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CHEMICAL CLEANING SOLVENTS
AMONATED CITRIC ACID FOR THE REMOVAL OF WATERSIDE
DEPOSITS FROM BOILERS ON OPERATING NAVY SHIPS
Interim Report No. 1
NAVSECPHILADIV RDT&E Project A-1385
(Subproject S 4638, Task 11f04)
5 June 1972

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**NAVAL SHIP ENGINEERING CENTER,
PHILADELPHIA DIVISION**

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NAVSECPHILADIV RDT&E Project A-1385
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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
SUMMARY PAGE	ii
ADMINISTRATIVE INFORMATION	iv
REPORT OF INVESTIGATION	1
Introduction	1
Evaluation Procedures and Results	2
Discussion	7
Conclusions	9
Recommendations	10
DISTRIBUTION LIST	11

ABSTRACT

The ammoniated citric acid formulation is not an effective descalant for the removal of moderate amounts of hard adhering deposits of the type that are normally present on the boiler watersides of operating Naval ships. Increasing solution concentrations as well as contact times does not significantly increase the solubilities of these deposits. However, ammoniated citric acid is effective in removing pre-operational deposits from new construction boilers. Additionally, the formulation will remove deposits high in iron oxide (90 percent and above).

SUMMARY PAGE

The Problem

This project was initiated to determine whether a 3 percent solution of ammoniated citric acid can remove nominal amounts of hard adhering waterside deposits from operating boilers. Additionally, to resolve whether it would be practical to clean boiler watersides with this descalant at scheduled intervals.

Findings

Although a nominal 3 percent solution of ammoniated citric acid (pH-4 - 4 hours; pH-10 - 3 hours), is an effective descalant for the removal of mill scale and other pre-operational deposits from new construction boilers, it is not considered to be acceptable for the removal of hard, adhering operational deposits. Bench tests with ammoniated citric acid were made on tubes removed from the boilers on the USS COONTZ (DLG-9). These tube specimens had low to moderate amounts of hard, adhering deposits ranging from 0.003 to 0.006 inches thick. The ammoniated citric acid removed only about 50 percent of the deposits after cleaning times up to 7 hours. In contrast, inhibited hydrochloric acid (MIL-STD-796 (SHIPS) of 3 Jan 1966) removed all the deposits within one hour of contact time. Additional tests on tubes obtained from three operating ships, confirmed results obtained with the COONTZ tubes. The ammoniated citric acid removed about 40 percent

of the deposits while inhibited hydrochloric acid completely cleaned the tube sections. The contact periods were approximately one hour for hydrochloric acid and seven hours for the ammoniated citric acid. Increasing acid strength to 4 percent and contact time to 9 hours did not significantly increase the solubilizing characteristics of ammoniated citric acid. Increasing contact time and acid concentrations beyond these limits is not practical.

Recommendations

It is recommended that ammoniated citric acid not be utilized for cleaning Navy boilers containing hard, adhering waterside deposits.

ADMINISTRATIVE INFORMATION

Authority for this project was granted under the Naval Ship Systems Command Work Request WP-2 5428, Amendment No. 2 of 3 Sep 1971. Costs for conducting the investigation were chargeable to Appropriation/ Sub-head 1721804.2475. The Navy Index Number is S 4638, Task 11604, Dart Number 1.3.16.

REPORT OF INVESTIGATION

INTRODUCTION

Ammoniated citric acid (pH-4 for 4 hours at temperatures ranging from 200 to 170 F; pH-10 for 3 hours at temperatures of 145 ± 5 F) has been successfully utilized to remove pre-operational deposits from new construction boilers. Three full scale cleaning operations have been completed. A prototype DLG-32 boiler was initially cleaned by this method. This operation was followed by the cleaning of the watersides on a plant saturated steam boiler. A shipboard trial was subsequently conducted on the boilers of the USS BLUE RIDGE (LCC-19). These latter boilers had been steamed for approximately 200 hours before cleaning and contained brushable deposits. Results obtained from these cleaning operations showed that ammoniated citric acid, under the procedures prescribed, accomplished the intended purpose of removing waterside deposits and passivating the corrosion sensitive surfaces without additional treatment. The operations were conducted with a minimal amount of boiler preparation as well as with shortened cleaning times. Additionally, less post cleaning boiler preparation was required in order to make the plants operational. Significant monetary savings were attendant with the ammoniated citric acid method.

