated in the formulation or chemical changes took place on storage. Further tests conducted by two analysts on freshly prepared synthetic samples and on the referee samples CR-10572 and CR-10594, using the pentabromoacetone precipitation method, showed that slightly low values, although acceptable, were obtained on the synthetic samples. Slightly lower values were obtained on the referee sample CR-10594 and very low and unacceptable citric acid values were obtained on the CR-10572 referee sample. No explanation could be offered for the high results obtained previously and the low results obtained this time on the CR-10594 referee sample. Although the samples were properly quartered, it appeared that either the citric acid was segregated or chemical changes took place upon storage. It was also of interest to note that, from telephone communications with Wyandotte, variations in the citric acid content were also noted by their analysts even to a greater extent than those obtained at the Laboratory. The Laboratory therefore recommended that more work should be done to solve the citric acid analytical problem. This information was reported periodically by reference (u).

No further work was conducted at the Laboratory on the improvement of the analytical procedure for the determination of the citric acid content in the "Boiler Scale Removing Compound" because this problem was referred to the Mare Island Naval Shipyard Chemical Laboratory. In addition, since the Laboratory indicated degradation of the constituents in the 3.17.1 formulation, Mare Island was requested to expose the synthetically prepared descalant mixtures to prolonged storage at room temperature and at 122 F. Analyses of these samples would help to further explain the erratic results obtained for citric acid and any other phenomena apparently due to decomposition of some of the constituents present in this compound.

Other Related Work

The following other investigations and operations, related to chemical cleaning of shipboard boilers, were conducted during this period:

Boiling Out of DLG-6 Test Boiler

The Bureau of Ships Technical Manual, Chapter 51 procedure for boiling out of shipboard boilers, when oil is present, was tried on a Laboratory boiler. The procedure for oil removal consists of adding the required amounts of tri-sodium phosphate (TSP) and wetting agent directly to the steam drum, filling the boiler with fresh water and applying steam to maintain a minimum pressure of 50 psi for at least six hours. This was done at the Laboratory to furnish information as to the rate of TSP dissolution, the rate of distribution of the dissolved TSP in the various boiler circuits, time required to attain equal concentration levels and general cleaning efficiency. Results of this trial showed that the dry TSP dissolved readily and was fairly well distributed throughout the boiler circuits. Successful removal of preservative from the boiler watersides was also accomplished. It was therefore recommended that the shipboard boiling out procedure for the removal of oil, as described in Bureau of Ships Manual, Chapter 51, be employed. This information was reported by reference (f).

Chemical Cleaning of Oil Contaminated Boiler Waterside Surfaces

During the Laboratory's investigation of "Tolerance of Combatant Boilers to Oil Contaminated Feedwater", NBTL Project B-436, it was found that the Fletcher class boiler waterside surfaces were coated with a hard, glossy, black asphaltic material when 15ppm of Navy grade special fuel oil was fed into the boiler feedwater for about 100 hours of continuous operation. The Laboratory was requested to conduct cleaning evaluations on "baked-on" oil deposits found in screen row tube sections. The cleaning agents tried were: chlorinated hydrocarbons, trisodium phosphate, sodium metasilicate, steam cleaning compound (Federal Specification P-S-751), Navy stock degreaser (Specification MIL-C-20207C) and commercially available household cleaners. Treatments were conducted at 212 F and at 30 psi in an autoclave, except that the hydrocarbons were used at room temperature. Results of these evaluations showed that the inorganic boiling out chemicals and the steam cleaning compound were completely ineffective in removing the "baked-on" oil deposits. The Navy stock degreaser was only effective as a cleaner when used at a 33% concentration by volume. Out of the commercial cleaners evaluated, only "Lestoil" proved to be effective when used at a 25% concentration by volume of water. Needless to say, the chlorinated hydrocarbons removed the "oily" deposits in less than 15 minutes at room temperature.

