FOREWORD

This is the final report on Armour Research Foundation (ARF) Project 8212, "Evaluation of Coating Systems for High Strength, Low Alloy Steel Exterior Missile and Rocket Casings", covering work performed at Armour Research Foundation under Contract No. AF 33(616)-7739. The work was initiated under Project No. 7381, "Materials Applications", and Task No. 738101, "Exploratory Design and Prototype Development". The program was conducted under the supervision of the Specialty Materials Section of the Applications Laboratory, Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division. Mr. A. S. Dalton was the project engineer.

Foundation personnel contributing to this work include L. C. Bennett, N. D. Bennett, J. Bruskiewicz, K. E. Hofer, Jr., D. Horwitz, E. H. Koeller, H. R. Nelson, H. Sheriff, M. G. Spak, D. G. Vance, and A. E. Vajda. Data for this program has been recorded in ARF Logbooks No. C10679, C11227, C11728, and C11956.

This report covers work performed from 3 January 1961 to 28 February 1962.

ABSTRACT

Existing coating systems were evaluated by exposing coated metal specimens to environments to which missile and rocket casings may be exposed during fabrication, storage, shipment and readiness. SAE 4340 steel was the substrate material. The protection afforded the substrate was evaluated by direct tests of the coatings or by the change in the performance of the coating or substrate following exposure to various adverse environments.

Sixteen coating systems were studied. Tension, fatigue, embrittlement, abrasion, adhesion, flexibility, stress-corrosion, thermal change and humidity, accelerated weathering, and salt spray corrosion were the tests made.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

W. P. Conrardy

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Chief, Materials Engineering Branch
Applications Laboratory
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I. INTRODUCTION*

The relative adequacy of various coating systems to protect rocket and missile casings has long been open to question in view of a lack of controlled experiments upon which to base valid coating comparisons. The subject program, performed by Armour Research Foundation, was directed toward establishing the capability of a number of available coating systems in protecting the SAE 4340 steel missile casings to which they are applied.

Information secured provides a basis for assessing the relative effectiveness of available coating systems in providing protection to a substrate material to which they are applied. The program was restricted to the investigation of selected presently available metal-preparation and coating systems most likely to provide the needed long-term protection against deterioration of high-strength low alloy steel exterior missile casings, and thus insure casing reliability. No process or coating development activity was included in the program.

Existing coating systems were evaluated by exposing coated-metal specimens to various environments known to affect missile and rocket casings adversely during their fabrication, storage, shipment, and readiness. The degree of protection provided the missile-casing material was judged either by tests of the coatings themselves, or by comparing the reduction of strength or performance of coated specimens tested following exposure to various adverse environments.

The program consisted of two basic activities. The first includes a series of tests of (a) the coatings themselves, (b) uncoated metal specimens, and (c) coated metal specimens subjected to various environmental exposures and then tested. These evaluations were performed by standard test procedures or modifications thereof. The results obtained provided data regarding inherent coating system capability, and by comparison of coated and uncoated specimen performance, the degree of protection the coating affords a steel missile casing subjected to adverse environments.

The second activity was the analysis of experimental results to obtain an insight into which types of coatings offer the best overall protection from the various environments encountered in service, and the influence of preparation techniques on coating effectiveness.

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* Manuscript released by the authors April 1962 for publication as an ASD Technical Documentary Report.

II. SCOPE OF PROGRAM

This investigation was prompted by the recognition that missile casing performance may be seriously compromised by failure of protective coatings to provide protection from adverse environments during fabrication, storage, shipment, and readiness. The performance of various organic protective coating systems was evaluated by investigating the effectiveness of coating processes with presently available materials including pretreatments, primers, and topcoat materials applied to a single type of high-strength, low-alloy steel.

