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DEVELOPMENT OF AN IMPROVED CORROSION INHIBITOR FOR WATER-ALCOHOL SOLUTIONS

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FOREWORD

This report was prepared by the Wyandotte Chemicals Corporation under USAF Contract No. AF 33(616)-2442. This contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 73122, "Corrosion and Corrosion Prevention", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. H. L. Stevens acting as project engineer.

This report covers period of work from April 1954 to July 1955.

Proprietary surfactants have been studied in this work in systems other than those for which they were designed. In fairness to the manufacturers of these compounds it should be emphasized that the results do not necessarily reflect their comparative value as surfactants in their more conventional applications.

The proprietary inhibitors that were evaluated for this specific use have been coded to prevent misapprehension on the part of competitive commercial suppliers.

ABSTRACT

A corrosion inhibitor was developed for use with alcohol-water injection fluid for aircraft engines. It inhibits corrosion of steel, stainless steel and aluminum alloys, is soluble in methanol, ethanol, water or mixtures of the liquids, and lowers surface tension of the mixtures. Although the inhibitor is chemically compatible with hard water solutions, inhibition efficiency is inversely proportional to water hardness. Solutions made with water of more than 100 parts per million hardness, require an excessive amount of inhibitor for inhibition of corrosion. The inhibitor is a mixture of dicyclohexylammonium nitrite, urea and 1-nitropropane in an anhydrous methanol solution. Data gathered from initial screening of 150 corrosion inhibiting compounds is presented in detail.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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TECHNICAL SUMMARY

The work covered by this report resulted in three inhibitor formulations, CR-2990-A1, CR-2990-A2, and CR-2990-A3. Subsequently they were evaluated by the Materials Laboratory of Wright Air Development Center. The conclusions of the Materials Laboratory are:

a. The three inhibitors are effective in methanol-distilled water solutions.

b. At an optimum concentration, effective inhibition can be obtained in both liquid and vapor phases of inhibited methanol-hard water solutions. The concentration of the three inhibitors needed for effective inhibition increases as the total dissolved solids of the water used for dilution of the alcohol increases. The amount needed to prevent corrosion of SAE 1010 steel and of 2024 aluminum alloy in a 26% methanol-hard water (450 parts per million calcium carbonate) solution is 2% of the mixture volume, or 8% of the methanol volume.

c. The three inhibitors adversely affect reciprocating engine performance (knock) numbers of aviation fuel almost in proportion to their concentrations.

In view of these facts, the inhibitors are considered to be effective for methanol-distilled or deionized water solutions. They may find use with waters of low hardness, but due to the large concentration of inhibitor needed, they are not appropriate for use with extremely hard water solutions that are found on many Air Force bases.

I INTRODUCTION

Alcohol-water mixtures are used as thrust acceleration fluids in aircraft jet and rotary engines. Corrosion has been experienced with these mixtures in the blending and refueling tanks, the supply tank and the injection systems. The corrosion preventative most commonly employed to the present time has been a soluble oil of the type covered by specification MIL-C-4339. This type of inhibitor is not entirely satisfactory for the following reasons.

a. The compound must be thoroughly dispersed in the water prior to addition of the alcohol.

b. Even with thorough dispersion, an oil layer tends to separate with time particularly when hard water is used.

c. Solids precipitated when hard water is used clog filter systems.

d. The inhibitor does not provide adequate protection to metals in the vapor phase.

The aim of this research program was the development of better corrosion inhibitors for use in aircraft alcohol-water injection systems. The protection of tanks used for storage and transportation was an immediate objective. The inhibitors were expected to have the following properties (as quoted from the amended Exhibit A of the contract):

1. The inhibitor may be a single compound, a mixture of compounds, or solution, provided the desired properties are obtained. The amount to be added shall not be excessive.

2. The inhibitor shall be suitable for mixing with undiluted methanol and ethanol, conforming to Specifications O-M-232 and MIL-A-6091 respectively, at the time of packaging, or at an Air Force Base in either concentrated or diluted form.

3. At the concentration level needed for inhibition, the inhibitor shall be soluble from -65°F. or 10°F above the freezing point of the solution, to 160°F or 10°F below the boiling point, in the following solutions: anhydrous methanol (Spec. O-M-232), a 95% ethanol-methanol mix (Spec. MIL-A-6091), and either of the above diluted with water over the 20 to 70% alcohol by volume concentration range. Separation with time shall not occur.

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4. The presence of the inhibitor shall not cause excessive precipitation over what would normally occur when the temperature of the solutions in 3 (above) is varied over the limits specified.

5. The inhibitor shall effectively inhibit corrosion in aircraft alcohol-water systems. For the purpose of a laboratory type evaluation, the effect of the inhibitor on 1020 steel, aluminum alloy 24S-T6, and aluminum alloy 24S-T6 coupled to Type 304 stainless steel is considered indicative of its performance in an actual aircraft system. The inhibitor shall inhibit in both liquid and vapor phases.

6. The inhibitor shall not form over 100 ppm non-combustible solids based upon the concentration used in a 50-50 alcohol-water mix.

7. The inhibitor shall provide a surface tension and interfacial tension equal to or less than that obtained with 0.05% Triton X-100 in a 30% alcohol-water mixture.

8. The cost and availability of the inhibitor shall not preclude its use in time of National Emergency.

9. The inhibitor shall have a reasonable shelf life, either by itself or when mixed in alcohol-water solutions.

10. The inhibitor shall be soluble in undiluted alcohol conforming to Specifications O-M-232 and MIL-A-6091 at a concentration equal to four times that needed to effectively inhibit corrosion in a solution of 25% alcohol, 75% tap water. Effective inhibition is considered to be as is described in article five above. If absolutely necessary, small amounts of water (up to four percent) may be added to anhydrous alcohol to increase the solubility of the inhibitor.

In general four major approaches to the problem were pursued:

1. A moderately comprehensive literature survey to provide a list of corrosion inhibitors for screening and to indicate corrosion test methods suitable for the present program.

2. A general corrosion screening program which included the examination of a relatively large number of candidate inhibitors to select those effective in the prescribed water-alcohol solutions.

3. Further examination of the materials that successfully passed the requirements of the general screening program, and of candidate agents for lowering surface and interfacial tension.

4. Comprehensive testing and evaluation of candidate inhibitors-surfactant combinations in order to establish at least three inhibitor formulas having the characteristics specified in Exhibit A.

Due to the multiplicity of characteristics required in a successful formula some exploratory portions of the work had to be conducted without regard to some of the requisites for an acceptable compound. For instance, many preliminary corrosion prevention, surface activity and solubility evaluations were carried out on formulations known to have excessive residual non-combustible solids as set forth under (6) of Exhibit A. Subsequently, modified systems were employed which met this requisite and were acceptable in other respects.

II EXPERIMENTAL PROCEDURES AND EVALUATION TECHNIQUES

In the initial phases of this work, a literature survey was conducted in order to compile a list of candidate inhibitors for screening purposes. During this literature survey various corrosion test methods which might be applied in the present problem were reviewed. No specific method suitable for evaluation of candidate corrosion inhibitors in these water-alcohol systems was found. The following procedures are based on methods found in the literature, modified by Wyandotte experience in corrosion testing.

GENERAL SCREENING TECHNIQUE

A screening method was developed that could rapidly cover a large number of compounds. It was recognized that the volume of the testing solution should be large enough to avoid any appreciable change due to chemical exhaustion of any ingredients of the solutions. Relying on past experience, a volume to area relationship was selected such that the approximately 5 square inch surface of the specimen was exposed to one liter of testing solution. A two quart Mason canning jar was selected as a suitable vessel. In control tests, duplicate specimens were tested, i.e., two in the liquid phase and two in the vapor phase as shown in Figure 1. In the screening studies only two specimens were used per jar, one in each phase which furnished the volume to area relationship in the liquid phase mentioned above. The specimens were suspended with

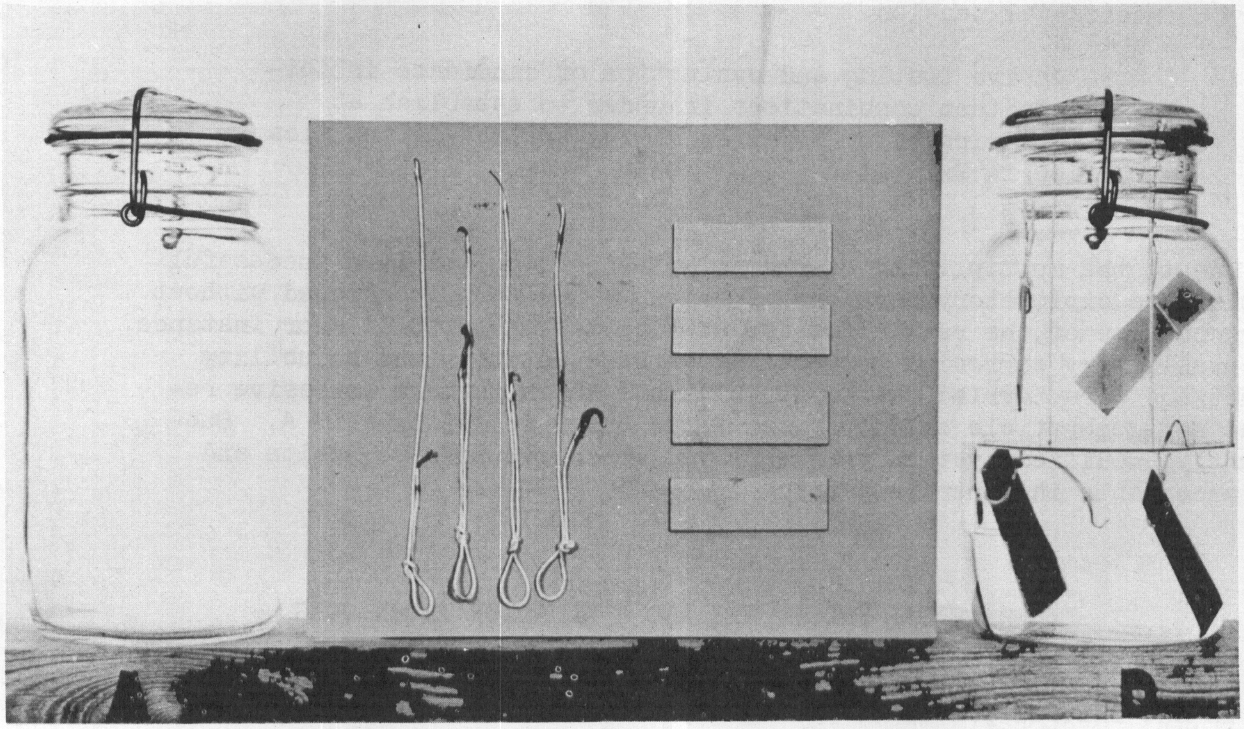

Fig. 1. Component parts and assembled corrosion test vessel used in general screening program.

A. Two-quart Mason jar.

B. Lengths of 1/16" diameter glass cord with slip-knot.

C. Metal test specimens.

D. Assembled unit. Note: This was a control test jar. Test specimens were suspended from the center of the coupon and only one to each phase.

1/16 inch diameter glass cord by fastening with a slipknot around the center of the specimen. The upper end of the cord was clamped to the metal fixture at the neck of the jar or held in place beneath the rubber jar ring. To prevent excessive fraying of the glass cord, the ends were fire-polished.

Preparation of Test Specimens.

In the initial screening phases of this work, two test metals were used, SAE 1010 cold rolled mild steel and aluminum alloy 2024-T3 (formerly designated 24S-T3). Coupons 3 inch x 3/4 inch x 1/16 inch were sheared from stock sheets. These specimens were sandblasted until a uniform surface was obtained. After sandblasting the coupons were degreased by an acetone dip, dried by air blast and stored in a desiccator until used. Subsequently, the coupons were handled with rubber tipped forceps or rubber gloves.

Water-Alcohol Solutions.

Inhibition of corrosion was studied in two alcohols, methanol (methyl alcohol) covered by Federal Specification O-M-232, and specially denatured ethanol (ethyl alcohol) covered by specification MIL-A-6091. The nominal composition of the latter is 90% ethanol, 5% methanol, and 5% water. It was required that corrosion be inhibited in solutions containing from 20 to 100% alcohol by volume of either of these alcohols. It was assumed (and confirmed later) that the 20% methanol in water would be the most corrosive toward the test metals so this solution was used in the initial screening work. Dilution of the alcohols was made with Wyandotte city tap water which has the following composition in ppm: silica (SiO_2) 2.4, calcium (Ca) 27.0, magnesium (Mg) 6.8, sodium (Na) 4.9, potassium (K) 1.1, bicarbonate (HCO_3) 88.0, sulfate (SO_4), 17.0, chloride (Cl) 10.0, (Ref.: Industrial Utility of Public Water Supplies, 1952 Part 1, Geological Survey Water Supply Paper 1299). To prepare a solution of candidate inhibitor, 1% by weight of the material was dissolved or suspended in 20% by volume methanol solution and allowed to stand over night. Frequently an incompatibility was encountered. Any gross floculation or sediment which appeared was removed by filtration or separated by decantation the following morning. Only the supernatant liquid in the latter case was employed for corrosion tests. It is recognized that this step eliminated knowledge of the exact concentration of the inhibitor in the solution but it appeared to be the most feasible approach in a rapid screening procedure. In some cases the inhibitor was completely soluble to the extent of 1% in the water-alcohol solution yielding a clear liquid. In other cases, a clear liquid resulted only after filtering or decanting. In a few instances a colored or opaque solution of the candidate inhibitor was used in the tests.

After the jar was prepared with the test specimen in place, it was exposed in a room thermostatted at 104° ± 3°F. Periodic observations were made of these specimens to observe the protective action of the candidate inhibitor. In order to determine the minimum time required for significant corrosion in these specific conditions, several untreated controls were run before inhibitor tests were started. Controls were also maintained during the testing period. A set of controls is shown in Figure 2. The steel and aluminum specimens were placed in separate vessels in order to avoid the possibility of complication due to mixtures of corrosion products. Periodic observations were recorded on specially printed record sheets.

Letter Method of Rating Inhibitors.

In order to record the relative degree of protection afforded by candidate inhibitors under the given test conditions, an arbitrary system of letter ratings was employed. Those metal specimens which appeared to have less than 20% of the surfaces attacked by the solutions after a stated exposure were rated "A"; specimens showing corrosion of 20-39% of the surface area were rated "B"; those corroded 40-59% were rated "C" and those corroded 60% or more were rated "D". In the tabular data each periodic observation made of the test panels is indicated by a numerical subscript which designates the time in days since the beginning of the tests. Compounds having a rating of "B" or higher for at least a 30 day period were selected for further study. Other materials showing a "B" grade protection for at least 20 days were grouped to be considered in the event that too many materials in the first group failed to meet other specified requirements. If either metal showed a degree of corrosion greater than a "B rating" in either the liquid or vapor phases the particular compound involved was tentatively dropped from further consideration.

Photographic Records.

As a given test was terminated, the specimens were removed from the solution and scrubbed briskly with a nylon bristle toothbrush under the running tap. The specimens were then rinsed in acetone, air dried and mounted with paper cement on white Bristol board. The specimens were aligned opposite the proper code number and beneath the heading which indicated the kind of metal and whether the exposure had been made in the liquid or the vapor phase. For purposes of comparison, each photograph includes a set of untreated control specimens in the initial sandblasted condition and a set of panels which had been exposed 20 days in a 20% by volume solution of methanol in water without inhibitor.

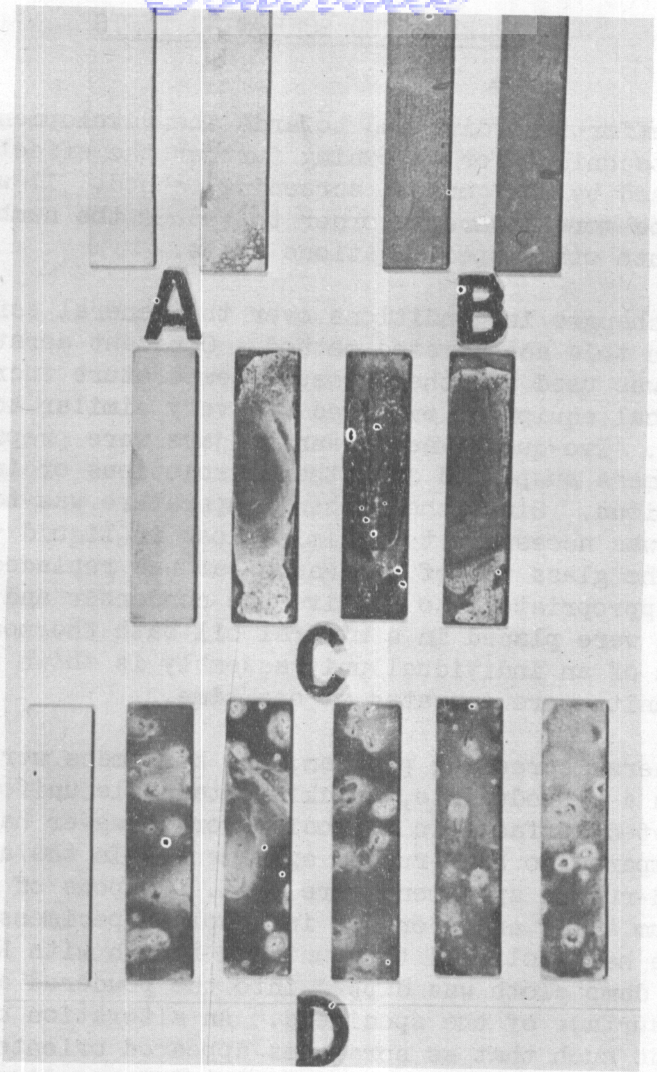

Fig. 2. Control specimens subjected to 20% by volume methanol solutions.

A. Aluminum Specimens

Left - untreated
Right - exposed 5 days in the liquid phase

B. Aluminum Specimens

Duplicate samples exposed 20 days in the vapor phase

C. Steel Specimens

Sample at left is untreated. (Stains are photographic in origin).
The other 3 samples were exposed 20 days in the liquid phase.

D. Aluminum Specimens

Sample on left is untreated. Other 5 samples were exposed 20 days in the liquid phase.

ACCELERATED SCREENING TESTS

A limited effort was directed towards the development of an accelerated corrosion technique for screening further the effective candidate inhibitors disclosed by the general screening method. It was intended that this procedure be more severe in order to reduce the number of inhibitors to be carried into other specifications tests.

Two major changes in conditions over the general screening techniques were employed in this accelerated method. Constant aeration by filtered, compressed air was used and the exposure temperature increased to 136° ± 1°F. The physical equipment employed was very similar to that used in the earlier program. Two-quart Mason canning jars were prepared as before with the metal specimens suspended in methanol solutions or in the vapor phase above the solutions. Since the higher temperature was to be employed a reflux condenser was necessary to minimize loss in liquid volume through the test period. The glass top of the Mason jar was replaced with a rubber stopper bored appropriately to receive the condenser and the air supply tube. The jars were placed in a mineral oil bath thermostated at 136° ± 1°F. A diagram of an individual unit assembly is shown in Figure 3. Sixteen of these units were operated at one time.

In the general screening program, the specimens were sandblasted in order to obtain a reproducible, quickly obtainable uniform surface. The use of sandblasted surfaces in corrosion work however has certain disadvantages as compared to hand-rubbed specimens. In the accelerated screening tests, hand-rubbed specimens were used. Coupons of 1010 mild steel, 2024-T3 aluminum alloy and, for use in coupled specimens, type 304 stainless steel were hand-polished to a uniform finish with No. 240 grit aluminum oxide. A damp cloth was dipped into the powdered aluminum oxide and rubbed on the surface of the specimens. An alteration of the direction of rubbing was made such that as scratches appeared oriented on one axis of the specimen subsequent strokes were directed perpendicularly until the previous scratch marks were removed. No imbedding of the aluminum oxide on the surface of the metal specimens could be detected.