Based on the success attendant with the removal of pre-operational deposits, it was decided to expand the investigative studies with ammoniated citric acid so as to include attempted removal of operational deposits.

EVALUATION PROCEDURES AND RESULTS

The boilers on the USN COONTZ (DLG-9) were scheduled for acid descaling. Tubes were removed from the boilers to determine whether these boilers would be suitable for evaluating ammoniated citric acid. Split tube specimens were crimped and showed that deposit thickness was nominal, ranging from 0.004 to 0.007 inches. Eight uncrimped tube sections were then exposed to a simulated cleaning with a 10 percent by weight solution of ammoniated citric acid. This solution was maintained at pH-4, with temperatures ranging from 160 to 170 F., for four hours. At the end of this period, the pH was raised to 7 by injecting ammonia into the acid solution. The cleaning was continued for an additional three hours at 145 ± 5 F. Results showed that only three of the tube specimens were successfully cleaned. Deposits remaining on the other five tube sections ranged from approximately 50 to 70 percent. When similar tubes were exposed to inhibited hydrochloric acid at 165 ± 2 F, the deposits were completely removed within an hour. Based on these results, it was recommended that the boilers on the COONTZ be descaled with a nominal 10 percent by weight solution of inhibited hydrochloric acid. The cleaning operation was successfully completed by a private contractor under the technical supervision of this Division.

Additional bench tests were conducted utilizing tubes obtained from the boilers of three operating ships. These tubes were selected because they had nominal amounts of hard adhering deposits ranging in thickness

NAVSECPHILADIV Project A-1385

from 0.003 to 0.006 inches. Deposits removed from these tubes were analyzed for major constituents present. Results, including tube sample designations, are given in Table I.

TABLE I

<u>Constituent</u>	<u>Expressed As</u>	<u>Sample Designation</u>		
		<u>Ship No. 1 Percent</u>	<u>Ship No. 2 Percent</u>	<u>Ship No. 3 Percent</u>
Iron	Fe ₃ O ₄	62.8	22.0	78.6
Calcium	CaO	5.6	36.0	2.9
Magnesium	MgO	7.7	5.7	1.0
Phosphate	P ₂ O ₅	15.5	28.3	6.4
Copper	CuO	2.1	0.3	0.7
Sulfate	SO ₃	0.7	1.4	0.4

The split tube specimens containing hard, adhering deposits (0.003 to 0.006 inches thick), representative of the analysis shown in Table I, were exposed to ammoniated citric acid. The pH was adjusted to 4 and held at this condition for 4 hours at temperatures ranging from 200 F down to 170 F. At the end of this period, the temperature was dropped to 150 F and ammonia was utilized to raise the pH to 9.5-10.0. Sodium nitrite was added to this solution to act as an oxidizing agent. The contact time with the tube specimens was continued for an additional 3 hours at 145 ± 5 F. The tubes were removed from the descaling solution and rinsed with a 0.05 percent solution of sodium nitrite. Visual examination showed that the

descalant did not remove the deposits completely from any of the tube specimens. It was estimated that the amount of deposit removed, from any of the tubes, was not greater than 40 percent.

Tests were made to assess whether longer solution contact time and higher descalant concentrations would materially affect the solubilizing properties of the descalant. The acid concentration was raised to 4 percent; contact times were 5 hours at pH-4 and 4 hours at pH-10. (Increasing acid concentrations and contact times beyond these limits is not considered practical.) Visual examination of the boiler tube specimens showed that the amounts of deposits removed were not significantly different from results obtained at the lower descalant concentration and acid contact time. It is interesting to note that a nominal 10 percent solution of inhibited hydrochloric acid (MIL-STD-796(SHIPS), 3 Jan 1966) completely removed the deposits from all the tube specimens in approximately one hour.

Solubility tests were conducted on two types of boiler waterside deposits. One sample represented a composite of deposits removed from the boiler watersides of approximately 30 operating ships. The other sample, composed principally of iron oxide, was employed to assess the effect of different deposit compositions on the solubility characteristics of ammoniated citric acid. Results of analysis are given in Table II.