A total of sixteen protective-coating system combinations were studied. The program included the comparative investigation of the following:

A. Pretreatments, including use of sand blasting and phosphoric acid etching for specimen cleaning.

B. Primers, including a wash primer, zinc chromate alkyd, and epoxy resin types.

C. Topcoats, including alkyd, chlorinated rubber, epoxy and polyurethane enamels.

D. One epoxy type fluidized bed applied enamel.

A total of ten test methods were employed in seeking to experimentally establish protective-coating effectiveness. Seven of these were performed in accordance with pertinent specification procedures in the following categories: Tension, Thermal Change and Humidity, Accelerated Weathering, Salt Spray Corrosion, Abrasion, Adhesion, and Flexibility. The evaluation also included an Embrittlement Study, a Sheet Fatigue Investigation and a combined Stress-Corrosion Study. The embrittlement study was performed in accordance with a previous WADC supported program*. Prepared fatigue specimens were evaluated using Tatnall-Krouse Sheet Fatigue testing machines. The ability of the coated specimens to resist a corrosive atmosphere while in a highly stressed state also was investigated using an experimental procedure proposed by ARF.

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* WADC TR 58-481, A New Look at the Hydrogen Embrittlement of Cadmium Coated High Strength Steels, December 1958.

III. SPECIMENS FOR EXPERIMENTATION

The investigation of coating effectiveness on missile casing, to be applicable, must deal with typical combinations of both coating and substrate materials. Missile casings are generally constructed from high strength steels. Consequently, the typical substrate to which coating systems were applied was an important parameter for the investigation.

A. Material

The material selected in advance and specified by the contract for program use was SAE 4340 steel as defined by Specification MIL-S-8844 Class I. The SAE 4340 steel in sheet form is not a steel mill warehouse stock item but is only available when rolled to order. Since our total material requirement for the program was small, it was not feasible to procure stock rolled to just this one order. While we could have placed an order for our requirements with a steel mill, it would have been held until a minimum roll order for the same material was received and then both would be run at the same time. Since it was impossible to know when such an order might be received, it was not possible to proceed on such an indefinite basis.

In discussing this situation with ASD personnel the suggestion was made that we attempt to procure our material requirement from firms using such material in their production. The Aeroproducts Division of General Motors Corporation in Vandalia, Ohio was one firm suggested as a possible supplier. Upon investigating we found that while Aeroproducts Division had SAE 4340 stock in the sheet thickness we required, the material was produced in accordance with MIL-S-5000. The principal difference between the MIL-S-5000 and MIL-S-8844 Class I specifications is in the magnetic inspection for small inclusions called for by the latter specification. Since this factor was not considered to be particularly significant in this program, the ASD Project Monitor approved use of the SAE 4340 MIL-S-5000 steel stock. With this approval, sufficient sheet material was purchased through the cooperation of Aeroproducts Division in blanks 15 in. x 63-1/2 in. x 0.100 in. thick to care for program requirements. Bar stock material required for the embrittlement study was obtained from a regular steel supplier. However, to have uniformity of material in all specimens, we procured bar stock material also produced in accordance with MIL-S-5000. Thus, both sheet and bar material conformed to the same specification although they were not from the same heat and lot.

The chemical analysis requirements for SAE 4340 steel produced in accordance with MIL-S-5000 and MIL-S-8844 are shown in Table I. The actual chemical analyses for sheet stock and for bar stock used for specimen fabrication are also presented in Table I.

Table I

CHEMICAL ANALYSIS OF SAE 4340 STEELS

	C	Mn	P	S	Si	Ni	Cr	Mo
MIL-S-5000	0.38 to 0.43	0.65 to 0.85	0.025 max	0.025 max	0.20 to 0.35	1.65 to 2.00	0.70 to 0.90	0.20 to 0.30
MIL-S-8844	0.38 to 0.43	0.65 to 0.85	0.025 max	0.025 max	0.20 to 0.35	1.65 to 2.00	0.70 to 0.90	0.20 to 0.30
Sheet Stock	0.41	0.70	0.007	0.014	0.30	1.83	0.81	0.25
Bar Stock	0.40	0.80	0.011	0.015	0.31	1.84	0.85	0.27

B. Specimen Fabrication

1. Applicable Specifications

The coating evaluation studies performed required specimens with a variety of shapes. Specimen geometry was frequently fixed by applicable military specifications. In those cases where the shape was not defined, the appropriate specimen configuration was determined by the requirements of the testing equipment. Table II summarizes coating evaluation tests used, applicable specifications or test references, and the identification of figures detailing specimen shapes.

