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VAPOUR SPACE INHIBITOR STUDIES

- PART I: THE EFFECT OF N-DECANOIC ACID ON THE OXIDATION CHARACTERISTICS OF STEAM TURBINE OILS
- PART II: DEVELOPMENT OF A LABORATORY METHOD FOR MEASURING THE PRESENCE AND EFFECTIVENESS OF VAPOUR SPACE INHIBITORS IN OILS

by

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DIVISION OF MECHANICAL ENGINEERING

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FOR MEASURING THE PRESENCE AND
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SUMMARY

PART I Previous work indicated the potentialities of low molecular weight organic acids as vapour space inhibitors for oils but a possible incompatibility with oxidation inhibitors was indicated. These confirmatory tests indicate very much shorter lives for blends containing either 4 methyl 2, 6 ditert-butyl phenol or phenyl- α -naphthylamine in the presence of 0.05 percent weight n-Decanoic acid as measured by the Oxidation Characteristics Test (ASTM D943).

PART II - The development of a potential laboratory glassware corrosion test method for measuring the presence and effectiveness of vapour space corrosion inhibitors is described.

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VAPOUR SPACE INHIBITOR STUDIES

INTRODUCTION

Following a report¹⁾ on the potentialities of low molecular weight organic acids as vapour space rust inhibitors for steam turbine oils, the Fuels and Lubricants Laboratory measured the effect of the addition of 0.05 to 0.10 percent weight n-Decanoic acid on the properties of finished oils and evaluated the Hot Plate Reflux and Cyclic Rust Test Methods²⁾. It was concluded that the Total Acid Number, Foaming Characteristics, and Load-Carrying Capacity of the turbine oils were altered by the VSI addition, but the changes were small and probably tolerable. However, a significant reduction in the Oxidation Characteristics of one oil was noted, indicating a possible additive incompatibility. Several more blends have been prepared from finished oils, base stock, amine, and phenol type antioxidants with n-Decanoic acid as a VSI additive. This study further the effect of this particular vapour space corrosion inhibitor on oxidation life. The tests and results are described in Part I of this report.

Work has continued on the development of a small-scale glassware laboratory apparatus and a suitable technique for measuring the presence and effectiveness of vapour phase corrosion inhibitors. Part II describes a proposed apparatus and method.

PART I

THE EFFECT OF N-DECANOIC ACID ON THE OXIDATION CHARACTERISTICS OF STEAM TURBINE OILS

Two qualified steam turbine oils (CGSB Specification 3-GP-357Ta) and one base stock were used for the test blends. Infrared analysis of extracts of the two finished oils indicated the oxidation inhibitor to be of a phenol type (4 methyl 2,6 ditert-butyl phenol) present in concentrations of approximately 0.2 and 0.4 percent by weight. Therefore the base stock was used to prepare samples containing phenyl- α -naphthylamine. From these basic blends test oils containing the n-Decanoic acid were prepared. Test procedures were varied (e.g. by adding metal deactivator or omitting the copper catalyst) to provide additional information. The samples prepared, test procedures, and results are summarized in Table I.

The basic method was ASTM Method D943 and the criterion of failure was the commonly employed Total Acid Number of 2.0 mg KOH per gram of sample. Initial TAN of acid blends was of the order of 0.20. Observations were made of weight of insolubles, water phase acidity, condition of the catalyst coils, and the appearance of oil and water phases at the end of the test. The relative amount of insolubles present is indicated in Table I.

Conclusions

These data indicate an incompatibility between the VSI additive, n-Decanoic acid, and the antioxidants 4 methyl 2,6 ditert-butyl phenol and phenyl- α -naphthylamine with respect to Oxidation Characteristics. A metal deactivator was ineffective in preventing oil deterioration. In the absence of copper, the blends were quite stable.