As the general screening program proceeded, it became apparent that the mild steel was more suitable than the aluminum for screening studies. Comparatively little weight loss was encountered with the aluminum specimens. Only the steel specimens therefore were used in certain intermediate phases of the general program. In order to establish a reliability of the accelerated method and a practicable exposure time necessary to produce significant weight loss data with steel, replicate untreated control specimens were run. The results of these studies conducted in 20% by volume methanol are shown in Table 1.

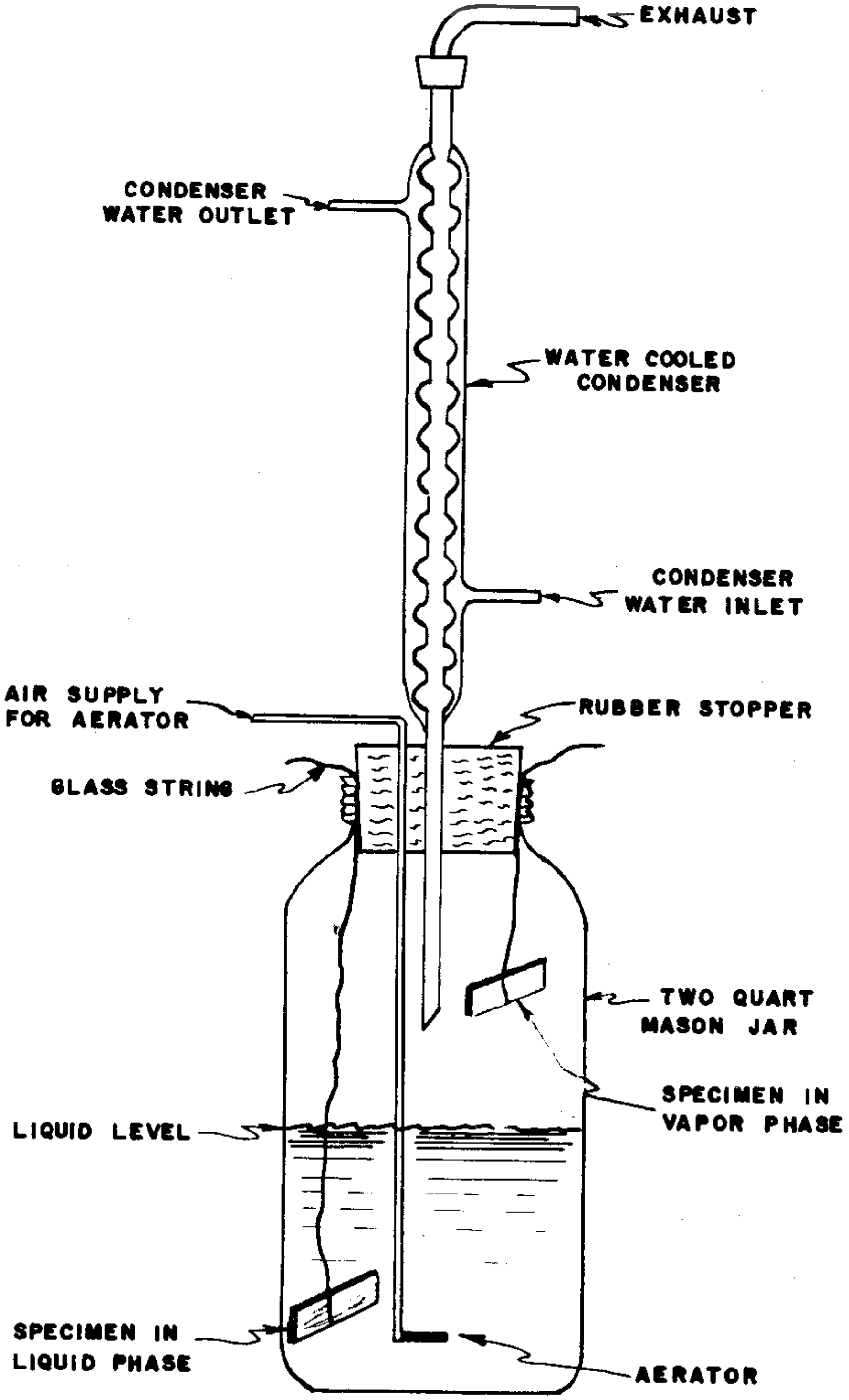

FIG. 3. ASSEMBLED CORROSION TESTING UNIT USED IN ACCELERATED PROCEDURE

TABLE 1

STUDIES OF AN ACCELERATED SCREENING TEST METHOD

Exposure in 20% methanol at 136° ± 1°F.

Metal	1010 Steel						2024-T3 Aluminum					
Exposure, Hours	24		16		8		24		16		8	
Exposure, Phase	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
Jar No. 1	-49.0	-21.8	-48.9	-34.7	-22.8	-33.2	-3.2	+4.1	-3.2	+5.4	-1.8	+3.5
2	-52.4	-75.9	-42.0	-67.3	-24.3	-18.7	-3.0	+3.8	-2.7	+3.6	-2.1	+2.7
3	-53.7	-28.3	-43.6	-55.6	-24.7	-26.4	-3.1	+2.5	-2.7	+4.4	-2.0	+3.9
4	-51.9	-77.1	-50.4	-47.0	-25.7	-17.7	-3.4	+4.6	-3.0	+3.0	-1.8	+4.4
5	-57.2	-27.2	-45.3	-30.8	-20.3	-10.3	-3.3	+3.1	-3.2	+5.0	-1.9	+4.1
6	-60.3	-34.9	-49.2	-43.5	-23.7	-24.3	-4.5	+4.8	-2.3	+5.9	-1.9	+3.4
Avg. Wt. Change, mg.	-54.1	-44.2	-46.6	-46.5	-23.6	-21.8	-3.4	+3.8	-2.8	+4.7	-1.9	+3.7
Range, mg.	11.3	55.3	8.4	36.5	5.4	22.9	1.5	2.3	0.9	2.9	0.3	1.8
Standard Deviation, mg.	4.0	32.8	3.4	13.5	1.9	7.9	0.77	0.88	0.11	1.25	0.038	0.60
Avg. Wt. Change,	-2.3	-1.8	-2.9	-2.9	-2.9	-2.7	-0.14	+0.16	-0.17	+0.28	-0.24	+0.46

The weight change data presented in Table 1 show several characteristic features of the method. It is apparent that in the vapor phase variation in weight changes significantly increases with longer exposures of steel specimens. Although it is recognized that vapor phase protection is an important requirement of an inhibitor, it was felt that the liquid phase tests would be more discriminatory and reliable for screening work. Observations on the length of exposure required to furnish reliable data in the liquid phase tests indicated that the 16 or 24 hour period would be adequate. Since an overnight test of 20 hours fitted well into the working schedule, this period was used in the accelerated screening program. As the number of experimental candidate inhibitors was narrowed to a few, a longer exposure period of 72 hours was used. In view of the time limitations of the contract, this was the longest period that could be given. While the results are believed to be indicative, it is recognized that much longer periods of testing, perhaps under other conditions, are necessary before sound conclusions may be drawn.

Since this evaluatory procedure was based primarily on weight changes, the specimens were cleaned of corrosion products before final weighing. An inhibited, acid cleaning solution (1) previously developed at Wyandotte for a similar purpose, was used on the mild steel specimens. For the aluminum specimens concentrated nitric acid was used. The cleaning procedure was as follows:

1. The specimen was removed from the alcohol-water solution and scrubbed briskly with a nylon toothbrush under the running tap.
2. The specimen was placed for one minute in the proper cleaning solution as indicated above.
3. The specimen was scrubbed once again under the running tap with the nylon toothbrush.
4. The specimen was dipped in acetone, dried in a filtered airblast and placed in a desiccator over night before weighing.

The use of the cleaning solution caused an average weight loss of 2 milligrams on non-corroded mild steel specimens. All the values presented in this report have been corrected for this weight loss. The aluminum control specimens cleaned in nitric acid remained at a constant weight.

In the later phases of the accelerated screening program, coupled specimens consisting of type 304 stainless steel and 2024-T3 aluminum alloy were included. In the preparation of the coupled specimens, a 5/16 inch diameter

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(1) 10% Naxonate G, 5% sodium bisulfate, 0.5% Pluronic F-68, 1.0% citric acid, 0.2% mercaptobenzothiazole, 83.3% water.

hole was drilled through each member of the couple centered at one end of the specimen. A one-half inch bolt of one-quarter inch diameter was placed through the two holes and a nut tightened with the fingers. The bolt and nut were made of type 304 stainless steel. The head of the bolt was in contact with the aluminum member to minimize scratching of the softer metal as the nut was tightened. Figure 4 is a photograph of the component parts and an assembled coupled specimen. In survey tests it was determined that the weight loss to the stainless steel member of the couple was negligible. Therefore in tables listing the results of weight losses to coupled specimens, the data are given for the aluminum member only. A supply of stainless steel specimens one inch wide already on hand was used and aluminum specimens cut in size to match. When the data were tabulated a size correction factor was applied in order to allow immediate comparison between weight change data for coupled and uncoupled aluminum.

SURFACE AND INTERFACIAL TENSION DETERMINATIONS

Since it is required that the surface and interfacial tension of the alcohol-water inhibitor meet certain requirements, it became necessary to include in an inhibitor composition a surfactant of suitable effectiveness. As these formulations were prepared the surface and interfacial tension values were checked in use alcohol solutions by the ring method using a Cenco-duNouy Interfacial Tensiometer. The standard procedures recommended by the instrument manufacturer were followed in these determinations. Values presented in this report have been corrected according to the usual methods.

III EXPERIMENTAL DATA AND DISCUSSION

The experimental program was first directed toward the evaluation of a large number of candidate inhibitors in a general screening procedure. Materials successfully passing this test were then examined to determine their ability to meet the other target requirements set up in Exhibit A of this contract. In general this involved evaluation of their solubility at lower temperatures and determination of the compatibility with selected surfactants. At a point in the work, promising inhibitors thus disclosed were next modified in order to meet the maximum non-combustible solids content requisite. Eventually the few selected compositions were further evaluated for corrosion protection against the test metals in comparison with the soluble oil covered by MIL-C-4339.

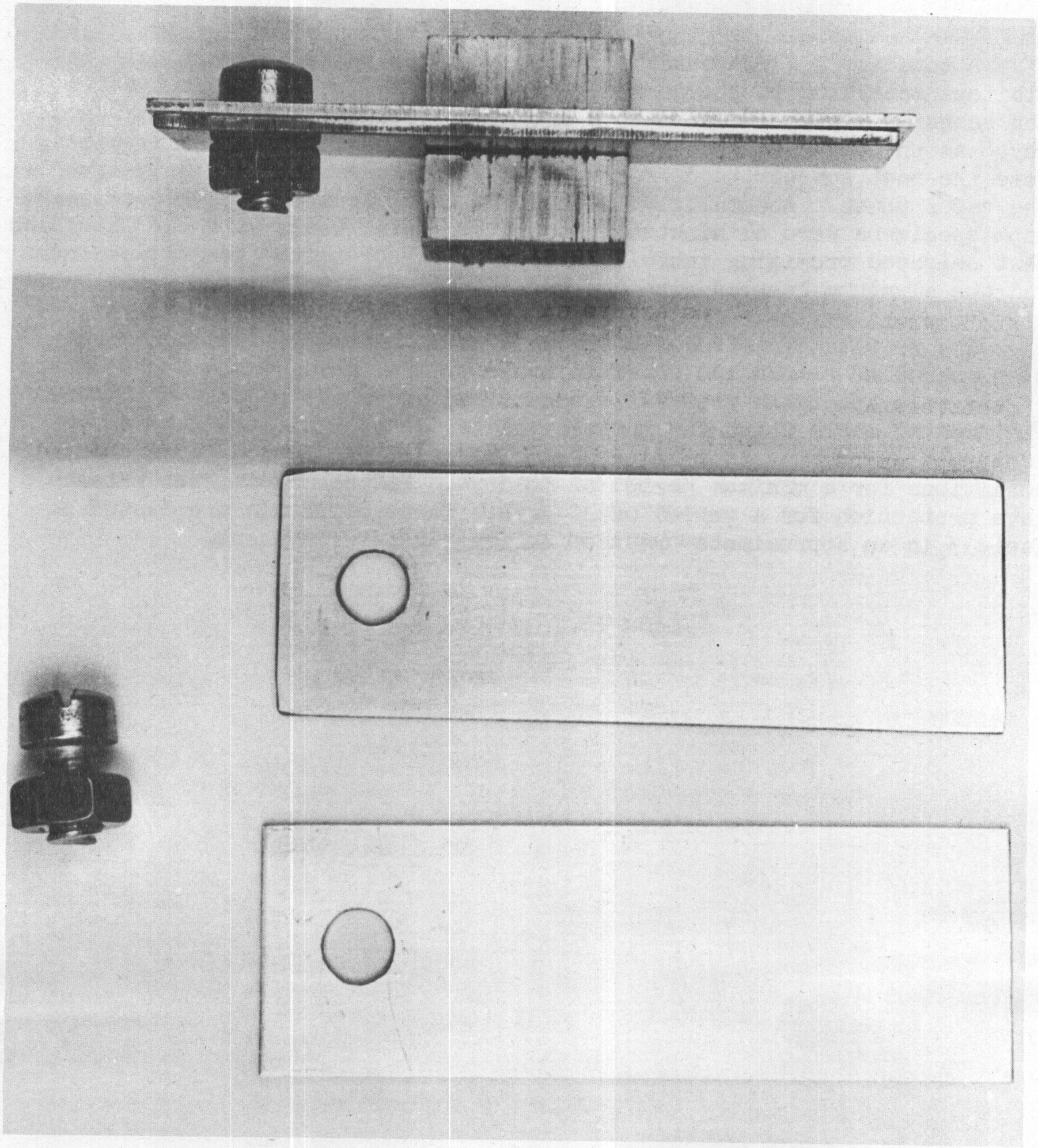

Fig. 4. The type 304 stainless steel-2024-T3 aluminum alloy coupled specimen used in corrosion studies.

GENERAL SCREENING TESTS

A total of 137 compounds was collected and tested as candidate inhibitors according to the general screening procedures described above. The tests initially included both SAE 1010 steel and 2024-T3 aluminum alloy. As the tests progressed it was recognized that the steel specimens were the most subject to corrosive attack. This was particularly true in the vapor phase. Accordingly in order to expedite the test program, aluminum specimens were eliminated from the screening tests with the provision that selected promising inhibitors would later be tested toward aluminum and the aluminum coupled with type 304 stainless steel.

The results of this screening work in terms of the letter designation method of rating are shown in Table 2. Following Table 2 photographs of the test specimens prepared as described above are presented (Figure 5). The data of Table 2 and the photographic evidence indicated that eleven compounds or combinations of compounds afforded protection under the test conditions for a minimum period of 30 days. Fifteen additional materials gave protection for a period of 20 days. These compounds are listed in Table 3 in an approximate order of decreasing effectiveness.

TABLE 2

PERIODIC OBSERVATIONS OF THE CORROSION OF SAE 1010 STEEL AND 2024-T3 ALUMINUM BY 20 PERCENT METHANOL-IN-WATER SOLUTION. INITIAL SCREENING PROGRAM

Exposure Temperature: 104° ± 3°F.
Maximum Inhibitor Concentration: 1%

Visual Corrosion Evaluation (a)

Subscripts refer to the number of days exposure

Code No.	Candidate Inhibitor (b)	Steel		Aluminum	
		Liquid phase	Vapor phase	Liquid phase	Vapor phase
Control	--	$D_{6\ 9\ 14\ 20\ 28}$	$A_{6\ 9\ 14}$ B_{20} C_{28}	$B_{6\ 9\ 14}$ C_{20} D_{28}	$B_{6\ 9}$ $C_{14\ 20}$ D_{28}
2507	Ethylenediamine	$A_{6\ 9\ 14\ 20\ 28\ 31}$	$A_{6\ 9}$ B_{14} C_{20} $D_{28\ 31}$	A_{6} $PFA_{9\ 14\ 20\ 28\ 31}$	$B_{6\ 9\ 14\ 20\ 28}$ C_{31}
2508	Dimethylaniline	$D_{5\ 12\ 21}$	$A_{5\ 12\ 21}$	$B_{5\ 12\ 21}$	$A_{5\ 12\ 21}$
2509	Proprietary	$A_{6\ 9\ 14}$ $B_{20\ 28\ 31}$	B_{6} $C_{9\ 14\ 20}$ $D_{28\ 31}$	A_{3} $PFA_{9\ 14\ 20}$ C_{28} D_{31}	$A_{3\ 9\ 14\ 20}$ $C_{28\ 31}$
2510	Proprietary	$D_{6\ 9\ 14\ 20\ 28\ 31}$	$B_{6\ 9}$ $C_{14\ 20\ 28}$ D_{31}	A_{6} PFA_{9} B_{14} $C_{20\ 28}$ D_{31}	A_{6} $B_{9\ 14}$ $C_{20\ 28}$ D_{31}
2511	Sodium benzoate	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$
2512	Acetamide-Potassium nitrite	$A_{5\ 14\ 21\ 28\ 30}$	$A_{5\ 14}$ $B_{21\ 28\ 30}$	$A_{5\ 14\ 21\ 28\ 30}$	$A_{5\ 14\ 21\ 28\ 30}$
2513	p-Phenylenediamine	$D_{5\ 12\ 21}$	$A_{5\ 12\ 21}$	$A_{5\ 12\ 21}$	$A_{5\ 12\ 21}$
2514	Proprietary	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7}$ B_{13} $C_{21\ 28}$ D_{37}	$A_{2\ 7\ 13}$ B_{21} C_{28} D_{37}	$A_{2\ 7\ 13}$ B_{21} C_{28} D_{37}
2515	Cyclohexylamine	$A_{5\ 11\ 19\ 26\ 35}$	$A_{5\ 11\ 19\ 26\ 35}$	$PFA_{5\ 11\ 19\ 26\ 35}$	$B_{5\ 11\ 19\ 26\ 35}$
2516	Catechol	$A_{2\ 7}$ $PFA_{13\ 21\ 28\ 37}$	$A_{2\ 7}$ $PFA_{13\ 21\ 28\ 37}$	$A_{2\ 7}$ $PFA_{13\ 21\ 28\ 37}$	$A_{2\ 7}$ $PFA_{13\ 21\ 28\ 37}$
2517	Urea-Potassium nitrite	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$

(a) and (b): See footnotes at end of table.