2. Specimen Details

The specimens required for all material and coating evaluations (except embrittlement tests) were prepared by shearing appropriately sized blanks from the 15 in. x 63-1/2 in. x 0.100 in. thick sheets. The sheared blanks were then machined to approximate size, hardened, and subsequently machine ground to their final shape. In order to minimize grinding stresses, coolant was used during the process. The orientation of any single type of specimen was always from the same direction in the sheet, even though the sheets were cross-rolled by the manufacturer. (Information on the original direction of rolling was not available.) This prevented mechanical property variations associated with grain orientation due to rolling from being a factor in the study. No attempt was made to simulate rolling conditions which might be present in large size sheets used for missile applications and hence slight differences between prototype and specimen behavior might be expected.

Table II

EVALUATION TESTS, APPLICABLE SPECIFICATIONS AND SPECIMEN DETAILS

Type of Test	Specification or Reference	Specimen Detail
Tension	Federal Test Method Stand 151 Method 211	Fig. 1
Fatigue	Tatnall-Krouse Sheet Fatigue Machine	Fig. 2
Embrittlement	WADC TN 58-581	Fig. 3
Thermal Change and Humidity	FTMS141 Method 6201	Fig. 4
Corrosion Resistance	FTMS141 Method 6061	Fig. 4
Accelerated Weathering	FTMS141 Method 6152	Fig. 4
Flexibility (Modified)	FTMS141 Method 6221	Fig. 4
Abrasion Resistance	FTMS141 Method 6192	Fig. 4
Adhesion	FTMS141 Method 6302	Fig. 4
Stress-Corrosion	Bent-Beam and Calcium Nitrate Salt Atmosphere Exposure	Fig. 4

The round notch embrittlement specimens were machined between centers to approximate size, heat treated and subsequently ground to final size. The details for sheet tensile, sheet fatigue, and round bar notch tensile embrittlement specimens are shown in Figs. 1, 2 and 3 respectively. Figure 4 presents a number of rectangular type specimens with a final ground thickness of 0.080 in. utilized for various environmental and mechanical tests. Figure 4a shows the type of specimen used for thermal change and humidity, salt spray corrosion, accelerated weathering, and for flexibility tests. The type of specimen used for observing coating abrasion resistance with the Taber Abraser is shown in Fig. 4b. The specimen used for measuring adhesion with the Arco Micro-Knife is shown in Fig. 4c, while the stress-corrosion specimen is shown in Fig. 4d.