TABLE I

RESULTS OF OXIDATION CHARACTERISTICS TESTS ON OILS AND BLENDS

Oil	% Phenol Antioxidant wt.	% Amine Antioxidant wt.	Added:		Hours to TAN = 2.0 mg/KOH/gr.	Remarks
			% n-Decanoic Acid, wt.	wt.		
A	-	-	-	-	more than 1000	Finished Oil - Company A. Insolubles slight.
A	-	-	0.05	-	500	Large amount of finely divided insolubles
A	-	-	0.05	-	more than 1000	Copper catalyst omitted. Insolubles slight
A	0.4	-	0.05	-	750	Insolubles slight
B	-	-	-	-	850	Finished Oil - Company B. Large amount of finely divided insolubles
B	-	-	0.05	-	300	Large amount of finely divided insolubles
B ₁	-	-	-	-	more than 1000	Finished Oil - Company B. (different batch) Insolubles slight
B ₁	-	-	0.05	-	450	Large amount of finely divided insolubles
B ₁	-	-	-	-	more than 1000	Copper catalyst omitted. Insolubles slight
B ₁	-	-	0.10	-	350	0.007% wt. metal deactivator added. Large amount of finely divided insolubles
C	-	0.2	-	-	800	Base Stock - Company B. Large amount of finely divided insolubles
C	-	0.2	0.05	-	250	Large amount of finely divided insolubles
C	-	0.4	-	-	1000	Moderate amount of insolubles
C	-	0.4	0.05	-	520	Large amount of insolubles

PART II

DEVELOPMENT OF A LABORATORY METHOD FOR MEASURING THE PRESENCE AND EFFECTIVENESS OF VAPOUR SPACE INHIBITORS IN OILS

In an earlier work²⁾, a slightly modified Hot Plate Reflux and a Cyclic Rust test were employed to assess the rust preventive properties of oils and blends containing vapour space corrosion inhibitors. The HPR test gave slightly more decisive and repeatable results than the Cyclic test and indicated trends pretty well. However it was felt desirable to develop a method that would permit better control of test conditions to improve repeatability and reproducibility. Control of test temperatures at various levels would also permit any steady state service condition to be reflected in the method. Finally, such a technique would be useful for laboratory assessment of potential VSI additives under a variety of temperature conditions.

After considerable experimentation the apparatus sketched in Figure 1 and illustrated in Figure 2 evolved, and a test method was devised. The method consisted of exposing a clean 1020 steel specimen to a 2-ml sample of oil in the PTFE cup for a 16-hour induction period, after which 2 ml of distilled water were introduced into the flask and the test continued for another 3 hours. During the test, the flask was supported in a bath maintained at 50°C, and cooling water at 30°C was circulated through the specimen holder. The test temperature of 50°C ambient and 30°C specimen were based on an extensive investigation by the Royal Canadian Navy into conditions causing corrosion (Note 1) in main propulsion gearing and lubricating oil systems of certain of their ships³⁾.

Blends of turbine oil base stock and n-Decanoic acid were assessed. A few runs were also made with base stock inhibited with an amine salt⁴⁾ supplied by the United States Navy. The test results were promising and the method distinguished clearly between the various levels of additives, as shown in Figure 3. Repeatability in the laboratory was good.

As a matter of interest, the "life" of the two inhibitors was compared at 210°F, using the apparatus and procedures of ASTM D972 (Note 2) in which oil blends containing 0.1 percent weight inhibitor were maintained in a sample cup at 210°F while 2 liters of air per minute were passed over the oil surface for 2, 4 or 6 hours. The residues were then subjected to the glassware corrosion test. The results, shown in Figure 4, indicate that the n-Decanoic acid had the longer "life" under these conditions. The acid, as shown in Figure 3, was required in greater concentrations to provide adequate protection under the usual test conditions.

In response to a request for laboratory test methods for assessing VSI oils, the procedure was submitted to the Task Group of Section II (Rusting and Corrosion) of ASTM Technical Committee C on Turbine Oils. To date, four rounds of co-operative testing have been completed by this group, resulting in some modifications to the original methods.

In the initial round, six sets of the laboratory apparatus were fabricated by a United States laboratory from NRC drawings, and six laboratories evaluated four commercial oils. The results are shown in Table II.

TABLE II

RESULTS OF FIRST ROUND OF CO-OPERATIVE TESTS

Sample	Description	Degree of Corrosion					
		1	2	3	4	5	6
A	Commercial Oil - Uninhibited (150 SUS)	Severe	Slight	Severe	Moderate	Stain	Severe
B	A-inhibited	None	None	Light	None	None	None
C	Commercial Oil - Uninhibited (400 SUS)	Severe	Severe	Severe	Moderate	Stain	Severe
D	C-inhibited	Moderate	None	Light	None	None	None

These results were considered very encouraging. As a check on the sensitivity of the specimens, the tests on samples A and C were repeated by Laboratory 4 using NRC 1020 steel specimens, and the NRC ratings of "severe" were reproduced in both tests. Further, Laboratory 6 reported good correlation between the results of the proposed method and the Hot Plate Reflux method.