Since the chlorinated hydrocarbons would present a potential hazard to operating personnel due to toxicity and since full strength must be used at a comparatively high cost, this cleaning agent was not recommended for cleaning the Fletcher boiler. Also, "Lestoil" was much more costly than the Navy stock degreaser. Since both products were equally effective in removing the "baked-on" oil deposits from the tube surfaces and since both cleaners have shown to have approximately the same flash, fire and explosivity characteristics, the Navy

stock degreaser was recommended for the removal of the asphaltic material from the watersides of the Fletcher boiler. It was also recommended that a thorough rinsing of the boiler should immediately follow the draining of the cleaning solution to avoid gelling of the cleaner. Safety precautions normally used in handling volatile solvents were to be exercised. The details of these evaluations were reported by reference (n). The Fletcher boiler was later cleaned with the Navy stock degreaser to remove the asphaltic material from its waterside surfaces. This information was reported by reference(u).

Chemical Cleaning of USS CONSTELLATION (CVA-64) Boilers

The Laboratory furnished technical assistance to New York Naval Shipyard in the chemical cleaning of the ship's boilers and superheaters. Since the superheater stainless steel sections were to be acid cleaned, it was recommended that a 10% solution of DETU-inhibited sulfamic-citric acid formulation be employed on the generating sides, economizers and superheaters because the systems were to be cleaned as one unit. For maximum boiler protection, particularly to Croloy steels and the prevention of copper plating, the inhibitor concentration was increased to 1.0% in the 10% descalant formulation. A detailed procedure,

playing the proposed 10% acid treatment, the mild acid (pH-2) rinse and the nitrite-phosphate passivating rinse, was prepared and presented to private contractors who would bid on the cleaning job. Based on Laboratory test results using inhibited sulfamic acid, no bottom blow disc corrosion was observed and therefore it was recommended that the ship's bottom blow systems should not be removed during the descaling operation.

The operation was performed by a private contractor under the supervision of Laboratory representatives. The operation was accomplished in two forty-hour periods, with four boilers cleaned during each period. Inspection of the boilers after cleaning revealed the following:

The watersides and steamsides of all boilers were considered to be generally clean and well passivated.

Large quantities of loosened deposits, particularly in the drums and headers, were noted in all boilers.

After-rusting was noted on some boilers, principally near the top of the steam drums.

Some of the vertical superheater circuits were apparently never filled with the cleaning solutions as evidenced by the condition of adjacent tubes where one tube was clean and well passivated, while a considerable amount of rust (presumed to be the original deposit) was present on the other tube.

The bottom blow valve discs and seats showed no adverse effects from exposure to alternate soaking and recirculation of the acid descalant.

No pitting or other signs of corrosive attack were noted on handhole and manhole plates examined at random.

From the unusually large amounts of loose scale, it was concluded that the boilers were heavily scaled and in need of chemical cleaning.

Based on Laboratory recommendations, the boilers were mechanically cleaned and all loosened deposits removed. Frequent blowdown was also recommended during the first few days of steaming to purge the boiler water of any loose deposits normally present after chemical cleaning. This information was reported periodically by reference (u).

Corrosion Behavior of 16% Chrome- 1% Nickel Desuperheater Alloy

Since desuperheaters on new constructions are composed of 16% Chrome - 1% Nickel, corrosion tests were conducted to determine the behavior of the alloy when exposed to various sulfamic acid solutions. Results of these tests showed the following:

Very high corrosion values were obtained (0.0199 lbs./ft.²/hr.) when new test specimens were exposed to the 20% solution by weight of the CR-7064-B

descaler formulation in the absence of corrosive additives. These corrosion values were about 20 times greater than those obtained on carbon steel and chrome-moly steel and about 200 times greater than the values obtained on 18-8 stainless steel. The 10% formulation was equally corrosive to this alloy.

For some unexplainable reason, the addition of ferric sulfate reduced the corrosion losses of this steel to negligible values. However, reducing the ferric iron concentration, caused extremely high corrosion. Addition of waterside scale to these solutions caused very high corrosion.