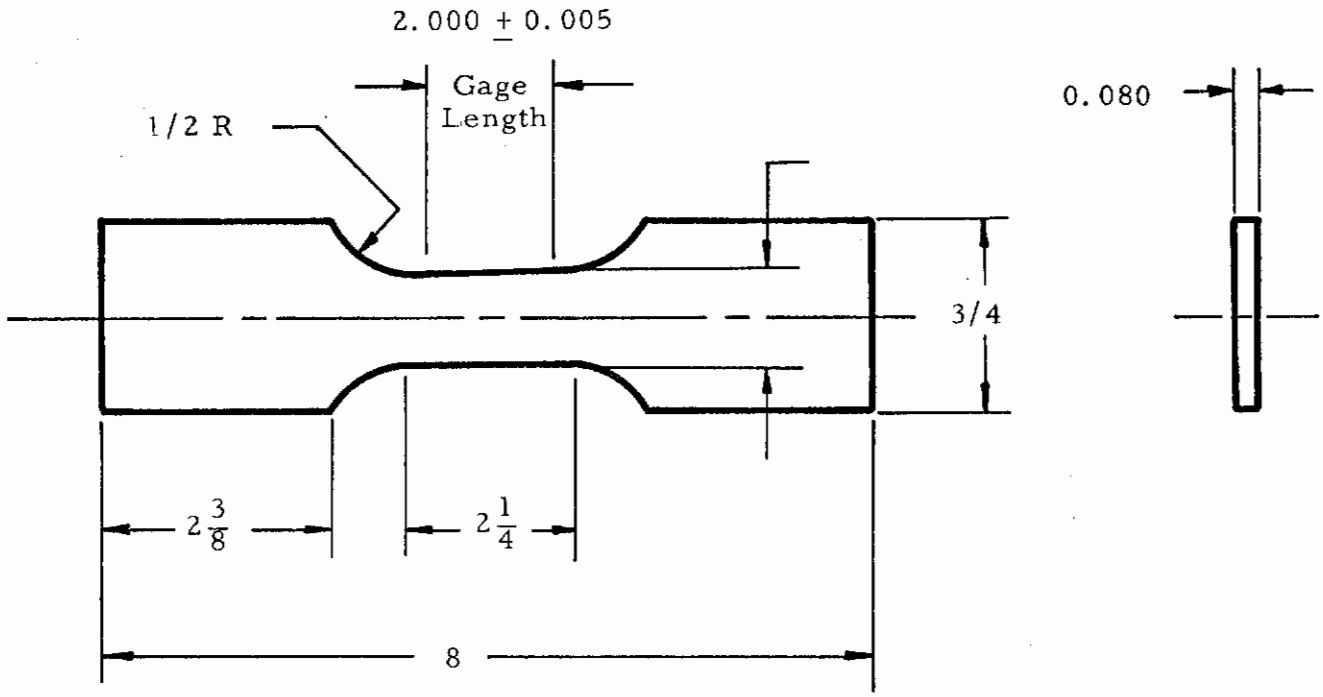

Fig. 1 TENSION SPECIMEN (All dimensions are in inches)