A second set of tests was arranged in which twelve laboratories participated. A source for the complete Vapour Space Corrosion Test apparatus was found and samples were prepared and distributed by NRC. The test oils contained 0.15, 0.075 and 0 percent n-Decanoic acid in a base stock. The selection was based on the results shown in Figure 3 and it was intended that pass, borderline, and fail samples be represented. All laboratories color-photographed the specimens after test and the 35-mm slides were returned to NRC for assessment by one experienced operator.

The results were generally in good agreement for the fully inhibited and uninhibited samples, although there was a spread of ratings from none to trace for the "pass" sample, and light to severe for the "fail" sample. The ratings for the intermediate sample ranged from no rusting to severe rusting (5 none, 3 trace, 3 light and 2 severe). Not all of the participants utilized the commercially available apparatus, and some of the spread of results was attributed to the use of specimens from different

sources. In confirmation, the laboratory rated the intermediate sample using the original 1020 steel specimens and those supplied with the commercially available apparatus. The results are illustrated in Figure 5. It appears that the common grade of steel now supplied is more rust resistant than the 1020 specified. The commercial specimens were presumed to be 1018 steel having a higher manganese content.

A third co-operative exchange was completed by the Task Group. Tests were run on a borderline (0.075 percent n-Decanoic) and pass (0.15 percent n-Decanoic) sample with specimens supplied by NRC. All the specimens were prepared from the same 1020 rod. Again good repeatability and reproducibility were obtained for the fully inhibited oil but the ratings for the intermediate sample ranged from no rusting and moderate rusting.

Since there appeared to be other factors entering into the test results, the laboratory undertook to investigate some of the parameters. A very significant factor appeared to be the humidity of the air to which the specimen was exposed just prior to the induction period (Note 3). It was also considered an expedient time to explore the feasibility of reducing the total test time so that an evaluation could be completed in one day.

A base stock containing 0.10 percent n-Decanoic acid and 1020 steel specimens were used for this investigation and tests were performed by

- (a) regular test method - uncontrolled humidity, 16-hour induction period and 3-hour test time;
- (b) heating the specimen during cleaning and mounting it in the specimen holder; blowing dry air through flask before insertion of the specimen; reducing the induction period to 4 hours and the test time to 2 hours.

The results, illustrated by the graph in Figure 6, indicate a much better repeatability for procedure (b). A slight modification to the apparatus was required for flushing with dry air. A side arm was added to the flask, as illustrated in Figure 7.

Subsequently, a fourth round of co-operative tests was initiated in the C-II Task Group. All specimens were obtained from one commercial source and were 1018 steel. It was decided to increase the severity of the test slightly by reducing the induction period to 3 hours, increasing the exposure time to 3 hours, and enlarging the holes in the PTFE cups to 0.063 inch. The method finally adopted is attached as Appendix A.

The results of the fourth round are summarized in Table III. The repeatability and reproducibility for 11 three samples was reasonably good. The performance of sample C was unexpectedly good but, since it is a purely arbitrary standard, it is considered that the final form of the method is slightly less stringent than that using 1020 steels. Consequently, sample C is a little on the "pass" side of the rating. Most co-operators also ran the Hot Plate Reflux method, and the results obtained by the two methods were comparable.

Comments

A relatively simple laboratory glassware Vapour Space Corrosion Inhibitor test method is presented that offers a versatile control of temperatures of environment and specimen and that demonstrates good repeatability and reproducibility, at least for uninhibited and adequately inhibited oils. Its value for evaluating oils in service has not yet been demonstrated by service trials.

Notes:

- Note 1. Since largely eliminated by adequate venting.
- Note 2. Test for the Evaporation Loss of Lubricating Grease and Oil.
- Note 3. Humidity was not recognized as a factor during the development of the test because the laboratory has a controlled humidity during the winter months to reduce the hazards associated with static electricity discharges and explosive vapour-air mixtures.

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TABLE III

RESULTS OF THE FOURTH ROUND OF CO-OPERATIVE VSI CORROSION TESTS

C - Partially inhibited
(0.075% n-Decanoic Acid)

A - Uninhibited base stock

B - Commercial inhibited

NRC Vapour Space Corrosion Test. (Appendix A)