TABLE 2 - (continued)

Visual Corrosion Evaluation (a)

Subscripts refer to the number of days exposure

Code No.	Candidate Inhibitor (b)	Steel		Aluminum	
		Liquid phase	Vapor phase	Liquid phase	Vapor phase
2518	Propylene diamine	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13}\ B_{21\ 28\ 37}$	$PFA_{2\ 7\ 13}\ PFC_{21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$
2519	Pyrogallol	$PFA_{2\ 7\ 13\ 21\ 28\ 37}$	$B_{2\ 7\ 13}\ C_{21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$	$A_{2\ 7\ 13\ 21\ 28\ 37}$
2520	Proprietary	$C_{5}\ D_{11\ 19\ 26\ 35}$	$A_{5\ 11}\ B_{19\ 26\ 35}$	$C_{5}\ D_{11\ 19\ 26\ 35}$	$A_{5\ 11}\ B_{19\ 26\ 35}$
2521	Benzotriazole	$B_{5}\ D_{11\ 19\ 26\ 35}$	$A_{5\ 11\ 19\ 26\ 35}$	$B_{5\ 11}\ C_{19\ 26}\ D_{35}$	$A_{5\ 11\ 19\ 26\ 35}$
2522	Naphthylamine	$D_{3\ 11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$	$D_{3\ 11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$
2523	Proprietary	$A_{3\ 11\ 18\ 27}$	$A_{3}\ B_{11}\ D_{18\ 27}$	$A_{3\ 11\ 18\ 27}$	$A_{3}\ B_{11\ 18\ 27}$
2524	Proprietary	$A_{3}\ D_{11\ 18\ 27}$	$A_{3}\ C_{11\ 18\ 27}$	$A_{3}\ D_{11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$
2525	β-Naphthylamine.HCl	$PFA_{3\ 11\ 18\ 27}$	$A_{3\ 11\ 18}\ D_{27}$	$PFA_{3}\ D_{11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$
2526	Dicyclohexylamine	$B_{3\ 11}\ C_{18\ 27}$	$A_{3\ 11}\ C_{18\ 27}$	$PFA_{3\ 11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$
2527	p-Toluenesulfonchloride	$D_{3\ 11\ 18\ 27}$	$A_{3}\ D_{11\ 18\ 27}$	$D_{3\ 11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$
2528	Resorcinol	$C_{3}\ D_{11\ 18\ 27}$	$A_{3\ 11\ 18\ 27}$	$C_{3}\ D_{11\ 18\ 27}$	$A_{3}\ B_{11\ 18\ 27}$
2529	Proprietary	$D_{3\ 11\ 18}$	$A_{3\ 11\ 18}$	$D_{3\ 11\ 18}$	$A_{3\ 11\ 18}$
2530	Sodium chromate-Sodium hydroxide	$A_{8\ 24}$	$C_{8\ 24}$	$PFA_{8\ 24}$	$A_{8\ 24}$
2531	Sodium metasilicate	$A_{8\ 24}$	$C_{8\ 24}$	$A_{8\ 24}$	$A_{8\ 24}$
2532	Sodium chromate-Calcium phosphate	$A_{8\ 24\ 29}$	$A_{8}\ B_{24}\ D_{29}$	$A_{8\ 24\ 32}$	$A_{8\ 24\ 32}$
2533	Potassium nitrite-Sodium molybdate	$A_{5\ 21\ 26}$	$B_{5\ 21}\ D_{26}$	$A_{5\ 21\ 26}$	$A_{5\ 21\ 26}$

TABLE 2 - (continued)

Visual Corrosion Evaluation (a)

Code No.	Candidate Inhibitor (b)	Subscripts refer to the number of days exposure			
		Steel		Aluminum	
		Liquid phase	Vapor phase	Liquid phase	Vapor phase
2534	Sodium chromate	$A_{5\ 21\ 28}$	$B_{5\ 21}\ D_{28}$	$A_{5\ 21\ 28}$	$A_{5\ 21\ 28}$
2537	p-Cyclohexyl phenol	$D_{5\ 21}$	$A_{5\ 21}$	$C_5\ D_{21}$	$A_{5\ 21}$
2538	Sodium perborate - Sodium phosphate	$A_{13\ 18\ 22\ 24}$	$A_{13\ 18}\ B_{22}\ C_{24}$	$PFA_{13\ 18\ 22\ 24}$	$A_{13\ 18\ 22\ 24}$
2539	Potassium nitrite	$A_{13\ 18\ 22\ 24}$	$B_{13\ 18\ 22}\ C_{24}$	$A_{13\ 18\ 22\ 24}$	$A_{13\ 18\ 22\ 24}$
2540	Sodium nitrate	D_{13}	B_{13}	PFA_{13}	A_{13}
2541	Sodium nitrate - Sodium chromate	$A_{13\ 18}$	$B_{13}\ D_{18}$	$A_{13\ 18}$	$A_{13\ 18}$
2542	Sodium chromate - Potassium nitrite	$A_{13\ 18}$	$B_{13}\ D_{18}$	$A_{13\ 18}$	$A_{13\ 18}$
2543	TSP - Potassium ferricyanide	$A_{13\ 22}$	$B_{13}\ C_{22}$	$A_{13\ 22}$	$A_{13\ 22}$
2544	Ammonium carbonate - Ammonium hydroxide	$A_{13\ 22\ 32}$	$B_{13\ 22\ 32}$	$A_{13\ 22\ 32}$	$A_{13\ 22\ 32}$
2545	Soluble Oil, MIL-C-4339	$A_{13\ 22\ 24}$	$B_{13}\ C_{22\ 24}$	$A_{13\ 22\ 24}$	$A_{13\ 22\ 24}$
2546	Proprietary	$A_{13\ 22\ 24}$	$B_{13}\ C_{22}\ C_{24}$	$A_{13\ 22\ 24}$	$A_{13\ 22\ 24}$
2547	Proprietary	$A_{7\ 18}$	$B_7\ C_{18}$	$A_{7\ 18}$	$A_{7\ 18}$
2548	2-Hydroxypropylamine nitrite	$A_{7\ 18}$	$B_7\ C_{18}$	$A_{7\ 18}$	$A_{7\ 18}$
2549	Proprietary	$A_{7\ 18}$	$B_7\ C_{18}$	A_{18}	A_{18}
2550	Proprietary	A_{31}	$B_{7\ 18\ 24\ 31}$	A_{31}	A_{31}
2551	Undecylenic acid	A_{31}	$A_{21}\ B_{31}$	A_{31}	A_{31}
2552	Tannic acid	$PFB_{7\ 10}$	$C_{7\ 10}$	$D_{7\ 10}$	$A_{7\ 10}$

TABLE 2 - (continued)

Visual Corrosion Evaluation (a)

Subscripts refer to the number of days exposure

Code No.	Candidate Inhibitor (b)	Steel Liquid phase	Steel Vapor phase	Aluminum Liquid phase	Aluminum Vapor phase
2553	Linoleic acid	B_{21}	B_{15} C_{21}	A_{21}	B_{21}
2554	Lactic acid	PFA_{1}	D_{1}	PFA_{1}	A_{1}
2555	Proprietary	A_{31}	A_{8} B_{31}	A_{31}	A_{31}
2556	Proprietary	A_{21}	A_{8} B_{15} C_{21}	A_{21}	A_{21}
2557	α-Naphthol	A_{8}	A_{8}	D_{8}	PFA_{8}
2558	Butylene oxide, mixed isomers	D_{7}	C_{7}	D_{7}	A_{7}
2559	Glycerol mono-oleate	$A_{6\ 13}$	B_{6} C_{13}	$A_{6\ 13}$	$A_{6\ 13}$
2560	Guanidine carbonate	A_{5}	C_{5}	PFA_{5}	A_{5}
2561	Proprietary	D_{6}	C_{6}	A_{6}	A_{6}
2562	Aluminum stearate	D_{5}	A_{5}	A_{5}	B_{5}
2563	Proprietary	$A_{6\ 13}$	A_{6} C_{13}	$A_{6\ 13}$	$A_{6\ 13}$
2564	Naphthenic acids	PFB_{30}	A_{30}	A_{19} PFA_{30}	A_{30}
2565	Proprietary	D_{1}	A_{1}	A_{1}	A_{1}
2566	Proprietary	D_{1}	A_{1}	A_{1}	A_{1}
2567	Proprietary	D_{1}	A_{1}	A_{1}	A_{1}
2568	Bone oil	$A_{8\ 14}$	B_{8} C_{14}	$A_{8\ 14}$	$B_{8\ 14}$
2569	Oleic acid	$A_{8\ 14}$	B_{8} C_{14}	$A_{8\ 14}$	$A_{8\ 14}$
2570	Sodium nitrite - Oleic acid	A_{30}	A_{30}	A_{30}	A_{30}
2571	Ethyl stearate	D_{7}	A_{7}	A_{7}	A_{7}
2572	n-Butyl benzoate	D_{7}	B_{7}	D_{7}	A_{7}
2573	Benzoic acid	PFA_{7}	D_{7}	D_{7}	A_{7}

TABLE 2 - (continued)

Visual Corrosion Evaluation (a)

Subscripts refer to the number of days exposure

Code No.	Candidate Inhibitor (b)	Steel		Aluminum	
		Liquid phase	Vapor phase	Liquid phase	Vapor phase
2574	Ricinoleic acid, sodium salt	A_{20}	B_{13} C_{20}	A_{20}	A_{20}
2575	p-Toluhydroquinone	D_7	C_7	D_7	A_7
2576	Tri-p-tolylphosphite	A_{13} C_{20}	B_{13} C_{20}	C_{13} D_{20}	A_7 PFA_{13} C_{20}
2578	Proprietary	D_6	B_6	A_6	A_6
2579	Proprietary	D_6	B_6	D_6	A_6
2580	Proprietary	A_{16}	B_{12} C_{16}	A_{16}	A_{12} B_{16}
2581	o-Dianisidine	D_6	B_6	D_6	A_6
2582	2,4-Tolylene diamine	A_{18} $C_{26\ 30}$	$B_{6\ 30}$	A_{30}	A_{19} $PFB_{26\ 30}$
2583	o-Toluidine	D_4	A_4	A_4	A_4
2584	m-Phenylene diamine	$D_{10\ 31}$	A_{10} B_{31}	A_{31}	A_{31}
2585	Proprietary	D_4	B_4	A_4	A_4
2586	Proprietary	D_4	B_4	A_4	A_4
2587	Proprietary	D_4	B_4	A_4	A_4
2588	Proprietary	D_4	B_4	A_4	A_4
2589	Dimethylethanolamine	A_4	D_4	A_4	D_4
2590	Diethylethanolamine	A_4	D_4		
2591	2-Mercaptoethanol	A_4	D_4		
2592	3-Dimethylamino-propylamine	A_4	D_4		
2593	3-Methoxypropylamine	A_4	D_4		
2594	3-Isopropoxypropyl-amine	A_4	D_4		

TABLE 2 - (continued)

Code No.	Candidate Inhibitor (b)	Visual Corrosion Evaluation (a) Subscripts refer to the number of days exposure Steel Liquid phase	 Vapor phase
2595	3-Isopropylaminopropylamine	A_4	D_4
2596	3,3'Iminobispropylamine	A_4	D_4
2597	2-Amino-benzenethiol	$A_{4\ 11\ 18}$	$A_4\ B_{11}\ D_{18}$
2598	3-Diethylaminopropylamine	A_4	C_4
2599	Formamide	D_4	C_4
2900	Dimethylpyrazine	D_4	B_4
2901	Dimethylisopropanolamine	A_4	D_4
2902	Diethylaminoethanol	A_4	D_4
2903	Proprietary	D_4	B_4
2904	Triethanolamine titanate	$B_4\ C_{11}$	B_{11}
2905	Tri n-butylamine	C_4	C_4
2906	Triethyl phosphate	D_4	B_4
2907	Tetramethyl ammonium hydroxide (10%)	$A_{4\ 11}$	$B_4\ C_{11}$
2908	Ammonium chromate	A_4	C_4
2909	Pyridine-N-oxide	D_4	B_4
2910	4-Picoline-N-oxide	D_4	B_4
2911	Proprietary	D_4	B_4
2912	Proprietary	D_4	B_4
2913	Proprietary	D_4	B_4
2914	Piperidine	A_{34}	B_{34}
2915	Proprietary	D_4	B_4

TABLE 2 - (continued)

Visual Corrosion Evaluation (a)
Subscripts refer to the number of days exposure

Code No.	Candidate Inhibitor (b)	Steel	
		Liquid phase	Vapor phase
2916	3,3'-Dimethoxybenzidine	D_4	A_4
2917	Proprietary	D_4	A_4
2918	Triacetin	D_4	C_4
2919	Proprietary	A_5	C_5
2920	Proprietary	B_5	C_5
2921	Proprietary	$A_{12}\ {}_{19}$	B_{12} C_{19}
2922	Proprietary	D_5	B_5
2923	Ammonium salt of perfluorooctanoic acid	A_5	D_5
2924	Ammonium salt of perfluorobutyric acid	D_5	D_5
2925	Sodium molybdate-Sodium tungstate	$A_{12}\ {}_{19}$	B_{12} C_{19}
2926	Sodium perborate - Sodium carbonate	A_5	C_5
2927	Proprietary	$A_5\ {}_{12}$	B_5 D_{12}
2928	Acrylamide - Sodium nitrite	$A_5\ {}_{12}$	B_5 D_{12}
2929	Proprietary	D_5	C_5
2930	Proprietary	D_5	C_5
2931	Stearamide - Sodium nitrite	A_5	C_5
2932	Stearamide - Ammonium chromate	A_5	C_5
2933	Proprietary	D_{12}	C_{12}
2934	Proprietary	D_{12}	C_{12}
2938	Proprietary	D_5	A_5

TABLE 2 - (continued)

Visual Corrosion Evaluation (a)
Subscripts refer to the number of days exposure

		Steel	
Code No.	Candidate Inhibitor (b)	Liquid phase	Vapor phase
2939	4-Cyclohexylcyclohexanol	D_5	A_5
2940	Proprietary	D_5	A_5
2941	Phenylundecanoic acid	D_5	A_5
2942	Dibenzylacetic acid	D_5	A_5
2943	Proprietary	D_5	A_5
2944	1,4-Butanediol	D_5	A_5
2945	Proprietary	D_5	A_5
2948	p-Methoxyphenol	D_8	A_8
2949	Proprietary	D_8	A_8
2950	Proprietary	D_8	B_8
2951	Proprietary	D_8	B_8
2952	Proprietary	A_8	C_8
2953	Proprietary	$A_{8\ 13}$	A_8 B_{13}
2954	Proprietary	$A_{8\ 13}$	$B_{8\ 13}$
2955	Proprietary	B_8	B_8
2956	Proprietary	D_8	A_8

(a) Letters refer to percent of surface area corroded:

A = less than 20
B = 20 to 39
C = 40 to 59
D = 60 or more
PF = "Protective film" (uniform discoloration)

(b) In two-component tests, equal parts of each material were placed in the alcohol-water solution.

TABLE 3

LIST OF 26 PROMISING INHIBITORS FROM THE GENERAL SCREENING PROGRAM IN DESCENDING ORDER OF EFFECTIVENESS

Exposure: 20% Aqueous methanol at 104° ± 3°F; liquid and vapor phase.

Metals: SAE 1010 steel and 2024-T3 aluminum

Code No.	Component
	A. Effective for 30 days (min.)
2517	Urea-potassium nitrite
2511	Sodium benzoate
2570	Sodium nitrite-oleic acid
2516	Catechol
2564	Naphthenic acids
2914	Piperidine
2551	Undecylenic acid
2555	Proprietary
2512	Acetamide-potassium nitrite
2544	Ammonium carbonate-ammonium hydroxide
2550	Proprietary
	B. Effective for 20 days (min.)
2532	Sodium chromate - calcium phosphate
2538	Sodium perborate - trisodium phosphate
2539	Potassium nitrite
2533	Potassium nitrite - sodium molybdate
2534	Sodium chromate
2518	Propylene diamine
2515	Cyclohexylamine
2556	Proprietary
2553	Linoleic acid
2507	Ethylene diamine
2519	Pyrogallol
2545	Soluble Oil, MIL-C-4339
2514	Proprietary
2546	Proprietary
2584	m-Phenylenediamine

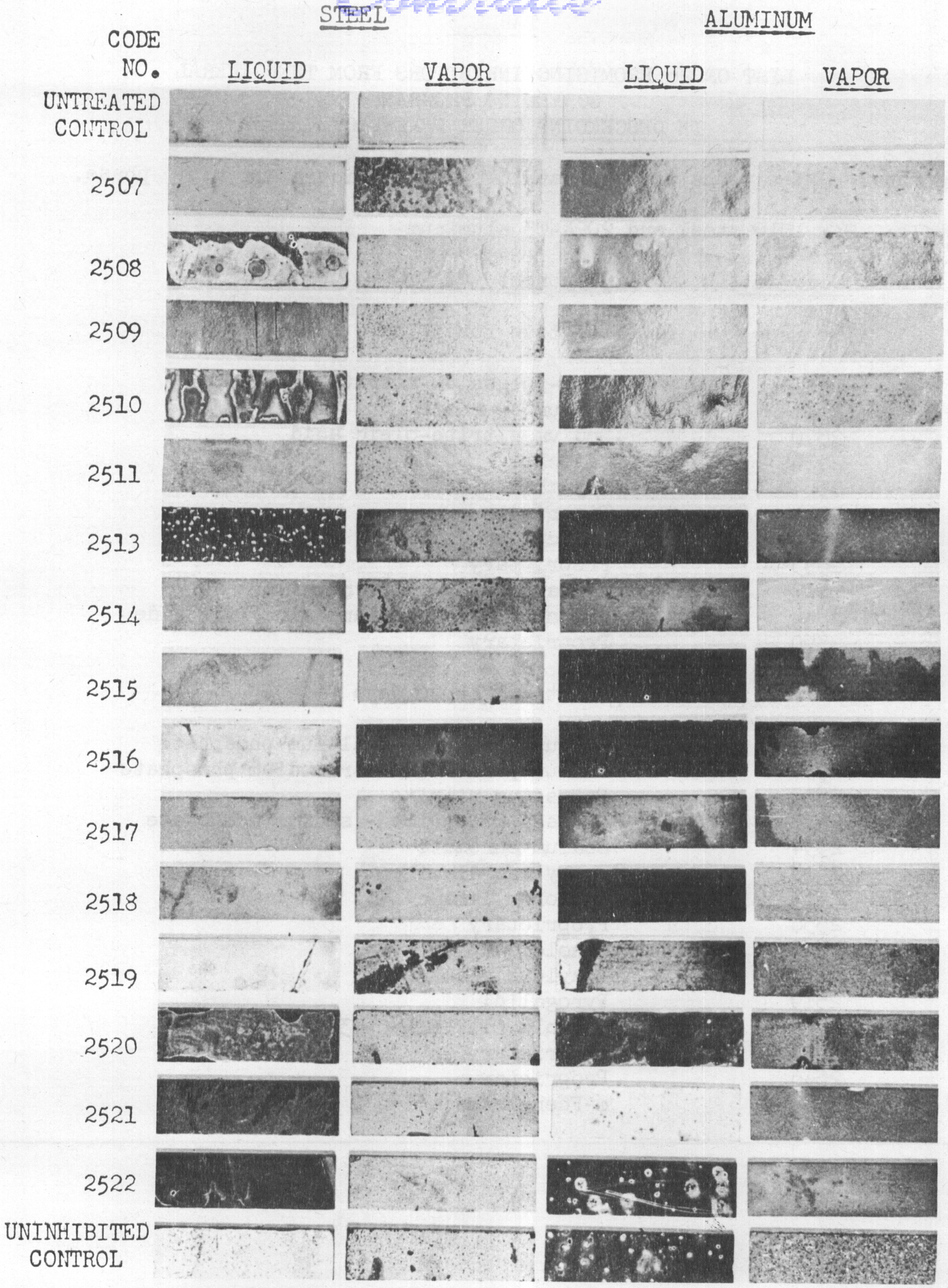

Fig. 5. Photographs of SAE 1010 steel and 2024-T3 aluminum specimens after use in evaluation of candidate inhibitors by the general screening method.