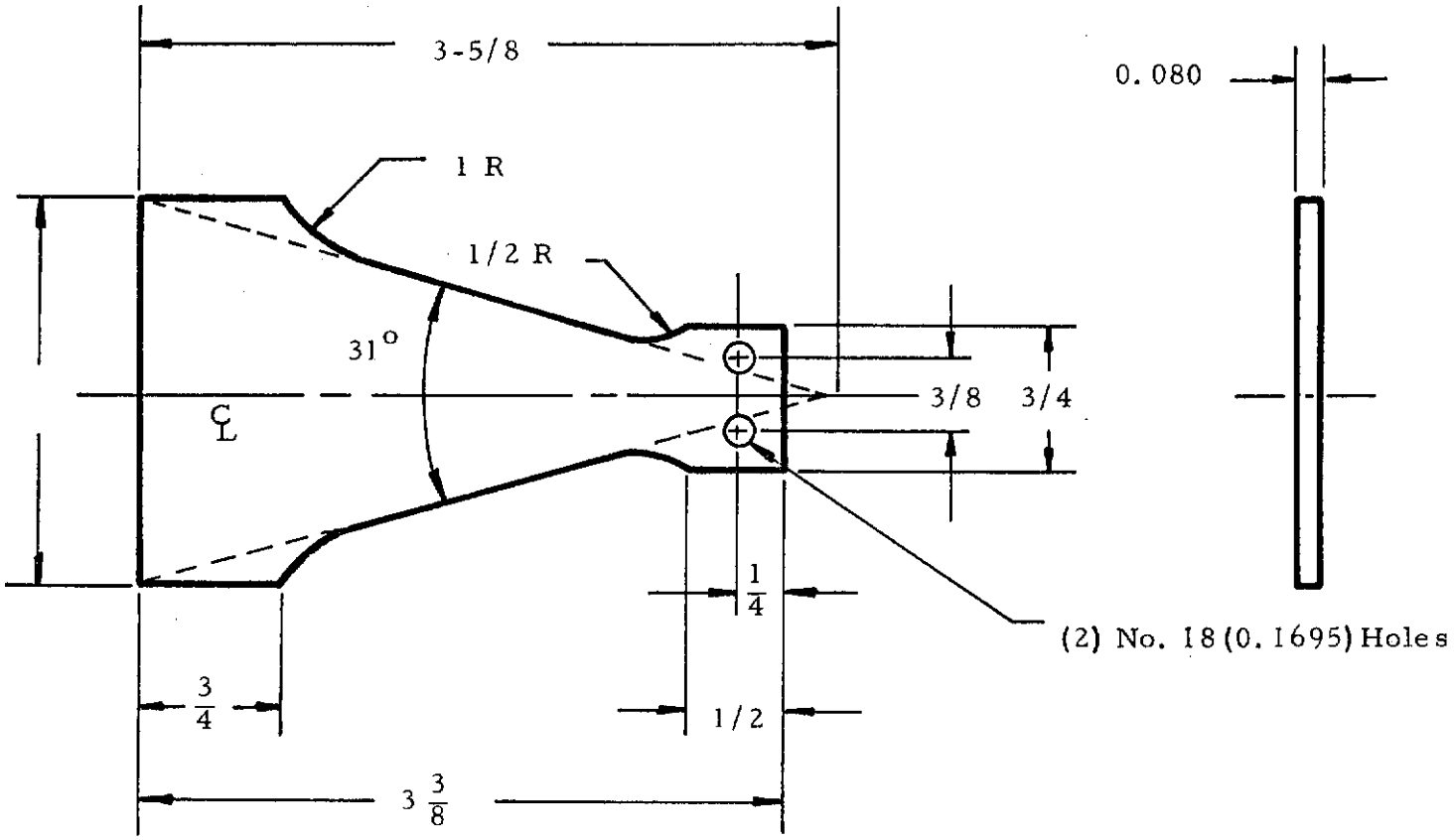

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Fig. 2 FATIGUE SPECIMEN (All dimensions are in inches)