Test Oils

Test Method

Laboratory	Rusting		
	Sample A	Sample B	Sample C
1	100% light - moderate	none	20% scattered light rust with several severe spots
2	100% very light	none	none
3	(1) fail (2) fail	(1) pass (2) pass	(1) pass (2) pass
4	(1) 50% rust (2) 60% rust (3) 60% rust	(1) none (2) trace (1 speck)	(1) trace (2 specks) (2) trace (3 specks) (3) trace (2 specks)
5	(1) 50% light (6 heavy spots) (2) 30% light (3 heavy spots)	none	none
6	(1) moderate (2) moderate	(1) trace (3 specks) (2) trace (2 specks)	(1) none (2) none
7	(1) 10% rust (2) 1% rust	(1) none (2) 3% rust	(1) none (2) none
8	(1) light (2) light	(1) none (2) none	(1) none (2) none
9	(1) 25% rust (2) 25% rust	(1) none (2) none	(1) none (2) none
10	(1) moderate (2) moderate	(1) none (2) none	(1) none (2) trace
11	(1) moderate (2) moderate	(1) none (2) none	(1) none (2) none

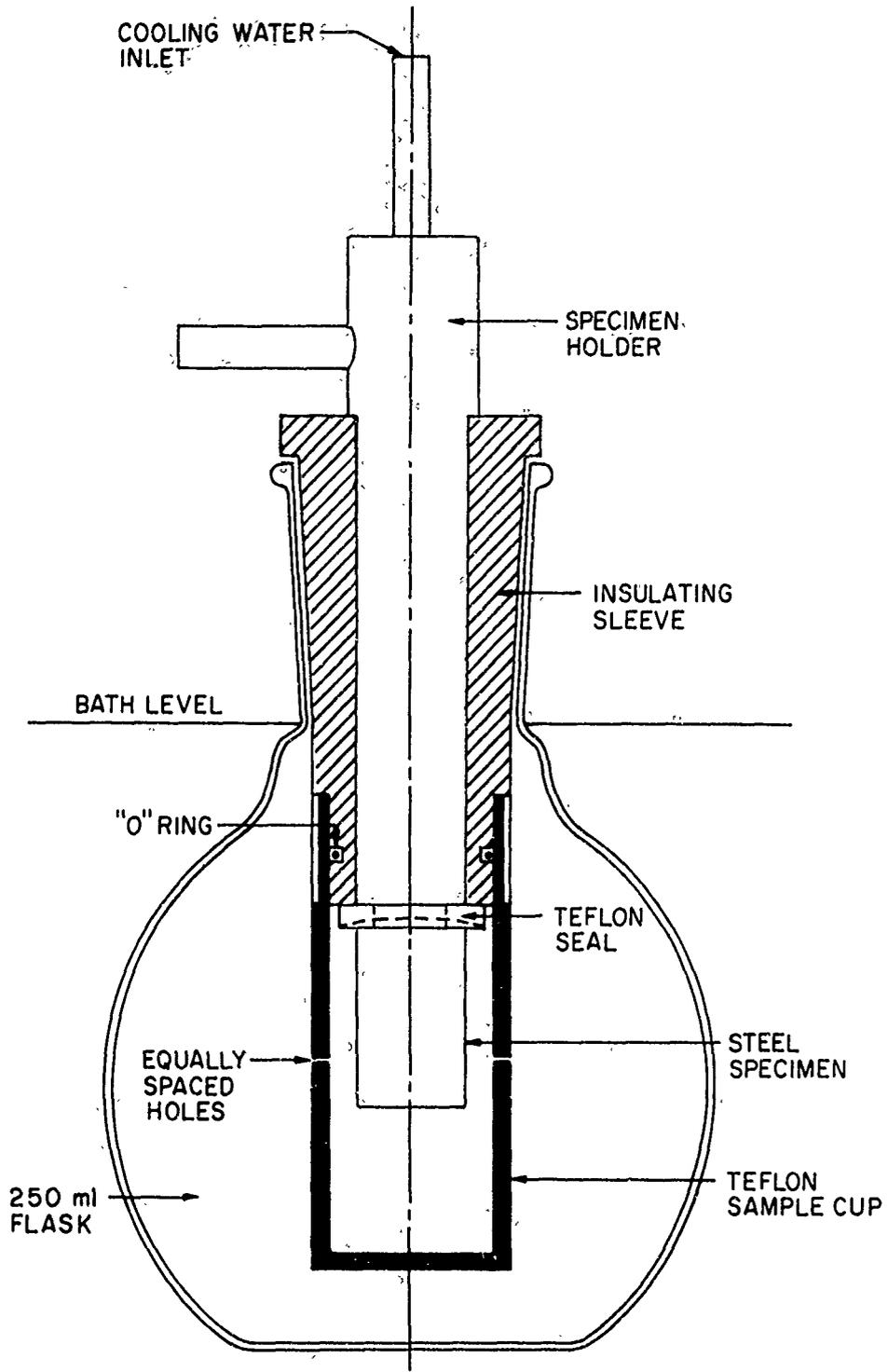
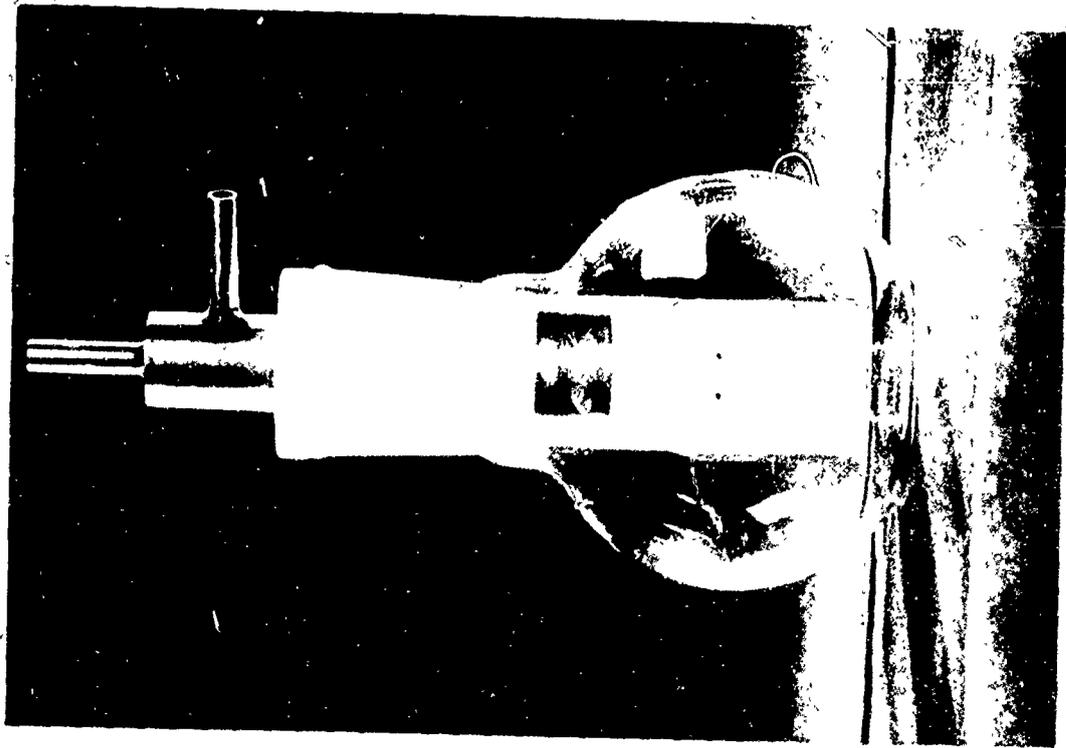