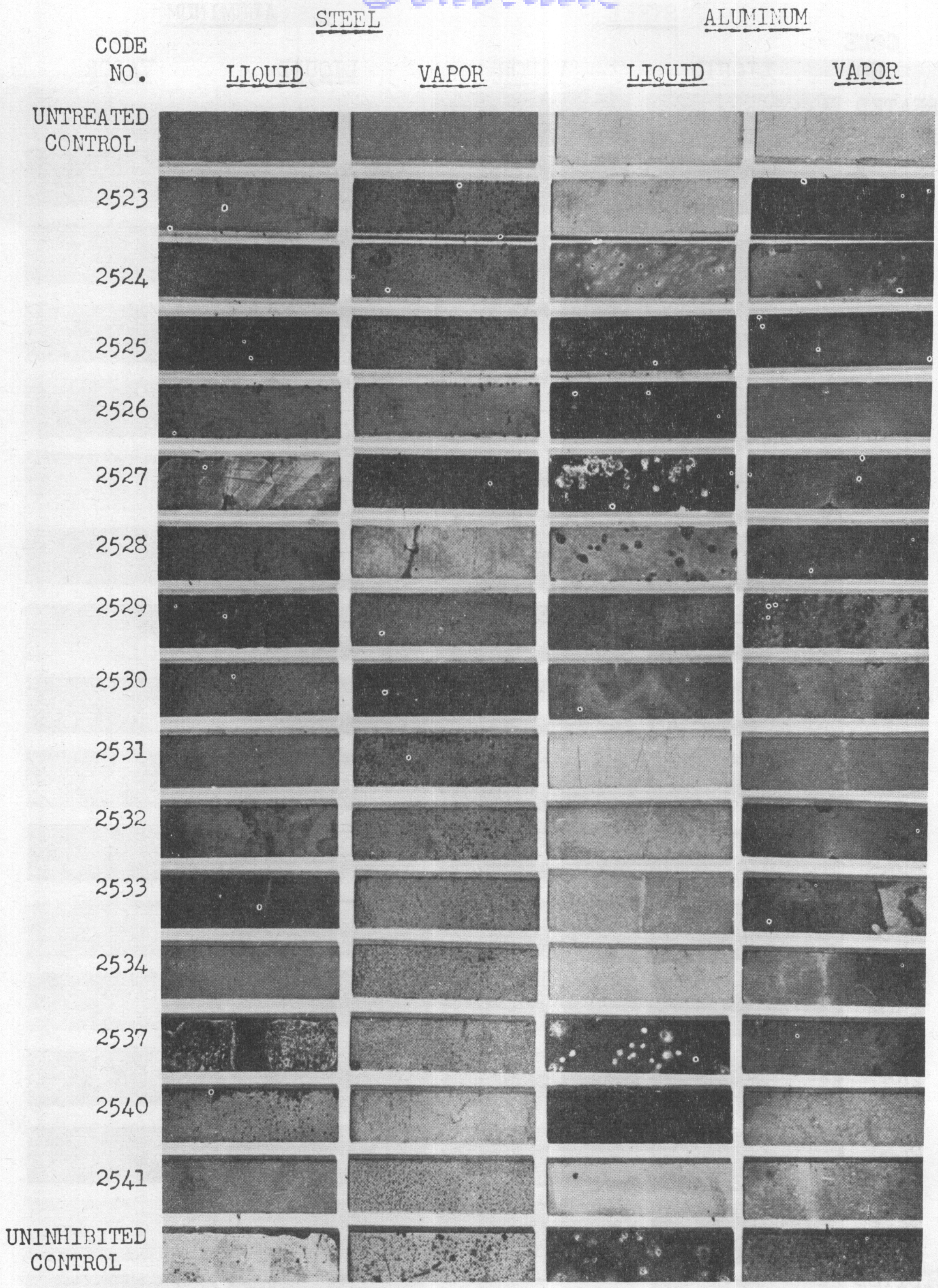

Fig. 5. (Continued)

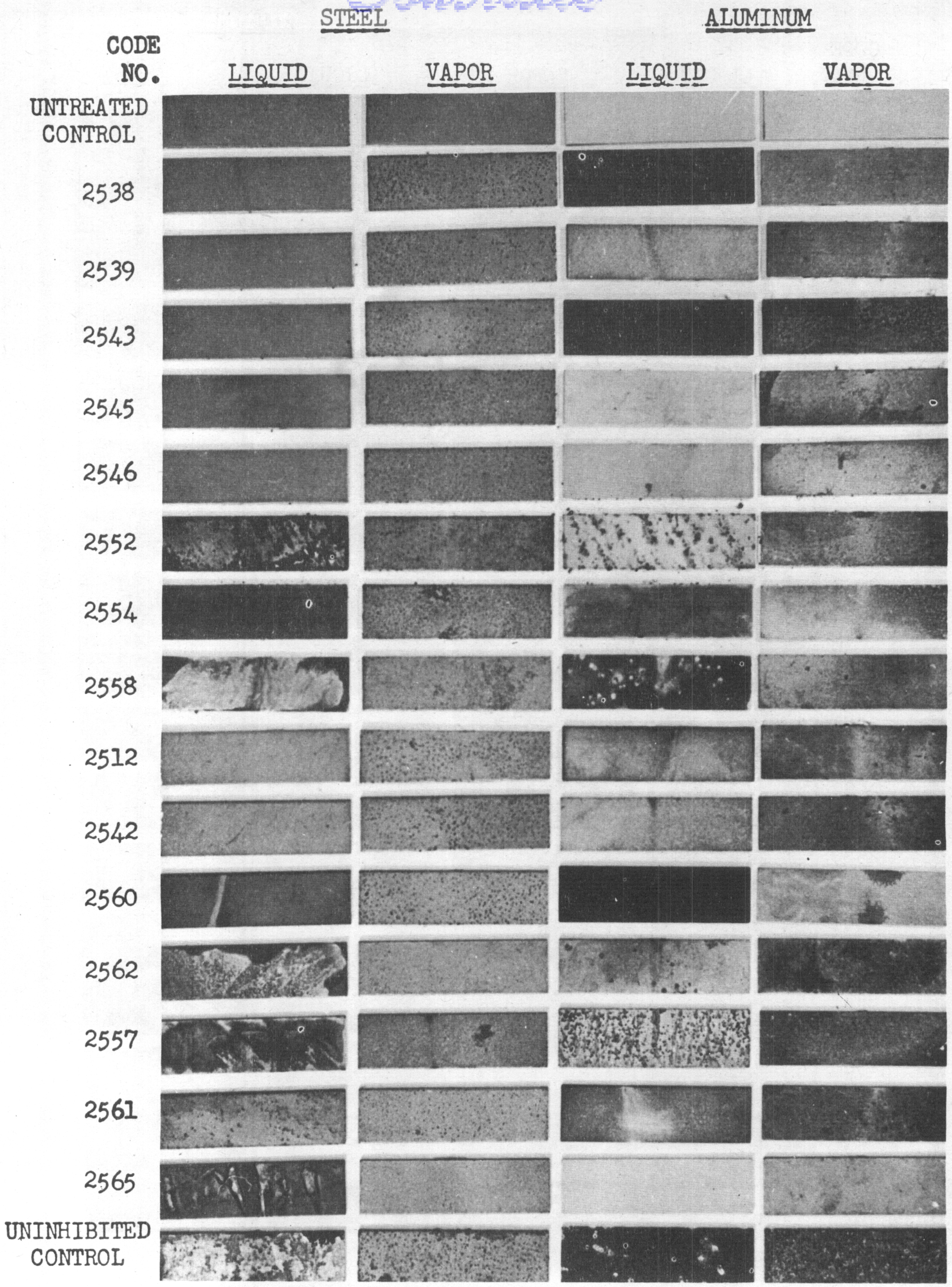

Fig. 5. (Continued)

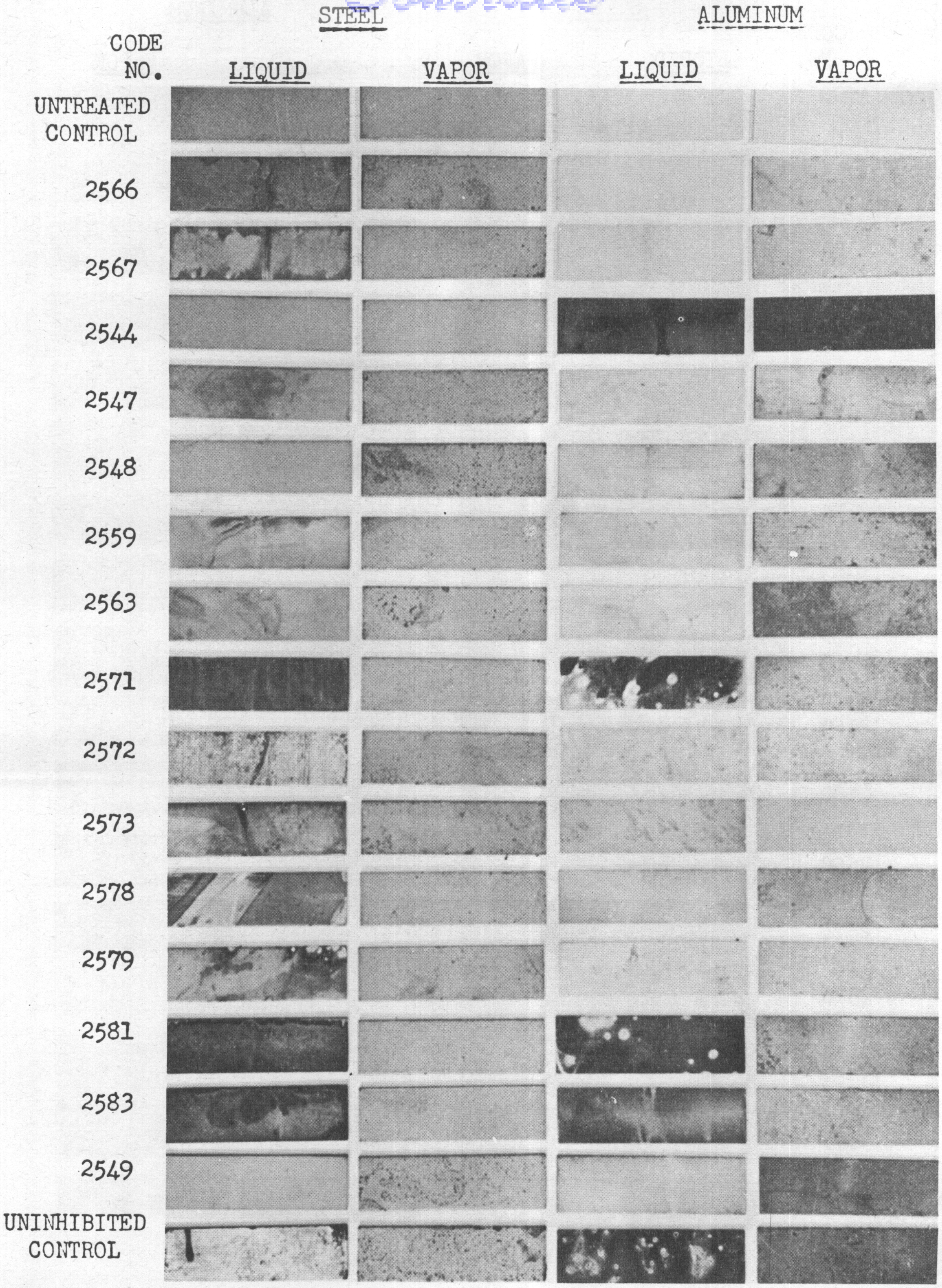

Fig. 5. (Continued)

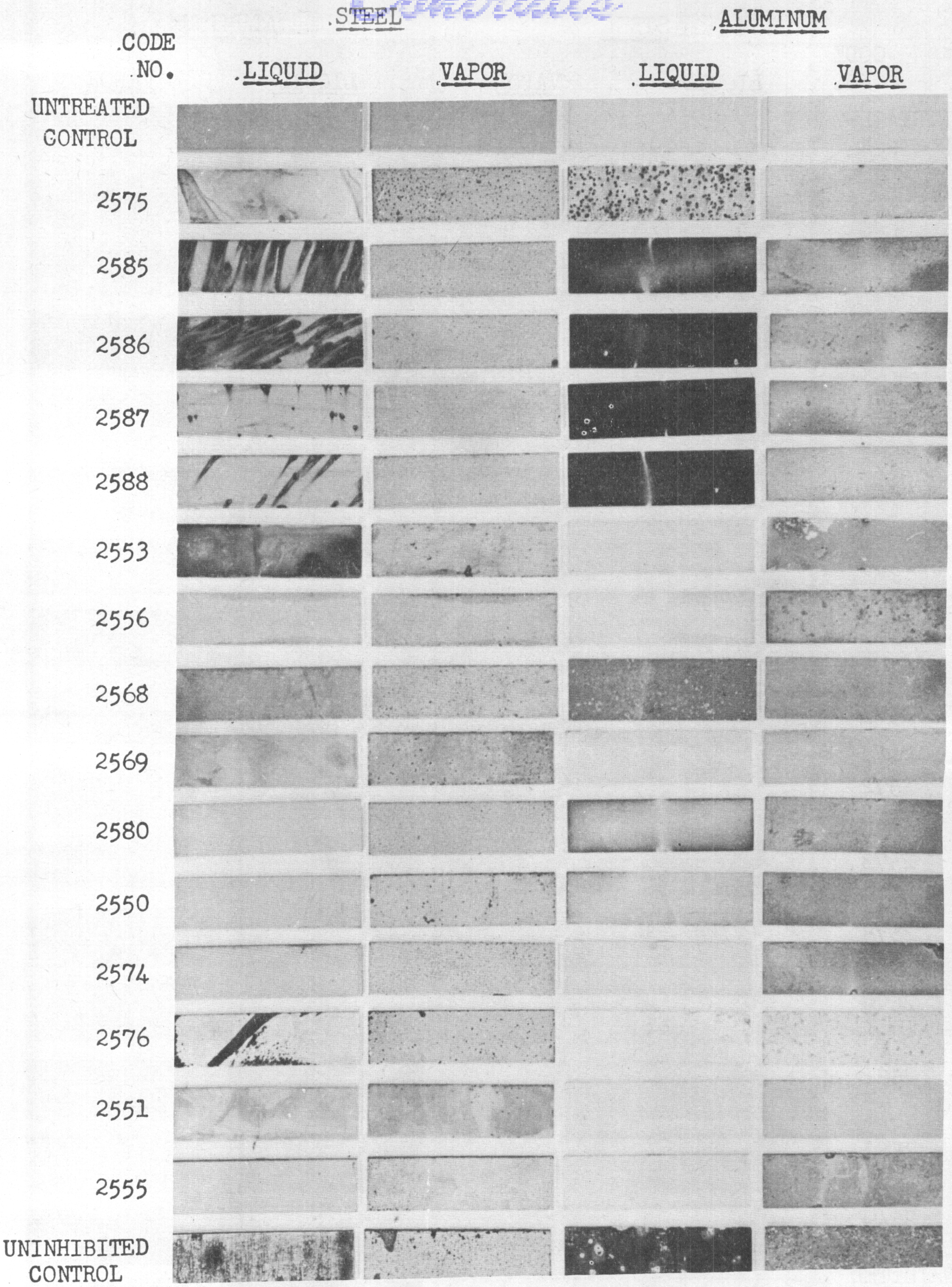

Fig. 5. (Continued)

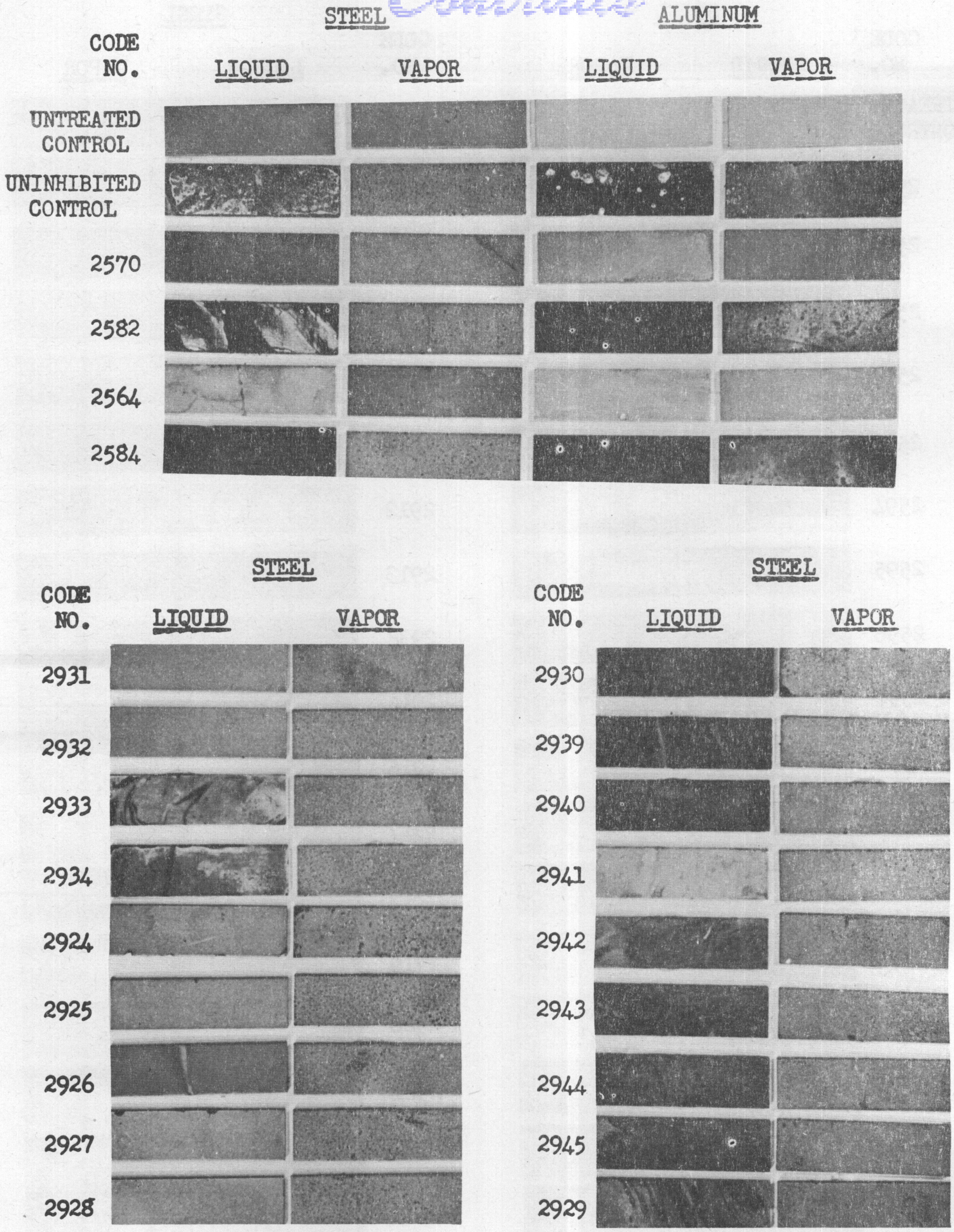

Fig. 5. (Continued)

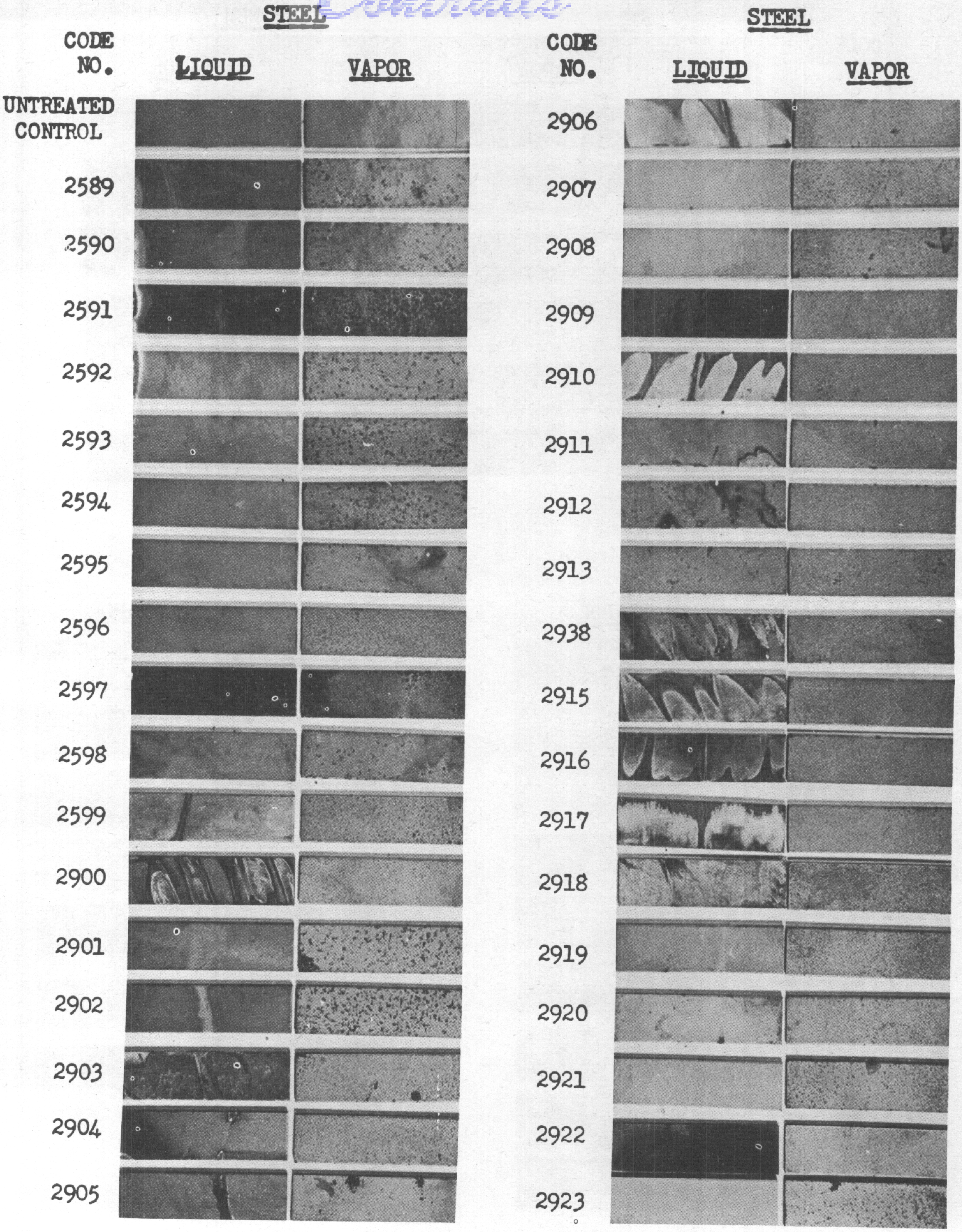

Fig. 5. (Continued)