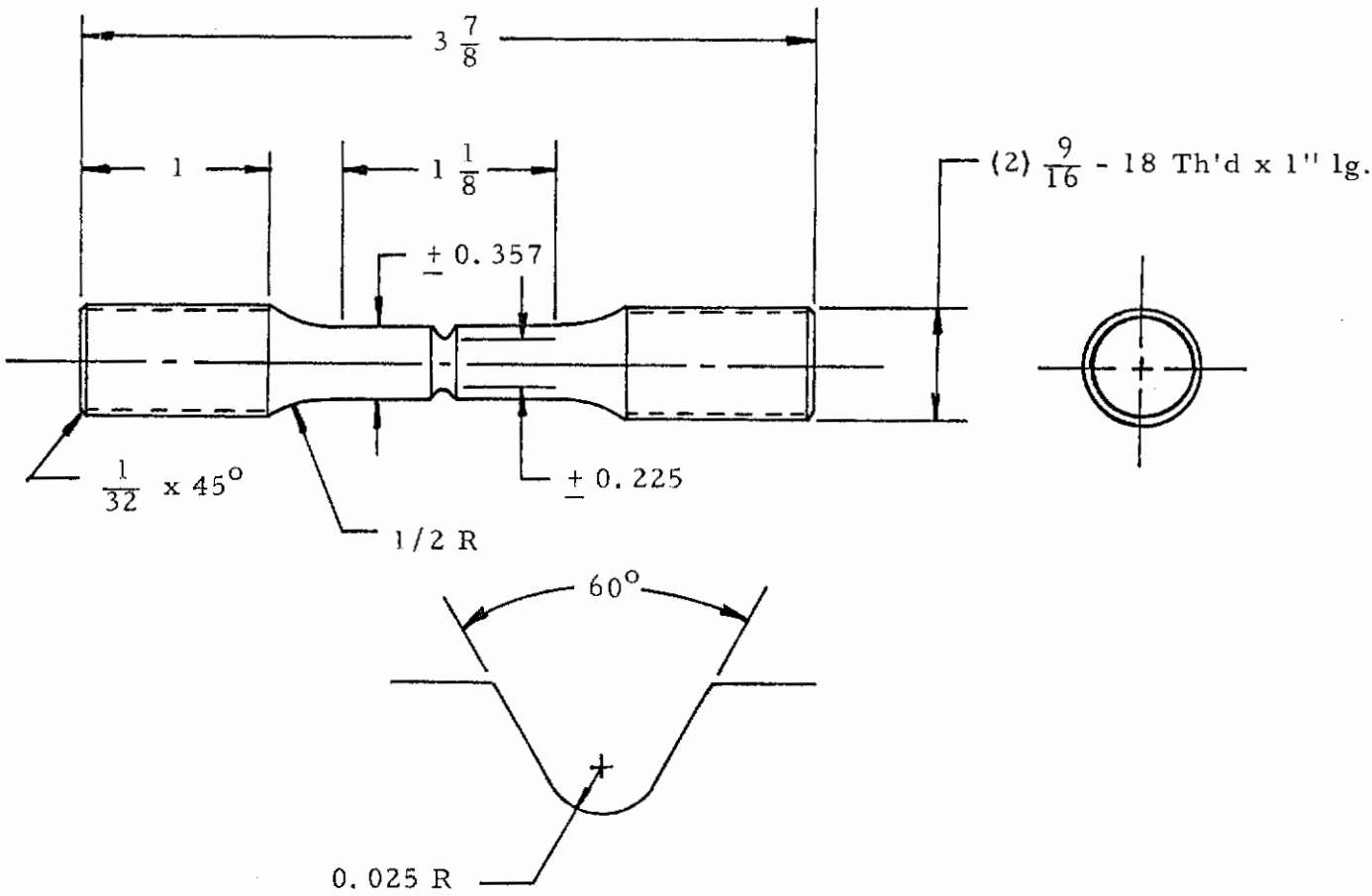
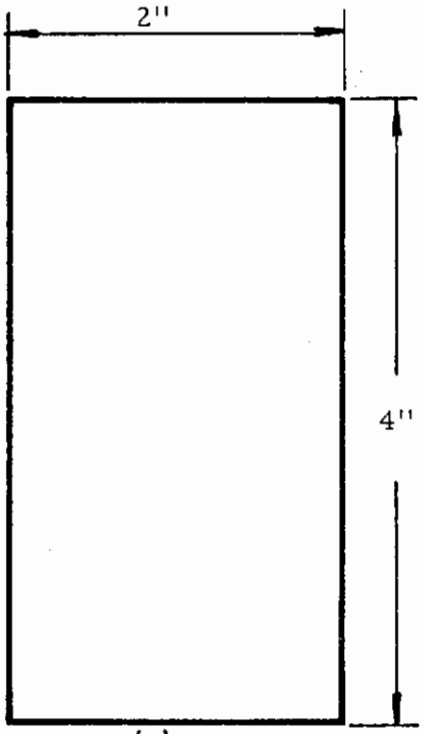
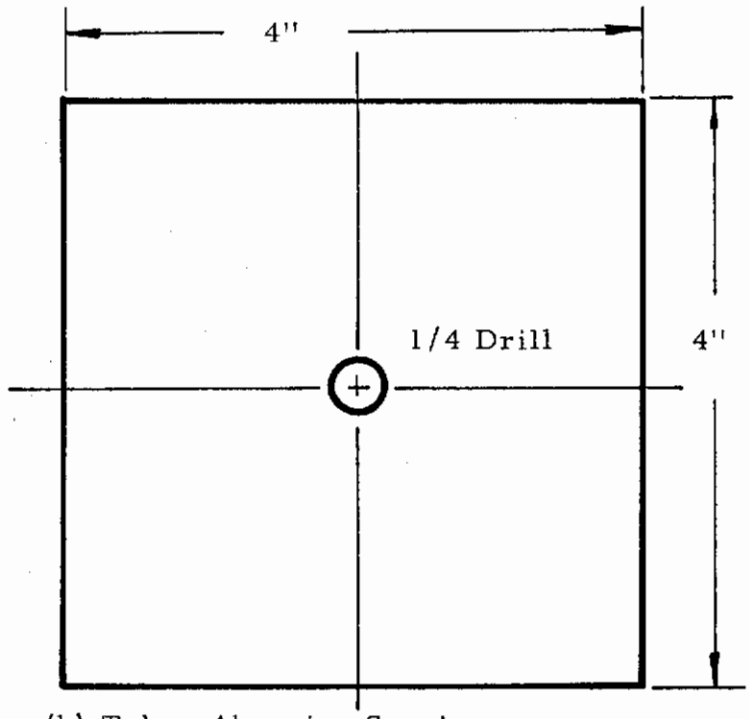