FIG.1: VAPOUR PHASE CORROSION INHIBITOR TEST APPARATUS



ASSEMBLED



EXPLODED VIEW.

FIG.2: VAPOUR SPACE CORROSION INHIBITOR TEST APPARATUS.

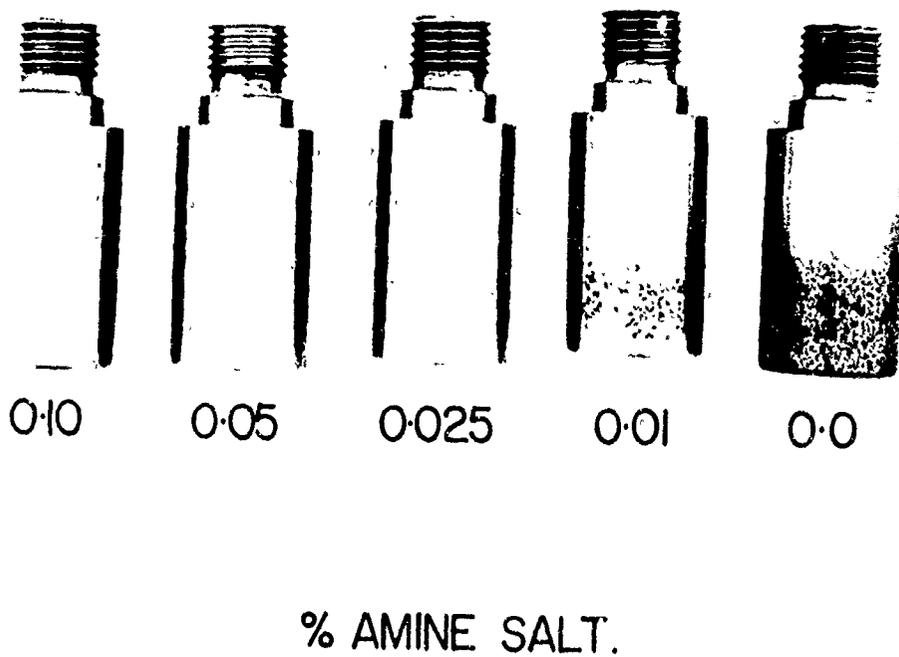
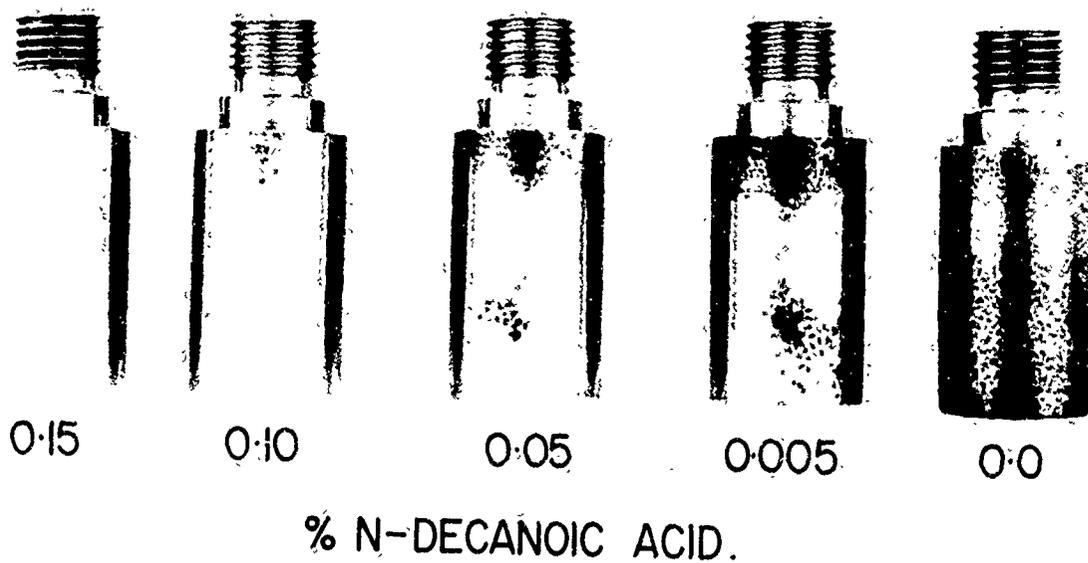
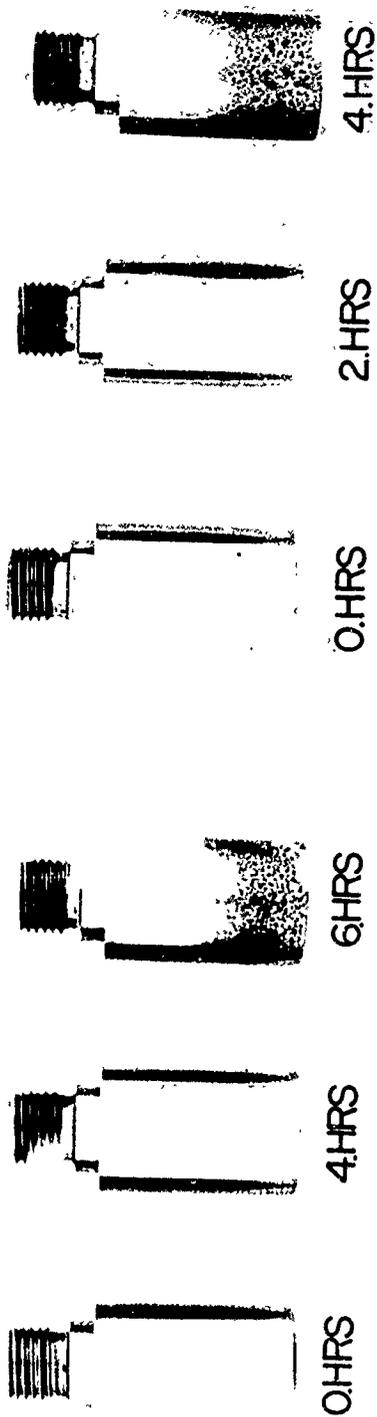