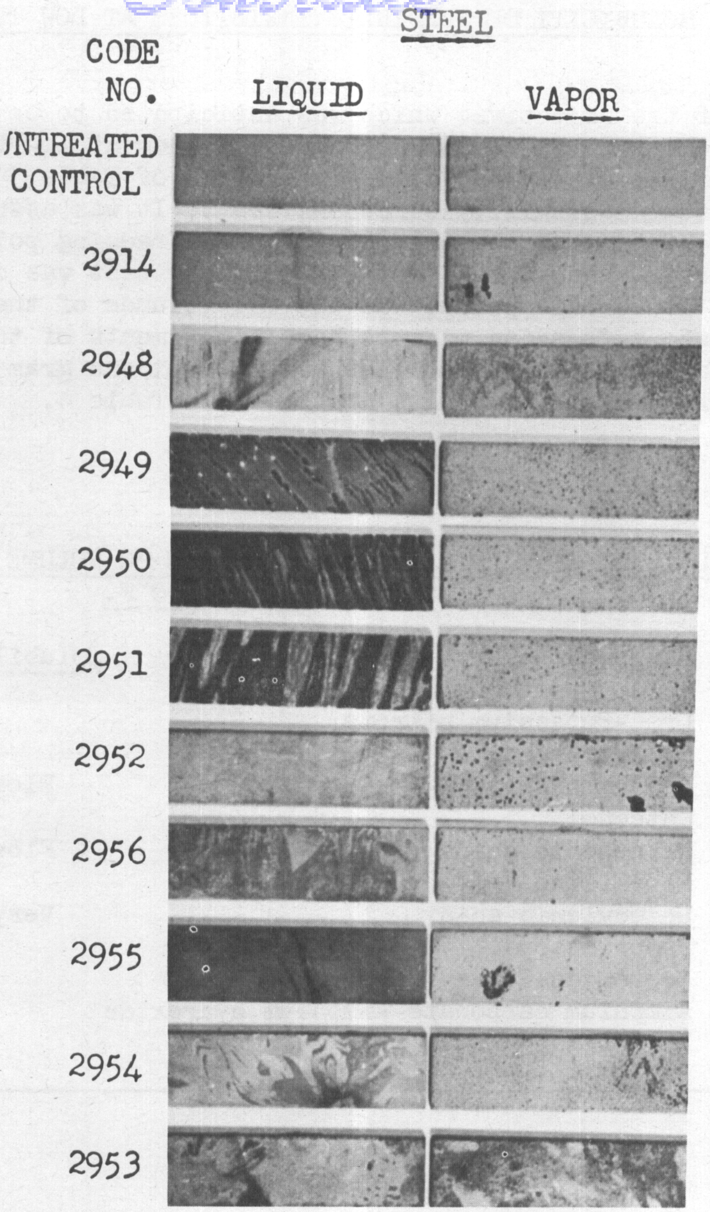

Fig. 5. (Continued)

SOLUBILITY OF CANDIDATE INHIBITORS AT LOW TEMPERATURES:

One of the objectives which was anticipated to be very restrictive is the requirement on solubility of the inhibitor at low temperatures. Accordingly the first eleven candidate inhibitors of Table 3 were taken through a low temperature solubility screening test. It was assumed that these solutions would freeze at about 18°F. (average freezing point of 20% methanol and denatured ethanol) and so the solubility test was conducted about ten degrees F. above this point. To 100 ml. volumes of the alcohol, cooled by plunging into a freezing mixture bath, increments of the candidate inhibitors were added to determine whether at least one gram would dissolve at this temperature. The results are shown in Table 4.

TABLE 4

SOLUBILITY OF CANDIDATE INHIBITORS IN 20 VOLUME PERCENT AQUEOUS METHANOL AT 26°-30°F.

Code No.	Compound	Solubility in 100 ml. grams.
2517	Urea-Potassium nitrite	1.0
2511	Sodium benzoate	1.0
2570	Sodium nitrite - Oleic acid	Floating separation
2516	Catechol	1.0
2564	Naphthenic acids	Floating separation
2914	Piperidine	1.0
2551	Undecylenic acid	Very slightly soluble
2555	Proprietary	1.0
2512	Acetamide-Potassium nitrite	1.0
2544	Ammonium carbonate-Ammonium hydroxide	1.0
2550	Proprietary	0.75

Three of the candidate inhibitors did not dissolve sufficiently at this temperature and were set aside. The remaining eight were carried into further tests.

SURFACE TENSION STUDIES ON SURFACTANTS IN METHANOL SOLUTIONS

Corrosion inhibitors to be used in this application are also asked to provide a surface tension equal to or less than that obtained with 0.05% Triton X-100 in a 30% alcohol-water solution. Since the inhibitors of Table 4 would not meet this specification, compounding with a surfactant became necessary. A number of wetting agents were selected on the basis of the manufacturers' information that the materials were soluble in alcohol. These were examined for their surface activity in 20-30% by volume methyl alcohol. The data obtained are presented in Table 6 and the surfactants are identified in Table 7 (page 36).

From Table 6 it is seen that Aerosol OT at concentrations above 0.05% was the most effective surfactant in this methanol solution concentration range. This material was therefore selected at an early stage for corrosion studies in mixtures with the candidate inhibitors which passed the low temperature solubility test. The amount of Aerosol OT was varied in order to observe the surface tension effects of the mixture when dissolved in 20% by volume methanol. The results of these studies are presented in Table 5.

TABLE 5

SURFACE TENSION OF 1% SOLUTIONS OF CANDIDATE INHIBITORS IN 20 VOLUME PERCENT METHANOL

Determinations by duNouy Tensiometer
at 77°F.

		Surface Tension, Dynes per Cm.				
		Weight Percent Aerosol OT				
Code No.	Inhibitor	0	0.01	0.05	0.10	0.20
----	None	53.0	35.1	30.4	23.8	24.9
2511	Sodium benzoate	49.6	32.9	25.0	23.8	24.8
2512	Acetamide-Potassium nitrite	50.1	31.6	24.3	24.4	24.5
2516	Catechol	45.5	34.0	27.4	23.5	25.4
2517	Urea-Potassium nitrite	50.9	31.2	24.0	25.1	24.3
2544	Ammonium Carbonate-Ammonium hydroxide	50.0	33.0	25.6	24.6	24.6
2550	Proprietary	40.2	31.9	32.4	32.5	32.4
2555	Proprietary	36.2	36.2	36.1	35.7	34.5
2914	Piperidine	41.2	35.5	29.6	27.1	27.1

TABLE 6

SURFACE TENSION OF SURFACTANT-METHANOL SOLUTIONS

Determination by duNouy Tensiometer at 77°F.

Surfactant	Weight Percent	Methanol Volume Percent	Dynes per Cm.
None	--	20	53.0
	--	25	47.0
	--	30	47.5
	--	60	33.0
Advawet 10	0.01	25	38.7
	0.05	25	30.8
	0.10	25	31.4
Aerosol OT	0.01	20,30	35.0,31.6
	0.05	20,30	27.4,27.7
	0.10	20,30	24.0,25.6
	0.20	20,25	25.0,24.8
	0.25	60	32.0
Alrosol B	0.01	25	28.7
	0.05	25	28.5
	0.10(a)(b)	25	28.3
Dergon OM	0.01	25	28.0
	0.05	25	27.5
	0.10	25	28.0
Igepal CA	0.01	25	30.7
	0.05	25	28.8
	0.10	25	29.5
Ninol 737	0.01	25	27.7
	0.05(a)	25	27.5
	0.10(b)	25	27.3
Ninol 1281	0.01	25	27.5
	0.05(a)(b)	25	27.0
	0.10(b)	25	29.0
Nonic 218	0.01	25	41.3
	0.05	25	33.3
	0.10	25	29.0
	0.20	25	29.3

TABLE 6 - (continued)

Surfactant	Weight Percent	Methanol Volume Percent	Dynes per Cm.
Oronite N1-8586	0.01	25	31.4
	0.05	25	31.0
	0.10	25	30.9
Pluronic L62	0.01	30	40.0
	0.10	30	36.8
	0.25	30	35.6
	0.01	60	32.7
	0.25	60	33.1
Quasol 95	0.01	25	30.9
	0.05	25	27.6
	0.10	25	28.0
Synthetics B-79	0.01	25	32.2
	0.05	25	30.6
	0.10	25	31.2
Triton X-100	0.01	20,30	29.0,26.5
	0.05	20,30	28.2,28.0
	0.10	20,30	30.0,30.0
	0.25	60	33.0
Tween 85	0.01	30	37.3
	0.05	30	34.5
	0.10	30	33.6
	0.25	30	33.6
Victawet 12	0.01	25	29.0
	0.05	25	27.4
	0.10(a)	25	26.8

(a) Became cloudy above this concentration.

(b) Foamed excessively at this concentration.

TABLE 7

IDENTIFICATION OF SURFACTANTS STUDIED

Advawet 10	Advance Solvents and Chemical Corporation	Alkylaryl polyether alcohol
Aerosol OT	American Cyanamid Company	Dioctyl ester of sodium sulfosuccinic acid
Alrosol B	Alrose Chemical Company	Fatty alkylol amide condensate
Dergon OM	Arkansas Company	Amino fatty acid ester
Igepal CA	Antara Division, General Aniline and Film Corporation	Alkyl phenoxy polyoxyethylene ethanol
Ninol 737	Ninol Laboratories	A fatty acid alkanolamide
Ninol 1281	Ninol Laboratories	A fatty acid alkanolamide
Nonic 218	Sharples Chemicals, Incorporated	Polyethylene glycol tertdodecylethioether
Oronite Nl-8586	Oronite Chemical Company	Alkylaryl sulfonate
Pluronic L62	Wyandotte Chemicals Corporation	Polyoxyethylene-polyoxypropylene block polymer.
Quasol 95	Quaker Chemical Products Company	
Synthetics B-79	Hercules Powder Company	An ethylene oxide condensate of an alkylated phenol
Triton-X-100	Rohm and Haas Company.	Alkylaryl polyether alcohol
Tween 85	Atlas Powder Company	Polyoxyethylene sorbitan trioleate
Victawet 12	Victor Chemical Works	Alkyl triester phosphate

Proprietaries No. 2550 and No. 2555 produced relatively low surface tensions in their own right when dissolved in 20% by volume methanol. However, they were found to be less susceptible to a decrease in surface tension by increasing concentrations of Aerosol OT than the other selected inhibitors. The surface tension of the alcohol systems containing the other six candidate inhibitors appearing in Table 5 was readily decreased by increments of Aerosol OT. These latter materials except piperidine were taken into accelerated corrosion tests. Piperidine was omitted because on standing a flocculent separation was observed.

ACCELERATED SURVEY CORROSION STUDIES WITH INHIBITOR-SURFACTANT FORMULATIONS

Since the two proprietaries in Table 5 appeared to be less subject to lowering of the surface tension by the addition of Aerosol OT, and since the piperidine system proved to be unstable, these candidate inhibitors were dropped from consideration and the remaining five taken into a corrosion study by the accelerated method described in the section on experimental procedures. The reliability tests also presented there indicated that mild steel specimens would yield more indicative results than those from aluminum and that the 20-hour exposure period would give useful indications.

The five candidate inhibitors were dissolved in 20% by volume methanol containing 0.07% Aerosol OT. Because of the limitations on the amount of non-combustible solids only this minimum which would yield a surface tension value comparable with that established for 0.05% Triton X-100 was used. The results of these corrosion studies are shown in Table 8.

TABLE 8

CORROSION STUDIES ON CANDIDATE INHIBITORS IN 20 VOLUME PERCENT METHANOL SOLUTIONS

Test Conditions

Each inhibited solution contained 0.07 weight percent Aerosol OT. SAE 1010 mild steel coupons sandblasted and exposed 20 hours at 136° ± 1°F. under continuous aeration. Data below are weight losses per coupon in milligrams. Uninhibited control specimens showed a weight loss of 44.4 mg. and 41.4 mg. in the liquid and vapor phases respectively (average of 3 replicates).

Inhibitor, Weight Percent	Acetamide-Pot. Nitrite (a)		Amm. Carbonate-Amm. Hydroxide(a)		Sodium Benzoate		Urea Pot.Nitrite(a)		Catechol	
	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase
1.00	0	0.7	0	0.3	0	1.0	0.3	2.0	87.4(b)	1.2
0.50	--	--	--	--	0.7	5.2	--	--	--	--
0.10	0	1.5	21.1	4.8	0	2.8	0.3	3.7	38.3	3.1
0.075	1.7	9.7	--	--	1.6	4.7	2.3	9.4	--	--
0.05	32.4	8.5	--	--	33.0	13.0	30.9	19.1	--	--
0.025	32.5	14.5	--	--	55.3(b)	12.9	28.0	54.5(b)	--	--
0.01	33.3	3.6	41.6	8.7	23.9	1.0	30.5	2.4	37.8	1.1
0.001	31.6	5.1	39.1	18.8	38.0	18.1	32.7	13.5	148.1(b)	4.4

(a) Equal part mixtures.

(b) Isolated data suggest that inhibitor may cause accelerated corrosion under some conditions.

The data in Table 8 suggested that the best three of the five inhibitors studied were sodium benzoate, equal part mixtures of acetamide and potassium nitrite and equal part mixtures of urea and potassium nitrite. Catechol was quite ineffective in the liquid phase. The result suggested that this material was actually corrosive toward mild steel. It is believed that this effect was due to the accelerated conditions of the test, namely the temperature of 136° ± 1°F. and the constant aeration of the alcohol solution. The ammonium carbonate-ammonium hydroxide combination was also relatively ineffective in the liquid phase at the 0.1 weight per cent concentration.

STUDIES ON PROMISING INHIBITOR SYSTEMS

The eleven most promising candidate inhibitors appearing in Table 3 had been narrowed to three. At this point these three materials were explored in detail in respect to the remaining target specifications.

Surface Tension Evaluations.

Hitherto, only 20, 25 and 30% methanol solutions had been studied. The next step was the evaluation of the effect of varying amounts of inhibitors on the surface tension, particularly in higher methanol concentration solutions. This phase of the program was developed around the three most promising candidate inhibitors as presented above. Table 9 shows the results of these studies.

It is apparent from these data that the surface tension of methanol through the middle range of concentrations is not effectively reduced by Aerosol OT. Increasing the amount of inhibitor had little or no influence on the surface tension of the middle and high methanol concentration range. In the lower to middle range, increasing the inhibitor concentrations of sodium benzoate tended to reduce surface tension slightly, but little or none for the other two systems. It was also seen in Table 6 that Triton X-100 was no more effective at the higher methanol concentrations than Aerosol OT. It became apparent about this time that the need for the low surface tension in the medium range alcohol solutions might not be required. It was learned through conferences at WADC that the surface activity target specification was intended for the thrust augmentation system to be used in J-47 turbojet engines for which about 26-27% alcohol solutions are specified. In reciprocating engines employing 50% alcohol the low surface tension requirement is not essential. This thinking made it unnecessary to continue the attempt to lower the surface tension in middle-range concentration alcohols. Aerosol OT, Triton X-100 and still other surfactants (See Table 6) showed promise of meeting the surface tension requirements for the lower concentration alcohol solutions.

TABLE 9

SURFACE TENSION OF METHANOL SOLUTIONS CONTAINING INHIBITORS AND AEROSOL OT

Determinations by duNouy Tensiometer at 77°F.

Aerosol OT, Weight Percent	Inhibitor, Weight Percent	Surface Tension, Dynes per Cm. Methanol, Volume Percent						
		20	30	40	50	60	70	100
		Inhibitor-Sodium Benzoate						
0	1.00	49.6	43.0	39.0	35.5	33.0	30.5	21.1
	0.50	48.5	42.5	38.0	35.5	33.0	30.5	21.2
	0.10	50.0	44.0	39.5	35.5	33.0	30.0	--
	0.00	53.0	47.5					
0.05	1.00	25.0	29.0	33.0	35.0	33.0	30.5	21.3
	0.50	27.0	25.5	34.5	35.0	33.0	30.5	21.5
	0.10	27.0	31.0	35.0	35.0	33.0	30.0	--
	0.00	27.4	27.7					
0.09	1.00	24.0	25.5	31.5	34.0	33.0	30.5	21.0
	0.50	25.0	26.5	32.0	34.0	33.0	30.5	21.1
	0.10	25.5	28.5	33.0	35.0	33.0	30.0	--
	0.00	24.5	26.0					
0.13	1.00	24.0	25.0	30.0	32.0	32.5	30.5	21.2
	0.50	25.0	25.5	30.0	33.0	32.5	30.0	21.1
	0.10	25.5	26.5	31.0	35.0	33.0	30.0	--
	0.00	24.0	24.0					
0.25	1.00	--	--	27.0	30.0	32.5	30.5	--
	0.50	--	--	28.0	31.7	32.5	30.5	21.3
	0.10	--	26.0	29.5	33.5	32.5	30.0	--
	0.00	25.0						

TABLE 9 - (continued)

Aerosol OT, Weight Percent	Inhibitor, Weight Percent	Surface Tension, Dynes per Cm.		
		Methanol, Volume Percent		
		20	45	70
		Inhibitor-Equal Parts Urea and Potassium Nitrite		
0	1.00	50.9	38.2	30.8
	0.50	51.1	38.1	31.5
	0.10	50.9	38.2	31.5
0.05	1.00	24.0	32.9	30.7
	0.50	25.3	34.8	30.4
	0.10	26.4	35.8	30.3
0.09	1.00	24.8	30.3	30.6
	0.50	25.0	32.7	30.7
	0.10	25.1	33.7	31.4
0.15	1.00	24.8	28.9	30.6
	0.50	24.8	30.8	30.5
	0.10	25.0	32.5	30.3
0.25	1.00	24.8	27.2	30.5
	0.50	25.1	29.0	30.4
	0.10	24.3	30.6	30.6
		Inhibitor-Equal Parts Acetamide and Potassium Nitrite		
0	1.00	50.9	38.1	30.9
	0.50	50.8	37.0	30.5
	0.10	51.0	38.0	30.8
0.05	1.00	25.1	34.4	30.8
	0.50	26.1	33.3	30.4
	0.10	25.6	35.1	30.8
0.15	1.00	25.1	29.1	30.6
	0.50	25.0	30.3	30.6
	0.10	24.5	34.1	30.9
0.25	1.00	25.0	27.8	30.6
	0.50	25.4	28.6	30.5
	0.10	24.4	29.9	30.8

Accelerated Corrosion Tests.