Addition of small amounts of RD-2508-P inhibitor (same as used in the CR-3909-C formulation) improved the corrosion protection.

Using the CR-7064-B formulation also caused evolution of hydrogen sulfide gas, presumably due to the breakdown of the diethylthiourea inhibitor. Under these conditions, the test specimens were badly chewed and pitted and were beyond recognition.

Although addition of ferric sulfate to the formulation offers good protection to the alloy, the additive is corrosive to other steels. Also, the use of RD-2508-P, although beneficial to this steel, may not be good for other steel systems.

In general, the behavior of this alloy when exposed to the various sulfamic acid descaling conditions is very much different from the behavior of any other boiler steel tested to date.

Based on the above information, it was recommended that the 16-1 desuperheaters be removed from the drums and not acid cleaned. This information was reported periodically by reference (u).

U. S. Navy Training File 161-92230

The Laboratory furnished technical assistance during the preparation of the

movie script, art work and preparation of chemical cleaning facilities on a Laboratory 692 class boiler and dockside near the USS KIDD (DD-661) for the shooting of the training film "Boilers and Their Operation - Chemical Cleaning of Boiler Watersides". The procedural steps in the cleaning operation were those used during the boiler descaling trial of the USS TAUSSIG (DD-746) and reported by reference (p), except that procedures for removing the bottom blow system, washing down of the boiler and alternate circulation were included. The step dealing with the removal of the bottom blow system during acid cleaning will no longer be required, based on Laboratory tests showing that no valve disc and seat corrosion takes place when exposed to sulfamic acid treatment. The details of the extent of technical direction of the U. S. Navy Training Film MN-92230 were reported periodically by reference (u).

DISCUSSION

Based on the above Laboratory and full scale boiler chemical cleaning trials, the solid descalant formulations CR-7064-B or 3.17.1, containing microfine silica as an anti-caking agent, can be used for chemical cleaning of boilers when performed by ships' personnel. Although these formulations are not quite as effective in the removal of certain tenacious waterside deposits from tube surfaces as inhibited hydrochloric acid, they are considerably superior to any other solid descalants evaluated. These solid formulations meet shipboard needs, i.e., they are non-toxic, easy and safe to handle, can be stored aboard ship, and can be mixed and used by ships' personnel without the need for technical supervision. Also, extensive chemical mixing equipment is not required. The use of inhibited hydrochloric acid does not meet these requirements.

These solid formulations can also be used with safety on boiler steels, including stainless steel superheater sections, except for Croloy 16-1 desuperheater alloy. Studies are continuing under a separate project to find suitable

Inhibitors that would offer maximum corrosion protection to this alloy when exposed to sulfamic acid treatment. Based on Laboratory data, this alloy also exhibits excessive metal corrosion when exposed to inhibited hydrochloric acid. Needless to say, inhibited hydrochloric acid cannot be used on 18-8 stainless steel superheaters.

Although these solid descalant formulations showed no appreciable degradation of the individual components when stored at 104 F and 75% R.H. for several months, storage at 122 F for over two months at Mare Island Chemical Laboratory indicated decomposition of the components with resultant evolution of obnoxious sulfur dioxide gas. Although the latter storage conditions are considered somewhat unrealistic, further studies are being conducted under a separate project to determine the extent of decomposition of the descalant when stored at 122 F. The final selection of suitable analytical procedures to be included in the specification for the procurement of the solid descalant will depend on the outcome of the analyses of the individual constituents in the formulation when stored under various conditions.

Other problems that are being studied in connection with solid descalants are the use of inhibitors that can better protect against copper plating and offer maximum corrosion protection to boiler steels when exposed to "spent" descalant solutions and when lower concentrations of descalants are used. The effect of lowering or increasing the DETU concentrations on corrosion and copper plating protection will also be investigated under a separate project.

CONCLUSIONS

It is concluded that:

The Wyandotte-designated solid descalant formulations CR-7064-B or 3.17.1 can be safely used during chemical cleaning of boilers by ships' non-technical personnel without the need of extensive cleaning equipment and without technical supervision.