FIG. 3: CORROSION vs PERCENT VAPOUR SPACE INHIBITOR

0.1% AMINE SALT

0.1% N-DECANOIC ACID



EVAPORATION TIME EVAPORATION TIME

FIG. 4: CORROSION AFTER EVAPORATION TEST

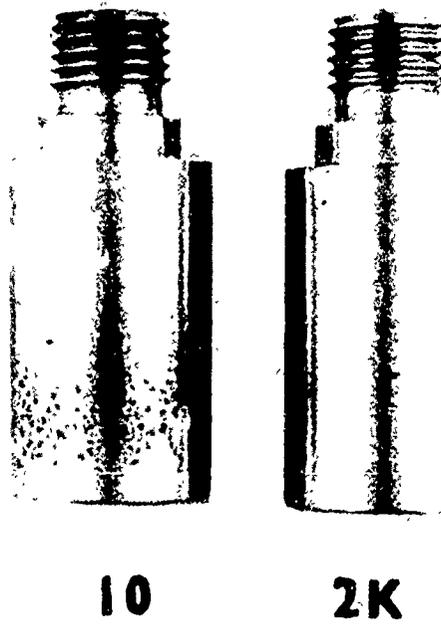


FIG. 5: COMPARISON OF RUSTING
OF DIFFERENT SPECIMENS

10 - 1020 STEEL
2K - 1018 STEEL

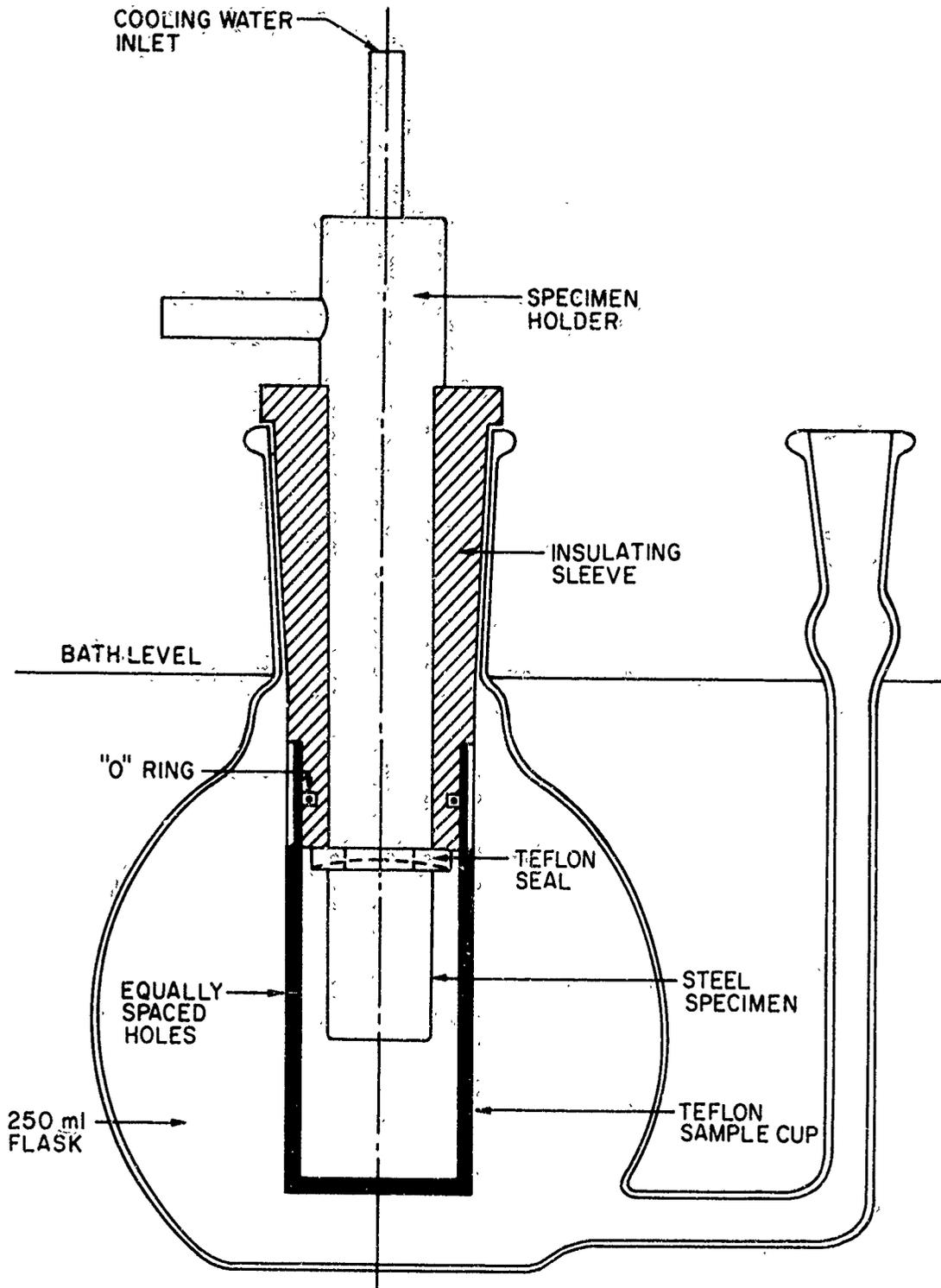


FIG.7: VAPOUR PHASE CORROSION INHIBITOR TEST APPARATUS
(MODIFIED)

APPENDIX A

PROPOSED TEST METHOD

CORROSION PREVENTIVE CHARACTERISTICS OF OILS CONTAINING VAPOUR PHASE CORROSION INHIBITORS

A-1. SCOPE

This method is intended for the determination of the vapour phase corrosion preventive characteristics of oils.

A-2 APPARATUS, REAGENTS, AND MATERIALS

Water bath, capable of maintaining a temperature of $50 \pm 1^\circ\text{C}$.

Specimen temperature regulating circulating system capable of maintaining a water temperature of $30 \pm 1^\circ\text{C}$ at both inlet and outlet of specimen holder.

Filtered dry air supply.

Test assembly as shown in Figures 1 to 5.

Adaptor threaded $3/8 \times 24$ UNF for holding corrosion specimen in a drill press chuck.

Abrasive paper, non-waterproof, Silicon Carbide, 400 grit.

Iso-octane.

A-3 PREPARATION OF APPARATUS

1. Wash glassware in hot water-detergent solution and rinse with tap water. Clean with chromic acid cleaning solution, rinse with tap water, then with distilled water, dry in an oven and cool to room temperature.
2. Wash teflon sleeve, seal, and cup in hot water-detergent solution, rinse with tap water, then with distilled water and allow to dry. Place in a dessicator until ready to use (at least 30 minutes).
3. Heat the metal specimen (Note 1) in an oven (approx. 220°F) to ensure that its temperature remains well above room temperature during the following cleaning procedure.

Mount the warm metal corrosion specimen in a suitable holder on a drill press or electric motor and rotate at approximately 1725 rpm. Prepare a fresh metal surface by applying silicon carbide paper to the rotating specimen.