Corrosion studies conducted to this point had been designed to screen out the less effective candidate inhibitors. The three most promising inhibitors were next taken into a more elaborate accelerated corrosion study as described in the section above on evaluation techniques. The results of these tests appear in Table 10. Ethanol was included in the test program for the first time.

Table 10 shows that in the absence of inhibitor, steel is far more subject to weight loss attack than the 2024-T3 aluminum alloy. At 100% by volume alcohol, however, very little corrosion with either metal was experienced. Generally, both vapor and liquid phase corrosion was largely inhibited by any of the three candidate inhibitors, with the exception of steel in the middle range concentrations of denatured ethanol containing sodium benzoate. The vapor phase corrosion of steel in 20% alcohol solutions might be further improved. The inhibitors have usually reduced the corrosion of the aluminum alloy in the liquid phase, but the effects in the vapor phase are not clearly defined. Increase in weight following exposure in the vapor phase is frequently seen.

Non-Combustible Solids.

The Air Force desired inhibitor systems which could be furnished and shipped in a concentrated form for addition to diluted or undiluted alcohol stocks. These will be referred to as inhibitor concentrates. They may comprise single or multiple inhibitors, usually in combination with surface active agents, and the combinations may be furnished in solid or liquid form, as for example dissolved in methanol.

The inhibited undiluted alcohol stocks subsequently would be diluted with water to meet the differing concentration requirements for jet and reciprocating engines and for different operating conditions. All the diluted alcohols must contain sufficient inhibitor concentrate to meet their corrosion protection requirements. The corrosivity problem normally becomes more difficult as dilution increases, hence the amount of inhibitor concentrate in the undiluted alcohol would be four times that fixed by the most dilute alcohol used, normally about 25%. In consequence higher concentrations of the alcohols would carry an excess of inhibitor concentrate, although the sodium benzoate-Aerosol OT system of Table 10 seems to be an exception.

Surfactants as well as the inhibitors might contribute solid residues. Exhibit A (page 1) required that the inhibited 50-50 water-alcohol mix should not carry over 100 ppm of non-combustible solid residues. Effective inhibition of corrosion of steel and aluminum has been accomplished by the three combinations of inhibitors and surfactants under specific conditions as shown in Table 10. Although it was recognized that these systems would not comply with the 100 ppm non-combustible solids limit other data were sought. Determinations of ignited solids residues appear in Table 11.

TABLE 10

STUDIES ON CORROSION INHIBITORS FOR WATER-ALCOHOL SYSTEMS

Test Conditions

Each solution contained 0.10 weight percent inhibitor and 0.07 weight percent Aerosol OT.

The SAE 1010 mild steel and 2024-T3 aluminum alloy coupons were hand polished with 240 grit aluminum oxide and exposed 72 hours at 136° ± 1°F. under continuous aeration.

Volume Percent Alcohol	Weight Loss, Mg.							
	O-M-232 Methanol				MIL-A-6091 Ethanol			
	1010 Steel		2024-T3 Al		1010 Steel		2024-T3 Al	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
Control - No Inhibitor or Aerosol OT								
20	86.6	158.0	4.6	1.1	91.9	138.0	8.4	0.5
45	72.7	78.8	1.3	0.8	93.8	41.4	1.4	0.9
70	0	0	0.6	0.5	34.8	7.5	0	1.1
100	0	0	0.8	0.3	0	0	0.2	0.9
Sodium Benzoate								
20	0	14.0	3.9	+0.4	0	5.7	3.2	0.1
45	0	0	0.7	1.2	58.3	39.8	0.3	+0.4
70	0	2.7	0.1	1.2	48.3	6.1	0.9	0.2
100	0	0	0.7	0.9	0	0	0.8	1.0
Equal Parts Acetamide-Potassium Nitrite								
20	0	22.1	3.7	0.1	0	17.8	0.2	+0.3
45	0	0	0.4	0.8	0	0	1.0	0
70	0	0	0.6	0.7	0	0	0.2	0
100	0	0	0.5	0.6	0	0	0.2	0.2
Equal Parts Urea-Potassium Nitrite								
20	0	15.8	4.2	+0.4	0	8.3	1.9	+1.4
45	0	0	0.5	1.6	0	0	0	+0.5
70	0	0	0.9	1.0	0	0	0.2	+0.4
100	0	0	0	0.4	0	0	0	+0.4

TABLE 11

NON-COMBUSTIBLE SOLIDS CALCULATIONS ON PROMISING INHIBITOR SYSTEMS

Ignited at 1000°C. to Constant Weight

Inhibitor Composition Weight Percent		Ratio(a)	Ash Determination, Weight Percent	Non-Combustible Solids Based On 50% Alcohol, ppm
Sodium benzoate	58.8	.10		
Aerosol OT	41.2	.07	19.9	677
Acetamide	29.4	.05		
Potassium nitrite	29.4	.05		
Aerosol OT	41.2	.07	25.4	866
Urea	29.4	.05		
Potassium nitrite	29.4	.05		
Aerosol OT	41.2	.07	19.7	670

(a) See Table 10

It is seen that the non-combustible solids residues calculated for a 50-50 alcohol-water mix are very high(1).

REDUCTION OF NON-COMBUSTIBLE SOLIDS IN PROMISING INHIBITOR SYSTEMS

The emphasis in this phase of the work was placed on (1) substituting a benzoic acid - amine combination for sodium benzoate, (2) the reduction of the relative amount of potassium nitrite in the systems with urea or acetamide, (3) complete replacement of potassium nitrite with an organic nitro compound and (4) search for a surfactant that in addition to fulfilling other requisites would contribute a minimum of non-combustible solids.

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(1) Were the actual requirements for corrosion protection in the 50-50 mix to be determined, the levels might very well be much lower and the problem of meeting the solids requirement less formidable. In any case the proper amount would have to be determined for each system. It might become possible in this way to utilize the effective potassium nitrite-urea or -acetamide inhibitor systems in a separate grade of booster fuel for reciprocating engines, should other advantages warrant this. Notwithstanding this possibility, all subsequent work was directed toward the reduction of non-combustible solids residues.

Substitute for Sodium Benzoate.

Although sodium benzoate had shown some promise as a water-alcohol inhibitor, the high non-combustible residue was undesirable. Combinations of benzoic acid with cyclohexylamine or dicyclohexylamine were tried at various molecular ratios, with and without 1-nitropropane, as possible substitutes for the sodium salt. These tests are shown in Table 12. Since these formulas carried 0.07% Aerosol OT which had been found to show 13.9% uncombustible solids this would contribute 700 x 0.139 = 92 ppm non-combustible residues. Since the other ingredients should contribute little or nothing to this total, all these formulas appear to meet requirements. Formulas 4, 5, 7 and 8 show the greater promise.

TABLE 12

PROTECTIVE EFFECT OF BENZOIC ACID-AMINE FORMULATIONS

Conditions: Solutions contained 0.1% inhibitor and 0.07% Aerosol OT in 25% methanol. Sandblasted SAE 1010 steel specimens exposed 20 hours at 136 ± 1°F. under continuous aeration.

	Inhibitor Composition, Weight Percent								
Component	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Benzoic Acid	57	40	40	10	25	40	10	25	40
Cyclohexylamine	43	60	--	50	50	50	--	--	--
Dicyclohexylamine	--	--	60	--	--	--	50	50	50
1-Nitropropane	--	--	--	40	25	10	40	25	10
Mol Ratio Amine/Acid	0.93	1.84	1.01	6.15	2.46	1.54	3.37	1.34	0.84
Wt. Loss, Mg.:									
Liquid phase	0.3	0.5	0.7	1.1	0	0	0	0	2.1
Vapor phase	21.2	6.9	24.4	1.7	2.4	3.4	1.2	2.2	6.5

In Formulas 1-9 (Table 12) the inhibitor is essentially a benzoate salt of an amine, with some excess or deficiency of amine in respect to the theoretical 1:1 ratio. The calculated ratios are shown for each formula. Good liquid phase protection has followed regardless of the ratio but vapor phase corrosion seems to depend on other factors. In the absence of nitropropane, corrosion was severe when the ratio of amine to acid was approximately 1:1 or less, representing presumably a neutral to acidic condition (Formulas 1 and 3). When the ratio was materially increased, vapor phase corrosion was reduced (Formula 2). Partial replacement of the amine by nitropropane, even at the expense of a reduced alkalinity and amine/acid ratio, materially reduced vapor phase corrosion in these systems, showing the value of this material (compare the formulas 2, 6, 5, 4 and 3, 9, 8, 7).

Reduction of Potassium Nitrite.

The inhibitor systems containing potassium nitrite with either urea or acetamide were modified by lowering the potassium nitrite and raising the organic inhibitor content. These were evaluated for corrosion protection in methanol systems through the range 25-100% by volume. The solutions were prepared by dilution of the specification methanol. For purposes of expediting the work, the shorter exposure period of 20 hours and use of sandblasted specimens were employed. The effect of this reduction of potassium nitrite in relation to corrosion inhibition is shown in Table 13.

The reduction of potassium nitrite through the range studied did not greatly influence either liquid or vapor phase protection against corrosion. Some improvement would be desirable in the 25% alcohol solutions. While modifications might be suggested which should improve both liquid and vapor phase protection and reduce non-combustible solids (which are still too high throughout Table 13) it was not practicable to carry this work further in the time available.

Replacement of Potassium Nitrite.

The use of the potassium nitrite salts stemmed from the earlier general screening program. As it became clear that the non-combustible solids residue specification probably could not be met by using this material, substitute organic nitro compounds were sought. In Table 14 data are shown on the comparative protection of steel in liquid and vapor phases by equal part mixtures of acetamide, urea or cyclohexylamine with selected organic nitrite salts and organic compounds containing the NO_2 group.

On the basis of the data presented in Table 14, it is evident that the dicyclohexylammonium nitrite when used with acetamide or urea was quite effective in the liquid phase but potassium nitrite was still the best in these combinations. For vapor phase protection of steel, 1-nitropropane used in conjunction with acetamide, urea or cyclohexylamine was especially effective. This work yielded a basis for the formulations evaluated in Table 15.

TABLE 13

EFFECT OF POTASSIUM NITRITE REDUCTION IN BINARY SYSTEMS WITH UREA OR ACETAMIDE

Conditions: Solutions contain 0.4% combined inhibitor and 0.1% Aerosol OT on 100% MeOH basis. Sandblasted SAE 1010 steel specimens exposed at 136 ± 1°F. for 20 hours under continuous aeration.

	Inhibitor Composition		Weight Loss per Specimen, Mg.							
			Methanol, Percent							
			25		50		70		100	
Inhibitor System	Organic %	KNO_2 %	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase
Urea - KNO_2	50	50	0.6	13.0	0	1.0	0	0.4	0	0
	66.7	33.3	5.3	14.1	0	0.5	0	1.0	0	0
	75	25	2.2	10.0	0.1	0.6	0	0.2	0	0
	80	20	4.3	14.6	0	0	0	0.3	0	0
Acetamide - KNO_2	50	50	0	26.0	0	0	0	0	0	0
	66.7	33.3	3.9	16.9	0	0.5	0	0	0	0.5
	75	25	6.3	19.4	0	2.8	0	0	0.3	0.7
	80	20	12.0	15.3	0.6	2.1	0.6	0.5	0.2	0.2

TABLE 14

PERFORMANCE OF ORGANIC NITRO COMPOUNDS VS. POTASSIUM NITRITE IN CORROSION INHIBITOR FORMULAS

Conditions: Solutions contained 0.1% concentration of equal part mixtures of nitro compound with acetamide, urea or cyclohexylamine, plus 0.07% Aerosol OT in 25% methanol. Sandblasted SAE 1010 steel specimens exposed at 136 ± 1°F. for 20 hours under continuous aeration.

	Weight Loss, Mg. per Specimen					
	Acetamide		Urea		Cyclohexylamine	
	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase
Potassium nitrite	1.1	28.0	2.6	15.0		
Diisopropylammonium nitrite	9.1	11.6	9.7	17.2		
Dicyclohexylammonium nitrite	2.8	16.0	4.6	19.4		
5-Nitrosalicylic acid	35.3	20.9	36.8	16.9		
1-Nitropropane	35.5	5.3	32.3	5.3	4.4	5.0
p-Nitrophenol	102.8	12.2	99.6	29.8		
m-Nitroaniline	18.1	16.5	17.4	20.7		

TABLE 15

PROTECTIVE EFFECT OF 1-NITROPROPANE FORMULATIONS

Conditions: Solutions contained 0.1% inhibitor and 0.07% Aerosol OT in 25% Methanol. Sandblasted SAE 1010 steel specimens exposed 20 hours at 136 ± 1°F. under continuous aeration.

Component	Inhibitor Compositions, Weight Percent										
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1-Nitropropane	75	75	10	20	10	20	10	20	10	20	45
Urea	25	--	40	40	40	40	--	--	--	--	--
Acetamide	--	25	--	--	--	--	40	40	40	40	--
Dicyclohexylammonium nitrite	--	--	50	40	--	--	50	40	--	--	55
Di-isopropylammonium nitrite	--	--	--	--	50	40	--	--	50	40	--
Wt. Loss, Mg.:											
Liquid phase	41.0	49.0	0.2	0	4.4	2.7	0	0	2.8	4.5	1.0
Vapor phase	2.1	1.9	3.0	1.0	5.9	3.7	2.2	3.0	2.7	5.2	3.5

The four formulas which showed the most promise are, in order, numbers 4, 7, 8, and 11. The vapor phase corrosion values are low and liquid phase values very low, and equal or better than obtained from previous potassium nitrite formulas. All contain nitropropane, from 10 to 45%. This appears to be essential for obtaining the low vapor phase corrosion losses since Table 14 indicates that neither of the ammonium nitrites when combined 50-50 with either urea or acetamide approached these low values. On the other hand urea or acetamide may not be essential to good results (Formula 11), and large amounts of nitropropane in combination with these failed completely to prevent liquid phase corrosion of steel.

Nonionic Surfactant Replacements for Aerosol OT.

Most of the formulas tested were made up with Aerosol OT since Table 6 had disclosed this to be the most effective surfactant. It had been indicated that the extremely low surface tension values obtainable with this agent in 25-30% alcohols would not be required. In order to reduce non-combustible residues further, five of the more effective surfactants were examined along with a reduced amount of Aerosol OT (0.03%) for their activity and compatibility in three promising inhibitor systems selected from Tables 12 and 15. Observations were made on stability at 23° and 140°F. Table 16

TABLE 16

SURFACTANT ACTIVITY AND COMPATIBILITY WITH CANDIDATE INHIBITORS IN 25 VOLUME PERCENT ALCOHOLS

Each solution contained 0.03 weight percent surfactant and 0.10 weight percent inhibitor. Storage period 65 hours.

	Methanol			Observations at End of Test (a),(b)			
	Surface Tension, Dynes/cm			Methanol		Ethanol	
Surfactant	Initial at 23°F	After Storage at 23°F.	After Storage at 140°F	23°F.	140°F.	23°F.	140°F.
Inhibitor: 10% Benzoic Acid, 50% Dicyclohexylamine, 40% Nitropropane							
Ninol 1281	27.2	27.0	27.0	S	s	Cd	C
Quasol 95	30.6	30.4	29.2	C	C	s	C
Dergon OM	27.7	28.1	28.2	s	s	S	C
Triton X-100	28.5	30.6	29.9	C	C	C	C
Victawet-12	28.1	27.3	28.4	C	C	C	C
Aerosol OT	28.4	28.7	28.6	Cd	Cd	Cd	Cd
Inhibitor: 40% Acetamide, 50% Dicyclohexylammonium nitrate, 10% Nitropropane.							
Ninol 1281	27.3	27.1	26.8	Cd	s	S	s
Quasol 95	31.6	28.8	32.1	s	C	C	C
Dergon OM	27.8	27.0	26.7	S	s	s	S
Triton X-100	28.9	29.2	29.4	C	C	C	C
Victawet-12	27.6	27.7	27.6	C	C	C	C
Aerosol OT	27.3	27.6	27.4	Cd	C	Cd	Cd
Inhibitor: 40% Urea, 40% Dicyclohexylammonium nitrite, 20% Nitropropane							
Ninol 1281	27.5	26.5	27.0	S	S	Cd	s
Quasol 95	31.8	28.2	31.7	C	C	s	C
Dergon OM	27.8	27.1	27.0	s	s	S	S
Triton X-100	28.0	29.4	29.2	C	C	C	C
Victawet-12	28.7	27.8	27.9	C	C	C	C
Aerosol OT	27.3	27.1	27.2	Cd	C	Cd	Cd

(a) C = clear, Cd = Cloudy, s = sediment, S = much sediment - after coming to room temperature.

(b) Undiluted alcohol solutions containing four times the above concentrations of inhibitor and surfactant all remained clear under similar conditions.

gives the results of these studies. The Aerosol OT formula is calculated to show about 42 ppm non-combustible solids, and the other formulas would be expected to show considerably less. From data on ash determinations of experimental formulas 7 and 8 of Table 12 and 4, 7 and 11 of Table 15 (to be presented in Table 17) the calculated non-combustible residues of inhibited 50-50 alcohol-water mixes should not exceed 10 ppm.

The selected candidate inhibitors showed very little effect on surface activity of 25% by volume methanol containing the surfactants. Although Quasol 95 was least efficient as a surfactant, poor compatibility was more generally the reason for rejection. The lower temperature caused more serious incompatibilities than the higher temperature. All the surfactants with the exception of two showed some degree of incompatibility at one temperature or the other in either methanol or ethanol. The two surfactants which seemed entirely compatible were Triton X-100 and Victawet 12. Inhibitor solutions with these surfactants remained clear in both alcohols at either temperature for the 65 hour test period. Victawet 12 was favored for its non-foaming characteristics. Although Aerosol OT was the most effective wetting agent in two of the three systems, it showed poorer compatibility with the candidate inhibitors.

CORROSION TESTS WITH SELECTED INHIBITOR SYSTEMS

As indicated in the section on experimental techniques, steel was the metal most indicative of the corrosion inhibition effects of experimental formulations. However, in order to comply with item five of Exhibit A, a more complete picture was required on the protection of aluminum and aluminum coupled with type 304 stainless steel. Further, the range of alcohols to be inhibited was to include use concentrations and undiluted methanol or denatured ethanol. Since the experimental inhibitors had been narrowed down to a few, it became appropriate to evaluate their effectiveness more completely. The weight loss data for the three types of metal specimens with the five most promising experimental inhibitors (Table 17) used in appropriate concentrations of either alcohol are presented in Table 18. Table 19 is a record of the visual observations made on the test specimen at the end of the 72-hour exposure period. Figures 6, 7 and 8 are photographs of the specimens after test.

TABLE 17

COMPOSITION OF SELECTED INHIBITOR CONCENTRATES

	Composition, Weight Percent				
	CR-2983-D	CR-2983-E	CR-2990-A1	CR-2990-A2	CR-2990-A3
Corresponding Earlier Formulation	No. 8 Table 12	No. 7 Table 12	No. 11 Table 15	No. 7 Table 15	No. 4 Table 15
1-Nitropropane	5.75	9.2	10.4	2.3	4.6
Dicyclclohexyl-ammonium nitrite	--	--	12.6	11.5	9.2
Acetamide	--	--	--	9.2	--
Urea	--	--	--	--	9.2
Dicyclohexylamine	11.5	11.5	--	--	--
Benzoic acid	5.75	2.3	--	--	--
Victawet 12	7.0	7.0	7.0	7.0	7.0
Methanol	70.0	70.0	70.0	70.0	70.0
Ash determination, weight percent	0.18	0.23	0.31	0.25	0.19

TABLE 18

WEIGHT LOSS DETERMINATIONS ON TEST SPECIMENS IN INHIBITED WATER-ALCOHOL SOLUTIONS

Hand polished specimens exposed 72 hours at 136 ± 1°F. with continuous aeration.