TABLE II

<u>Constituent</u>	<u>Expressed As</u>	<u>Ships' Composite Sample</u>	<u>Ship Sample</u>
Iron	Fe ₃ O ₄	71.7	94.3
Copper	CuO	12.2	1.2
Magnesium	MgO	1.6	0.1
Calcium	CaO	2.6	0.2
Phosphate	P ₂ O ₅	3.4	0.8
Zinc	ZnO	2.3	-
Nickel	NiO	0.6	0.1
Manganese	MnO	0.3	-
Silicon	SiO ₂	1.0	-
Sulfate	SO ₃	0.8	0.2

Based on predetermined volumes, 0.1 and 0.5 percent of the waterside deposits were placed into beakers. Ammoniated citric acid was then poured into the beakers to the specified volumes. The solubility determinations were conducted under simulated conditions (pH-4 - 4 hours at 200 - 170 F; pH-10 nitrited - 3 hours 145 ± 5 F). For comparative purposes, tests were also made with a nominal 10 percent solution of inhibited hydrochloric acid using a simulated MIL-STD-796 (SHIPS) procedure. Solubility results are given in Table III.

TABLE III

	<u>Deposit Present, %</u>	<u>Deposit Solubilities, %</u>	
		<u>Ships' Composite Sample</u>	<u>Ship Sample</u>
Ammoniated Citric Acid	0.1	67.8	92.0
	0.5	38.0	90.0
Hydrochloric Acid	0.1	100.0	100.0
	0.5	98.2	98.8

Data presented in Table III show that

a. With the ammoniated citric acid formulation, approximately 70 percent of the composite waterside deposit was dissolved when only 0.1 percent of the sample was present in the solution. However, when the test was repeated with 0.5 percent of the composite, solubilities decreased significantly. Only about 38 percent was dissolved. In contrast, practically complete dissolution of the deposits were obtained with inhibited hydrochloric acid, regardless of deposit concentration.

b. With the ship sample, which was composed of more than 90 percent iron oxide, solubilities in ammoniated citric acid were about 90 percent on both deposit concentrations. Needless to say, hydrochloric acid practically dissolved the samples in their entirety.

DISCUSSION

Results obtained during this study have shown that ammoniated citric acid is an excellent descalant for the removal of iron and copper oxide deposits from boiler watersides. This is borne out by the very good solubility results obtained on the "ship deposit" sample where very high amounts of iron oxide and some copper oxide were present. Additionally, the results of the full scale cleaning operation conducted on the boilers of the USS BLUE RIDGE (LCC-19) (Final Report of NAVSECPHILADIV Project AP-39 of 10 Jun 1971) showed that this descaling formulation is a practical, efficient means for removing pre-operational deposits from new construction boiler watersides. Less boiler preparation and considerable savings in time and money are attendant with ammoniated citric acid when compared to the present Navy cleaning procedures for removing pre-operational deposits. However, ammoniated citric acid is ineffective in removing nominal amounts of hard, adhering operational deposits from boiler watersides. This was demonstrated by the failure of this acid solution to completely descale the watersides of the tube specimens removed from operating ships. In fact, based on bench evaluations, it was decided not to descale the boilers on the USS COONTZ (DLG-9) with the ammoniated citric acid formulation. This ship had been selected for a full scale

trial to assess the effectiveness of this descalant for removing nominal amounts of operational waterside deposits. The boilers on the COONTZ were successfully descaled with inhibited hydrochloric acid.

Solubility results confirmed bench scale cleaning evaluations on tubes removed from operational ships. When only a small amount of the composite waterside deposit was exposed to ammoniated citric acid, solubilities were considered to be fair. However, when amounts similar to the quantities of waterside deposits that could be expected with normal ship's operation were present, solubilities were poor and unacceptable. It had been anticipated that ammoniated citric acid would dissolve the iron oxide matrix to remove the deposits. (The deposits contained about 72 percent iron oxide and 12 percent copper.) However, this did not occur with moderate amounts of deposits present. It is conceivable that the other constituents present in the deposit acted to retard the solubilizing properties of the ammoniated citric acid.

CONCLUSIONS

It is concluded that:

a. Ammoniated citric acid would not effectively remove moderate amounts of hard, adhering deposits normally found on the boiler watersides of operational ships.

b. Ammoniated citric acid will effectively remove moderate amounts of hard, adhering deposits containing high amounts of iron oxide (90 percent or more). Deposits of this type are normally found in new construction Navy boilers.

RECOMMENDATIONS

It is recommended that ammoniated citric acid not be used to remove hard, adhering operational deposits from the watersides of boilers on operational Navy ships.