These descalants can be used with safety on all boiler steels except Croloy 16-1 desuperheater alloy.

These solid descalants, although not quite as effective as hydrochloric acid in the removal of certain waterside deposits, are considerably better than the CR-3909-C or CR-5923 descalant formulations. When properly used, they will remove most of deposits encountered in naval boilers.

Sulfamic acid does not attack bottom blow valve discs and seats so that removal of these systems is not required during chemical cleaning.

Further investigation is needed on the following problems:

Corrosion protection for Croloy 16-1 alloy steel.

Storage stability of the formulations at various temperatures.

Improvement of the analytical procedures for inclusion in the purchase specification for the solid descalant.

Corrosion protection of steels when exposed to "spent" sulfamic acid solutions.

Prevention of copper plating when "spent" solutions or lower concentrations of descalants are used.

RECOMMENDATIONS

It is recommended that:

The solid descalant formulation, consisting of 89% of crystalline sulfamic acid, 5% of anhydrous citric acid, 5% of diethylthiourea and containing up to 0.3% of microfine silica as an anti-caking agent be selected for shipboard chemical cleaning of boilers.

This formulation be used on stainless steel superheaters but not on Croloy 16-1 desuperheater metal. These latter units should be removed and the flanges in the drum protected from acid attack.

A 10% solution by weight of the descalant be used for normal amounts of

boiler waterside deposits and 20% concentration when the deposits are unusually heavy.

BUSHIPS Instruction 9510.29 of 5 February 1958 be revised to require that the inhibited sulfamic-citric formulation be used for making up the strong descalant solution (10 or 20% by weight) and the mild acid rinse (pH-2) solution instead of the inhibited sodium bisulfate - citric acid formulation. The metal passivation step should remain as is. The instruction should also require the use of a small stainless steel mixing tank (nominal capacity ~ 80 gallons) similar to the one employed during the descaling trial of USS TAMSSIG (DD-746) boilers and also shown in the Navy Training Film MN-92230. The utilization of rubber tank assembly should be deleted. The instruction should also caution against washing down of the passivated metal surfaces with water for the removal of loosened deposits, otherwise after-rust will take place. If the boiler is to remain open after a hydrostatic test, the water used to fill the boiler shall contain about 0.5% of sodium nitrite in order to retain the passivating film on the metal. A requirement should be included that frequent blowdown be used during the first few days of steaming in order to remove the loosened fine deposits.

Further work be continued in the following areas:

Corrosion behavior of Alloy 16-1 steel.

Corrosion protection for 16-1 flanges and nipples, not removable from the drum.

Development of improved analytical procedures for the constituents present in descalant formulation 3.17.1.

Storage stability of CR-7004-S and 3.17.1 descalant formulations.

Copper plating inhibition by diethylthiourea and other sulfur-bearing compounds.

Corrosion protection to boiler metal when exposed to "spent"
descaling solutions.

Any other corrosion problems associated with shipboard chemical
cleaning of boilers.

Naval Boiler and Turbine Laboratory Project Report No. P-360 DEVELOPMENT OF FACILITIES FOR SHIP- BOARD CHEMICAL CLEANING OF BOILERS, Final Evaluation Report, by S. Greenberg 30 November 1962 46 pp. UNCLASSIFIED Several descalants that can be safely handled by non-technical ships' personnel were evaluated for chemical (over)	1. Chemical Cleaning of Boiler Water- sides I. S. Greenberg II. Wyandotte Chemicals Corporation III. R007-08-04 Task 0614 UNCLASSIFIED
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cleaning of shipboard boilers. The selected descalant must be a non-toxic, water-soluble solid formulation and its solutions possess scale removing properties similar to inhibited hydrochloric acid and at the same time be non-corrosive to boiler steels. A descalant formulation, consisting of 89% sulfamic acid, 6% citric acid and 5% diethylthiourea meets these requirements and is recommended for shipboard use.

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