		Weight Loss Per Specimen, Mg.									
		SAE 1010 Steel				2024-T3 Aluminum				Coupled 2024-T3 Al(a)	
		Methanol		Ethanol		Methanol		Ethanol		Methanol	Ethanol
Inhibitor Concentrate	Alcohol, Volume Percent	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Liquid Phase
Control	25	51.8	104.4	96.1	73.2	6.4	+0.9	5.5	+3.2	2.4	3.1
MIL-C-4339(b)	25	0.5	0	0	13.3	0.1	0.3	0.2	0	0.8	1.0
	50	0	0	0	0	0.3	0.5	0.5	0	0.8	0.6
CR-2990-A1(c)	25	0	0	0	2.6	2.4	0.9	2.3	+2.1	0.5	+1.1
	50	0	0	0	0	0.9	0.2	0.5	+0.2	0.5	+2.9
	Undil.	0	0	0	0	0.5	0.5	0.5	0.7	0.2	+0.3
CR-2990-A2(c)	25	0	0	0	0	0.9	+2.0	2.3	+2.1	1.4	0.7
	50	0	0	0	0	0.1	0.6	0.6	+0.8	0.1	+0.8
	Undil.	0	0	0	0	+0.2	+0.4	0.5	0.5	0	0.2
CR-2990-A3(c)	25	0	0	0	0	2.0	+0.9	2.0	+3.4	0.5	1.9
	50	0	0	0	0	0	0	+0.3	+0.3	0	+0.4
	Undil.	0	0	0	0	0.2	0	0.3	0.7	0.5	0.2
CR-2983-D	25	95.4	5.0	119.0	30.8	2.6	+1.4	4.9	+1.3	3.1	2.6
	50	0	0	163.9	3.2	0.1	0	0.8	+0.3	1.0	0.8
	Undil.	0	0	0	0	0.7	0.4	0.1	+0.1	+0.2	+0.2
CR-2983-E	25	28.5	0	54.7	7.3	4.2	+2.3	2.4	+3.0	2.6	2.7
	50	0	0	20.7	0	0.5	+1.1	0.6	+0.8	0	0
	Undil.	0	0	0	0	0.5	1.0	0.1	0.4	+0.1	+0.3

(a) No significant weight loss occurred to the 304 stainless steel member of the coupled specimens. Weight loss or gain (+) shown by the aluminum alloy.

(b) Solutions made up by diluting 0.5 ml. to 100 ml. by water.

(c) 1.77 g. Inhibitor Concentrate (CR-2990-A1, -A2, or -A3 -- approximately 2.04 ml) added to 100 ml of specification alcohol to produce an undiluted inhibited alcohol. 25 and 50 volume percent alcohols prepared by diluting 25 or 50 volumes of inhibited undiluted alcohol to 100 volumes with water.

TABLE 19

VISUAL OBSERVATIONS ON SPECIMENS FROM TESTS SHOWN IN TABLE 18

		SAE 1010 Steel				2024-T3 Aluminum				Coupled 2024-T3 Al(2)	
		Methanol		Ethanol		Methanol		Ethanol		Methanol	Ethanol
Inhibitor	Alcohol, Volume Percent	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase	Liquid Phase
Control	25	C(1)	CP	C	CP	TP(1)	T	T	t	T	TP
MIL-C-4339	25	c	c	nc	cp	nc	t	nc	t	nc	nc
	50	nc	c	nc	c	nc	nc	nc	t	nc	nc
CR-2990-A1	25	nc	nc	c	nc	T	t	T	t	T	T
	50	nc	nc	c	nc	nc	t	t	t	t	t
	Undil.	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
CR-2990-A2	25	nc	c	nc	nc	nc	t	T	t	T	T
	50	nc	nc	nc	nc	nc	t	T	t	t	t
	Undil.	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
CR-2990-A3	25	nc	nc	nc	nc	T	t	T	t	T	T
	50	nc	nc	nc	nc	T	t	t	t	T	T
	Undil.	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
CR-2983-D	25	C	c	C	cp	T	T	T	T	T	T
	50	nc	nc	C	cp	t	T	T	T	tp	T
	Undil.	nc	nc	c	nc	nc	nc	nc	nc	nc	nc
CR-2983-E	25	C	c	C	CP	T	t	T	t	Tp	Tp
	50	nc	nc	C	nc	t	T	t	t	T	t
	Undil.	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc

(1) Key: T = Tarnish C = Corrosion P = Pitting nc = No change
t = Slight tarnish c = Slight corrosion p = Slight pitting

(2) The observations are recorded for the outside surfaces of the coupled aluminum specimens (see Fig. 8). The inside surfaces showed a similar but less uniform effect. No change to the surfaces of the stainless steel member of the couple was discernable.

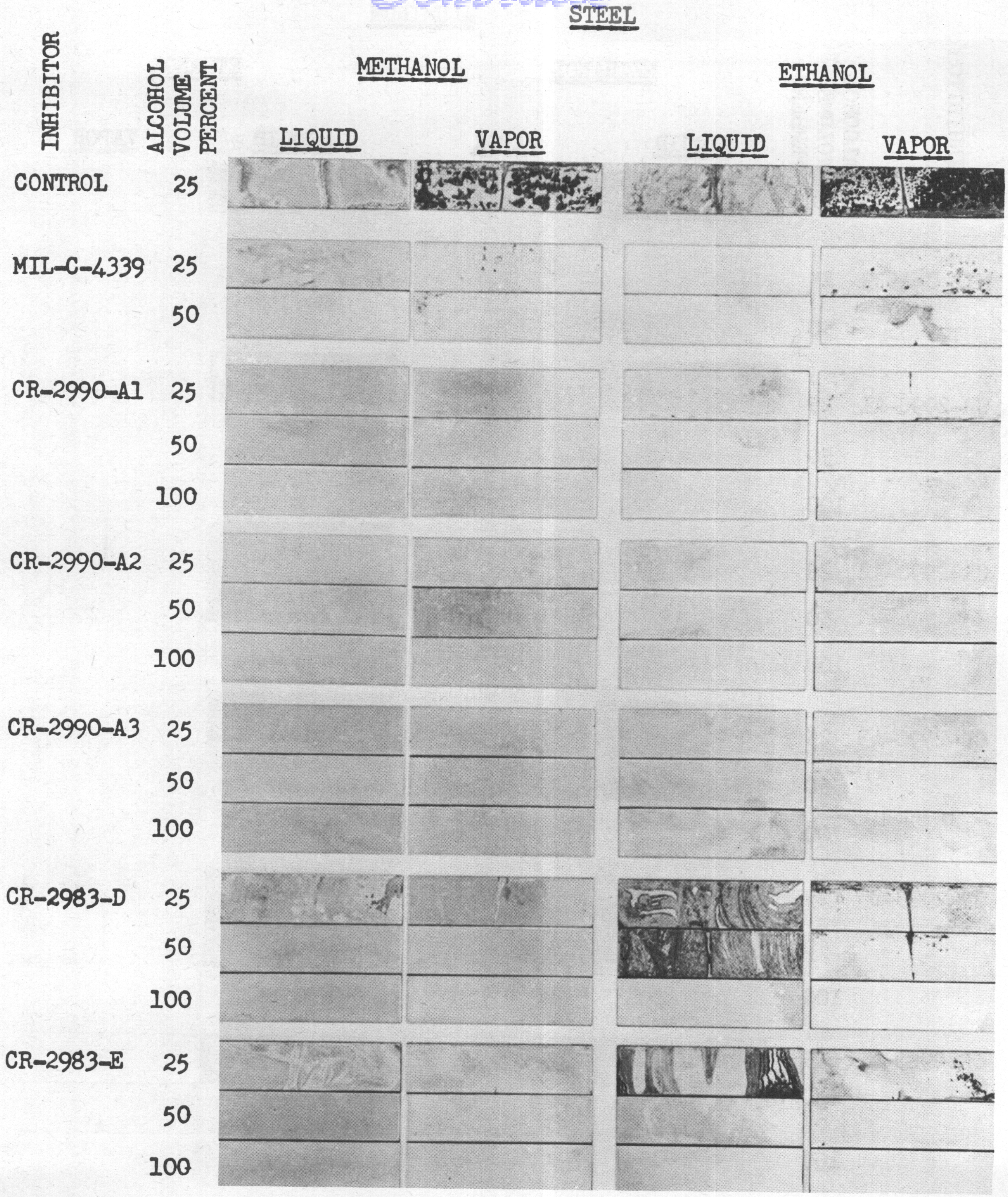

Fig. 6. Steel specimens used in tests described in tables 18 and 19.

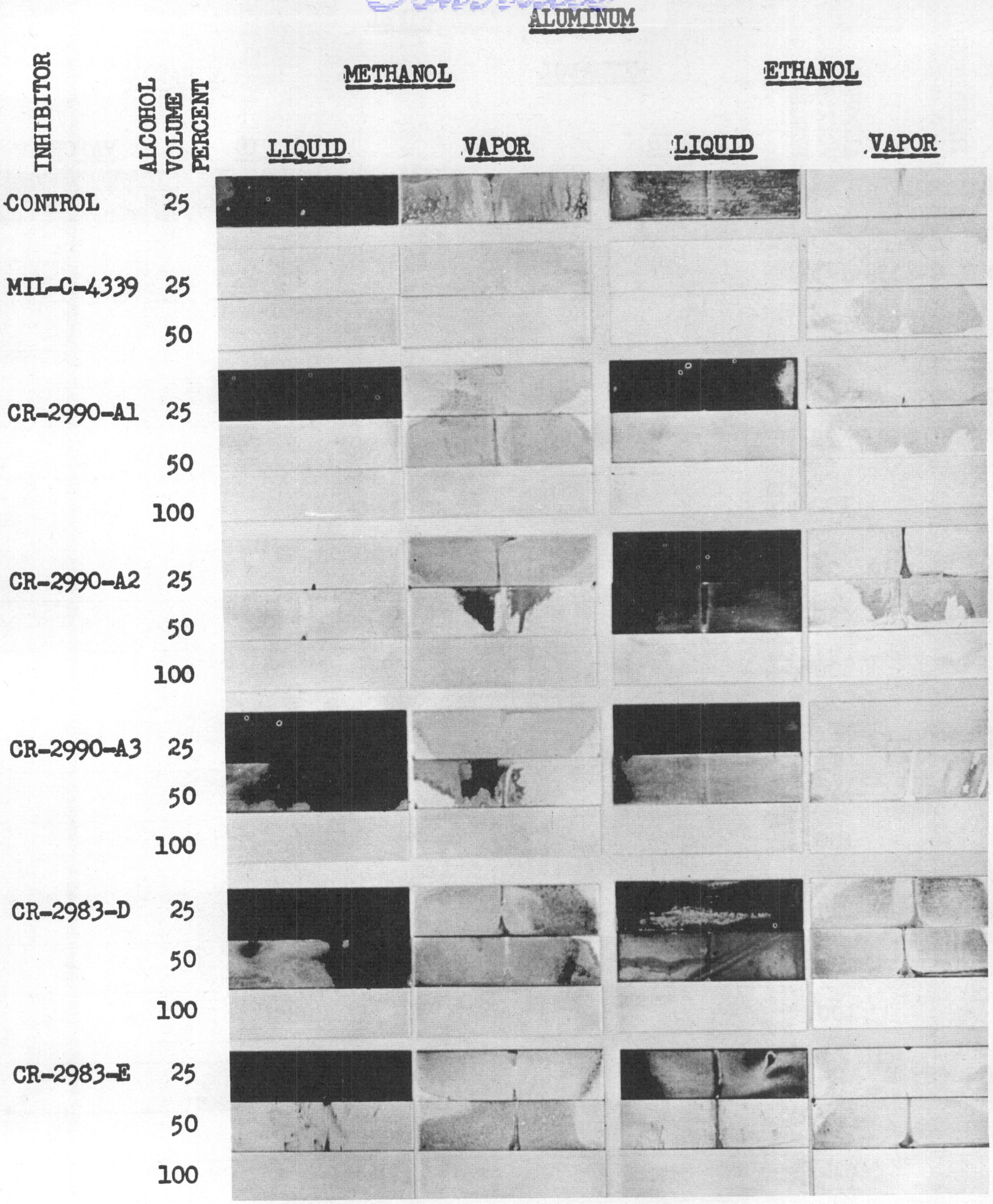

Fig. 7. Aluminum specimens used in tests described in tables 18 and 19.

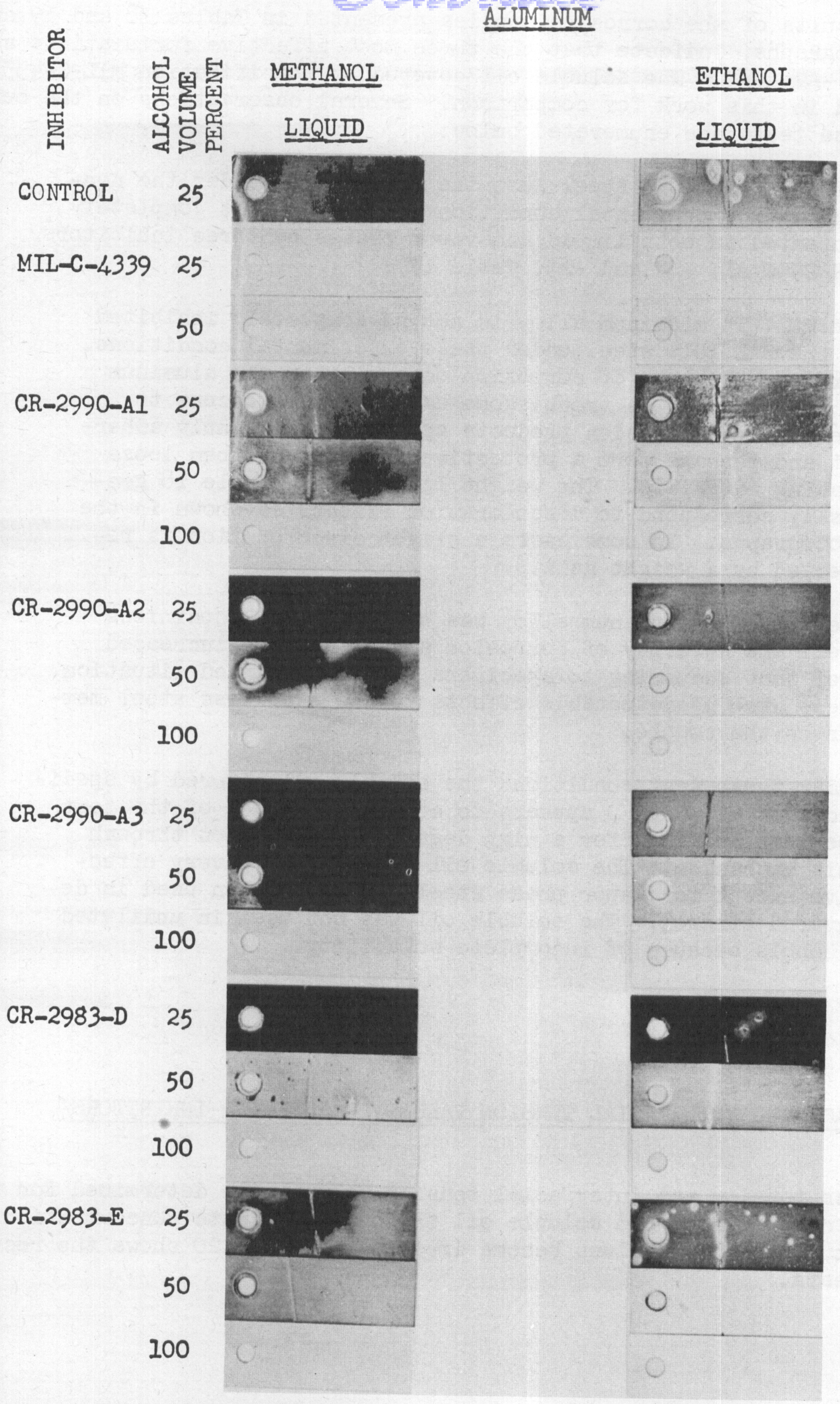

Fig. 8. Coupled aluminum specimens used in tests described in tables 18 and 19.

The results of the corrosion studies presented in Tables 18 and 19 and in the photographs, indicate that the three most effective formulations are CR-2990-A1, -A2, -A3. The soluble oil covered by specification MIL-C-4339 was included in this work for comparison. Several observations on the outcome of these tests are enumerated below:

1. Although SAE 1010 steel lost the most weight under the non-inhibited experimental conditions, it was almost completely protected in both liquid and vapor phases by three inhibitors (CR-2990-A1, -A2 and -A3, Table 17).

2. The 2024-T3 aluminum alloy is not as completely inhibited as the SAE 1010 steel under these experimental conditions. However, the type of corrosion occurring to the aluminum is probably not as troublesome as that which occurs to steel. The corrosion products appear to be tightly adherent and perhaps form a protective film rather than loose flaking materials. The weight loss data of Table 18 generally correspond to discoloration effects as shown in the photographs. In some cases a slight discoloration is reflected by a weight gain.

3. When 2024-T3 aluminum alloy was coupled to 304 stainless steel the severity of corrosion attack was not increased over that occurring to specimens in the uncoupled situation. There were no detectable effects to the stainless steel member of the couple.

4. Under these test conditions the soluble oil covered by specification MIL-C-4339 appears to coat the surface of the test specimen and to offer a high degree of protection through this mechanism. The soluble oil appears to be very effective except for vapor phase steel corrosion when used in denatured ethanol. The soluble oil was not used in undiluted alcohols because of incomplete solubility.

SURFACE AND INTERFACIAL TENSION VALUES OF SELECTED INHIBITORS

Surface tension and interfacial tension values were determined for the best three compositions and soluble oil in the approximate concentration of alcohols at which these values become important. Table 20 shows the results of these tests.

TABLE 20

SURFACE AND INTERFACIAL TENSION OF INHIBITED 25% BY VOLUME ALCOHOLS

Solutions contain 0.5 parts inhibitor per 100 parts 25% alcohol by volume.

Determinations by duNouy Tensiometer

	Dynes per Cm at 77°F.(b)			
	Surface Tension		Interfacial Tension (a)	
Inhibitor Concentrate	Methanol	Ethanol	Methanol	Ethanol
MIL-C-4339	30.5	30.7	1.4	1.4
CR-2990-A1	27.6	27.8	9.0	8.7
CR-2990-A2	27.7	27.3	9.1	8.6
CR-2990-A3	27.7	27.5	9.4	8.8

(a) Interfacial tension against Nujol.

(b) Triton X-100 at 0.05% in 30% methanol-water solutions shows surface and interfacial tension values of 28.0 and 4.9 respectively. These are the target values.

Recent conferences with military personnel of WADC have cast some doubt on the need for very low surface tension in a water-alcohol thrust augmentation system. Nonetheless it was recommended that a low surface tension value be maintained if possible. The three experimental formulations meet the specification. The interfacial tension values of these solutions however do not meet the 0.05% Triton X-100 in 30 volume percent alcohol requirement. The consequence of failure to meet this specification is unknown to the writer. On the other hand the soluble oil meets the interfacial tension and fails the surface tension requirements.

COMPATIBILITY OF INHIBITORS WITH HARD WATERS

Since it was known that the Air Force has encountered difficulty with hard waters when using the MIL-C-4339 soluble oil as a corrosion inhibitor in alcohol-water systems, the compatibility of experimental inhibitor concentrates in methanol diluted with hard water was checked. The experimental work conducted previously used dilutions made by 6-7 gr. Wyandotte city tap water. The three inhibitors were prepared in solutions containing 25 volume percent O-M-232 methanol and MIL-A-6091 denatured ethanol and 75 volume percent of 10, 30 and 50 grain artificial hard water according to specification USN (BuShips) 51-1-19. This formula calls for calcium and magnesium chlorides but no carbonates. The solutions were allowed to stand at room temperature for 15 days. The results of these tests are shown in Table 21:

TABLE 21

STABILITY OF 25% METHANOL SOLUTIONS DILUTED FROM INHIBITED METHANOL BY HARD WATERS

Conditions: 15 Days at Room Temperature.