Finish abrading the specimen with a fresh strip of 400 grit paper 1-1/4 inches wide, by drawing the strip firmly 4 times across the face of the specimen. The flat bottom is finished by moving the strip to and fro against it with a short stroke for 10 seconds. Finally wipe the rotating specimen with a clean lintless material such as surgical gauze to remove surface debris and immerse the specimen immediately in iso-octane, being careful not to touch the specimen with the fingers.

A-4 PROCEDURE

Stopper the flask and place it in the bath, which is at the test temperature of $50 \pm 1^\circ\text{C}$, approximately 30 minutes before starting the test.

When the flask has been in the bath at least 15 minutes, blow dry air into it via the side arm for a minimum of 2 minutes. The flow rate should be approximately 3000 ml/min. Then stopper the side arm.

Warm the iso-octane containing the specimen (in the 50°C bath) in order to maintain the temperature of the specimen above ambient.

Shake the sample vigorously and transfer 2 ml to the sample cup.

Remove the metal specimen from the warm iso-octane. Install the insulating sleeve on the specimen holder, which is at the test temperature $30 \pm 1^\circ\text{C}$. Insert the gasket and mount the specimen in its holder.

Mount the sample cup on the teflon sleeve and place the assembly in the flask, as shown in Figure 7 of the main report (Note 2).

At the end of the induction period (3 hours) add 2 ml of distilled water to the flask through the side arm.

Continue the test for 3 hours. Remove the metal specimen, being careful not to wipe off any rust, and describe its appearance.

A-5 REPORT

Report the degree of rusting - trace, slight, moderate, or severe, and the approximate percent of area covered.

Notes

- Note 1. Severely corroded specimens should be discarded but moderate pitting may be removed with coarser paper. The marks produced by this coarse paper must be removed with 400 grit paper before the final finish.
- Note 2. If more than one apparatus is being used it is more convenient to assemble the specimen holder, sleeve, gasket, and specimen and place them in a flask, similar to the test flask but without the side arm, that contains a small quantity of drierite. They can remain there for a reasonable length of time until the sample cups are added and they are then placed in the test flask.