Inhibitor Concentrate	All Permanent Hardness, Grains/Gal.		
	10	30	50
MIL-C-4339	40% (a)	90% (a)	100% (a)
CR-2990-A1	None (b)	None	None
CR-2990-A2	None	None	None
CR-2990-A3	None	None	None

(a) MIL-C-4339 soluble oil contains 85% oil. All of it (100%) appeared to have separated following dilution with 50 gr. water, and lesser proportions with the other waters.

(b) All CR-2990 inhibited solutions clear. Very small amounts of fine crystalline sediment noticed in each case, independent of water hardness.

A very small amount of sediment developed but was judged to be of little consequence in the use of these solutions as fuel boosters. The soluble oil was studied in parallel. Definite separation of the oil from the water-alcohol mixtures was observed to be proportional to the hardness of the water used in the solution. At the end of 15 days it was estimated that complete separation had occurred with the 50 grain water, about 90% separation in 30 grain water and about 40% separation in a 10 grain water.

FOAMING CHARACTERISTICS OF INHIBITORS

The CR-2990 inhibitor concentrates contain an amount of surfactant to produce a minimum surface and interfacial tension when used in alcohols diluted to the 20-30% by volume level. Previous work disclosed that the choice of surfactants of those investigated was restricted to Triton X-100 and Victawet 12 on the basis of effectiveness and compatibility. The latter was selected for formulation because of the far lower level of foaming it induced, particularly in diluted alcohols. Although no specific foaming tests were conducted, observations of relative foaming were readily available from the reflux type corrosion test runs during which compressed air was continuously distributed through the solution by fritted tubes. Foaming was practically non-existent in diluted alcohol solutions containing the CR-2990 inhibitors. Minor foam on the surfaces of aerated solutions dissipated instantly.

INHIBITOR CONCENTRATE SAMPLES CR-2990-A1, -A2, AND -A3 FOR WADC

It was hoped initially that stable concentrates of the ingredients of the CR-2990 formulas could be prepared so that the addition of one volume to 99 volumes of the undiluted alcohols would be sufficient. Although the ingredients could be gotten into solution at room temperature, difficulty reversible solids separation occurred on slight cooling. The maximum concentration which appears at all practical is 30% ingredients dissolved in 70% by weight undiluted methanol. Such solutions have remained stable and clear at room temperature for many weeks and are believed to remain stable at temperatures down to 32°F. and perhaps lower. No investigation of the addition of a few percent water has been made as an aid to increasing solubility. Further studies are obviously desirable.

The approximate densities of the Inhibitor Concentrates as obtained by weighing 500 ml. volumes in graduated cylinders in air, without corrections, are:

	Apparent Density	Apparent Lbs./Gal.
CR-2990-A1	0.860	7.18
CR-2990-A2	0.862	7.20
CR-2990-A3	0.878	7.33

The amounts of any of these concentrates at present suggested to be used are as follows:

17.7 g. or 20.4 ml./liter of undiluted alcohol

147.5 lb. or 20.4 gal./1000 gal. of undiluted alcohol

Addition to undiluted alcohol followed by water dilution may prove more satisfactory than addition of the concentrates to diluted alcohols. Safety precautions in handling the concentrates similar to those for undiluted methanol are suggested. Exposure to temperatures below 32°F. are not advised under present knowledge. Should this occur the stocks should be examined for any non-homogeneity and reconstituted by warming by steam coils or warm storage and thorough mixing.

STABILITY OF INHIBITOR SYSTEMS IN METHANOL AND ETHANOL

Figures 9 and 10 outline the stability requirements according to item 3 of Exhibit A, and Table 22 presents the fundamental data upon which these requirements are based. The points designated by "+" represents the compositions of systems made up and tested at the temperatures indicated. The upper limits were in general 160°F. (which is more than 10° below the boiling point range for most of the water-alcohol compositions) and the lower limits were 10° above the freezing point of the corresponding systems, or -65°F., whichever is the higher. The tests were made by preparing the water-alcohol systems at ambient temperature, lowering the temperatures as indicated and adding the recommended amounts of Inhibitor Concentrates (see Table 17). In all cases the materials went into clear solution without evidence of phase separation, turbidity or instability. However, when several times the recommended amounts of the materials were added to the more dilute alcohol systems at near freezing temperatures cloudiness resulted. When inhibited undiluted alcohols were diluted to use concentrations, no turbidity or cloudiness was

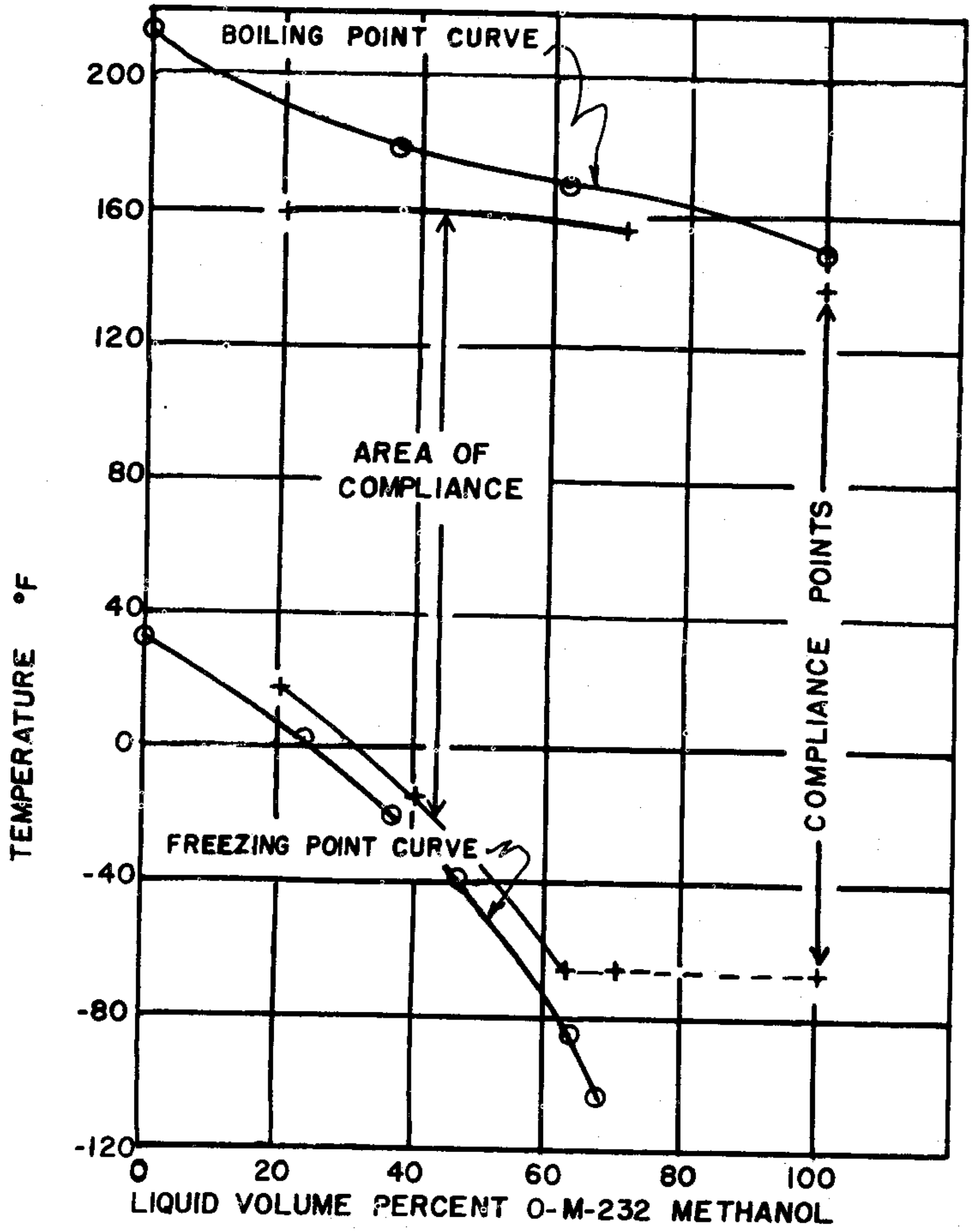

FIG.9. COMPLIANCE OF INHIBITOR CONCENTRATES WITH O-M-232 METHANOL SOLUBILITY REQUIREMENTS OF EXHIBIT A

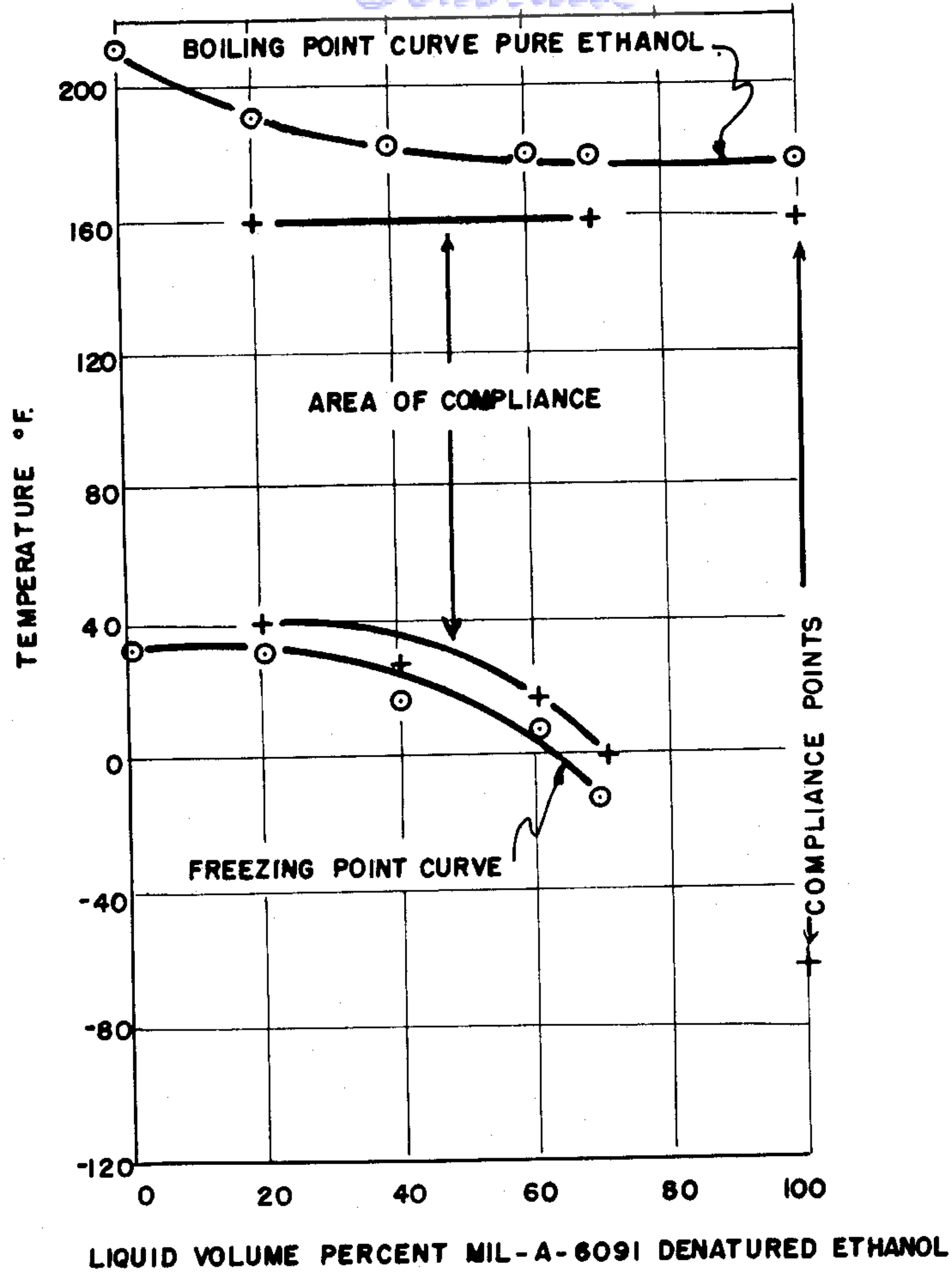

FIG. 10. COMPLIANCE OF INHIBITOR CONCENTRATE WITH MIL-A-6091 DENATURED ETHANOL SOLUBILITY REQUIREMENTS OF EXHIBIT A

TABLE 22

FREEZING AND BOILING POINT DATA FOR ALCOHOL SOLUTIONS

Methyl Alcohol				Ethyl Alcohol		MIL-A-6091 Denatured Ethanol
Mol % (MP) Weight % (WP) (a)	Volume %, (b)	F.P. °F.	B.P. °F.(a)	Volume, %	B.P. °F.(c)	Determined: F.P., °F.
0	0	32 (a)	212	0	212	32
20 WP	24.3	3 (a)	--	20	191	-30
20 WP	36.9	-20 (b)	180	40	183	-14
40 WP	47.1	-38 (a)	--	60	179	- 5
40 MP	62.0	-85 (b)	167	70	177	-13
60 WP	67.7	-103 (a)	--	100	173	< -65
100 WP	100.0	--	149			

(a) The Technology of Solvents and Plasticizers, Arthur K. Doolittle, John Wiley & Sons, Inc. (1954).

(b) Calculated.

(c) Handbook of Chemistry and Physics, Chemical Rubber Publishing Co.

observed. The amounts of inhibitor ingredients used corresponded to 0.4 weight percent not including surfactants, on the undiluted alcohol basis, or to 20.4 volumes approximately of any one of the CR-2990 formulas to 1000 volumes undiluted methanol or ethanol.

Solutions of 25% inhibited methanol and denatured ethanol have stood with perfect clarity for many weeks at room temperatures.

The soluble oil is not entirely soluble in the undiluted alcohols at any temperature. When soluble oil at a concentration of 0.5% by volume was added to use-dilution alcohols an oily phase separated in all cases with the exception of samples held near room temperature. The soluble oil would not appear to comply with item 3 of Exhibit A.

The long term stability of the CR-2990 systems in diluted or undiluted alcohol at very low or very high temperatures could not be checked within the time available.

IV SUMMARY AND CONCLUSIONS

1. Following a literature search, 137 candidate corrosion inhibitors were examined for their effectiveness in prescribed water-alcohol solutions.
2. This screening program disclosed 26 materials or combinations that afforded considerable protection to mild steel and aluminum in both liquid and vapor phases.
3. Eleven of the twenty-six materials were selected for their good protective qualities. These were examined more closely for fulfillment of other target specifications. The three inhibitors found to be the most effective of this group were sodium benzoate, a mixture of equal parts of urea and potassium nitrite and a mixture of equal parts of acetamide and potassium nitrite. These three systems were found to exceed the specified non-combustible solids limits when used at levels necessary to attain the desired corrosion protection.
4. The Inhibitor Concentrates described in (5) complied fully with requirements as to non-combustible solids and vertually all of the other requirements--see (6) below. In spite of this, further investigation of the inhibitor compositions under (3) may be justified for non-reciprocating engine service since most and possibly all the other requirements of Exhibit A can be met with formulations of this basic type.

5. In attempts to reduce the amount of non-combustible solids, substitutions were made which resulted in the following three Inhibitor Concentrate systems:

	Weight Percent		
	CR-2990 -A1	CR-2990 -A2	CR-2990 -A3
Nitropropane	10.4	2.3	4.6
Dicyclohexylamine nitrite	12.6	11.5	9.2
Acetamide	--	9.2	--
Urea	--	--	9.2
Victawet 12	7.0	7.0	7.0
Methanol	70.0	70.0	70.0
	100.0	100.0	100.0

6. The proposed Inhibitor Concentrates and Soluble Oil MIL-C-4339 conform to the requirements of Exhibit "A" as follows:

Exhibit "A" (Amended)	Inhibitor Concentrates CR-2990-A1, -A2, -A3	Soluble Oil, MIL-C-4339
I.A.1	Complies Methanol solution of mixture of inhibitors with surfactant. Probable use level 2 gal./100 gal. undiluted methanol or ethanol.	Complies
I.A.2	Complies May be mixed with diluted or undiluted methanol or ethanol at any time. Individual ingredients of the concentrates may be mixed with undiluted alcohols at the point of alcohol manufacture if preferred.	Fails Not entirely soluble in undiluted alcohols
I.A. 3	Complies Soluble (to an extent greater than required for corrosion inhibition) in undiluted methanol and ethanol at -65° and +160°F., and at 10°F. above the freezing point and 10°F. below the boiling point of 20-70 volume percent alcohols.	Fails Not entirely soluble in undiluted alcohols, or in diluted alcohols at extreme temperatures.
I.A. 4	Complies The inhibited solutions reamin stable and clear within the limits of I.A. 3.	Fails Produces opaque, milky emulsion in all alcohol dilutions.

Exhibit "A" (Amended)	Inhibitor Concentrates CR-2990-A1, -A2, -A3	Soluble Oil, MIL-C-4339
I.A. 5	Complies The inhibitor systems show promise of effective prevention of corrosion of steel in both liquid and vapor phase exposures. They also show promise of good liquid and vapor phase protection to aluminum alloys, perhaps a little less effective than toward steel. However, the corrosion products formed appear to be rather adherent and may yield secondary protection.	Complies May be a little less effective for protection of steel and a little more effective toward aluminum than the proposed inhibitor concentrates. Appears to function through deposition of an oily or greasy surface coating.
I.A. 6	Complies The non-combustible solids computed for the amounts of inhibitor concentrates to be used in 50-50 alcohol-water mixes should not exceed 10 ppm.	Compliance Unknown
I.A. 7	Complies (Surface Tension) Fails (Interfacial Tension Against Nujol)	Fails (Surface Tension) Complies (Interfacial Tension)

Dynes/Cm.	0.05% Triton X-100 in 30% Methanol (Standard)	Inhibitor Concentrates In 25% Methanol	Inhibitor Concentrates In 25% Ethanol	Soluble Oil in 25% Methanol	Soluble Oil in 25% Ethanol
Surface Ten.	28	27.6-27.7	27.3-27.8	30.5	30.7
Interfacial Ten.	4.9	9.0-9.4	8.6-8.8	1.4	1.4

While the surface tensions of either 50% alcohol solution will exceed the Triton X-100 standard, it is believed this is no longer an important consideration.

Exhibit "A" (Amended)	Inhibitor Concentrates CR-2990-A1, -A2, -A3	Soluble Oil, MIL-C-4339
I.A. 8	Believed to Comply The cost of the materials used will be much higher than for soluble oil. Present production of dicyclohexylamine nitrite is believed to be about sufficient for tentative A.F. requirements. No reason can be foreseen why the several licensed manufacturers would not increase production, if marketable. One present producer of cyclohexylamine would gladly increase production if commercially warranted and others might be encouraged to enter the field. Production, production capacity and costs for Victawet 12 and nitropropane have not been investigated. Normally a large new stable market would encourage expansion of any needed facilities and materially reduce costs.	Complies Low cost and probably unlimited supply.
I.A. 9	Complies Shelf life apparently unlimited as a concentrate or following addition to alcohols, diluted or undiluted.	Compliance Unknown
I.A. 10	Complies The inhibitor concentrates in proportions at least four times the levels needed for corrosion inhibition of 25% alcohol solutions may be added to undiluted alcohols O-M-232 or MIL-A-6091 without the necessity for addition of water. See I.A. 3 also.	Fails Must be dispersed in water followed by addition of alcohol.

Exhibit "A"
(Amended)

Additional Qualifications	Inhibitor Concentrates CR-2990-A1, -A2, -A3	Soluble Oil, MIL-C-4339
1. Hard Water Compatibility	Acceptable	Fails
	Compatible with 10, 30 and 50 gr. artificial hard waters (U.S.Navy Spec. 51-1-19) used to dilute inhibited methanol and ethanol concentrates to 25 volume percent alcohol. Trace of fine crystalline sediment noticed after 15 days, independent of water hardness.	Separation of oil noticed, proportionate to hardness of water used. Estimated separation of oil 40-100%.
2. Foaming Characteristics	Acceptable	Acceptable
3. Engine Knock Characteristics	Believed Acceptable	Compliance Unknown
	No tests run.	
4. Safety Hazards	Believed Acceptable	Acceptable.
	Essentially the same as for undiluted alcohols	None.

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