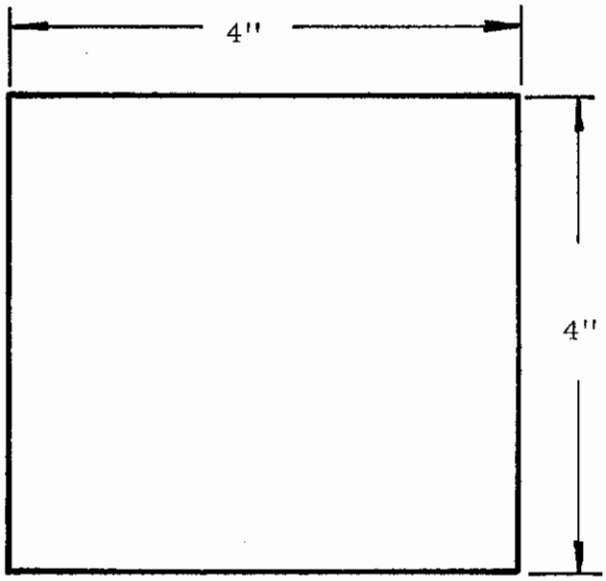
Fig. 3 ROUND, NOTCH TENSILE, EMBRITTLEMENT SPECIMEN
(All dimensions are in inches)



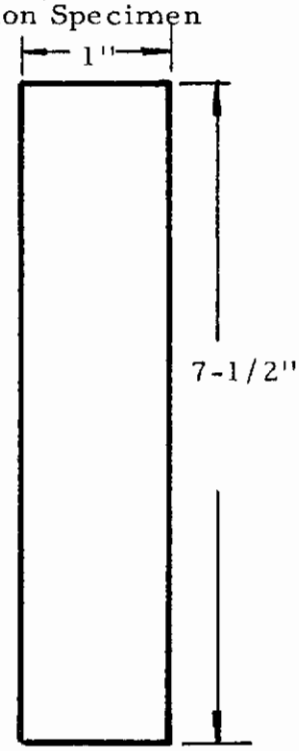
(a)
Thermal Change and Humidity, Accelerated Weathering, Salt Spray Corrosion, and Flexibility Specimen



(b) Taber Abrasion Specimen



(c)
Adhesion Specimen



(d)
Stress Corrosion Specimen

Fig. 4 SPECIMENS FOR VARIOUS ENVIRONMENTAL AND MECHANICAL TESTS (All specimens ground to 0.080 in. thickness)

3. Heat Treatment

The requirements of the contract specified that all evaluations be made with SAE 4340 material heat treated to an ultimate tensile strength of approximately 280,000 psi. The specific heat treatment used to bring the material to the required tensile strength was determined experimentally. Several groups of tensile specimens were subjected to slightly different heat treat cycles, after which their hardness and ultimate strength was determined. From these results the heat treat cycle required to bring the SAE 4340 steel stock to an ultimate strength level of approximately 280,000 psi was selected. The heat treat cycle utilized consisted of heating specimens in a neutral fused salt to 1525°F, followed by a salt solution quench. Specimens were subsequently drawn in air at 400°F for three hours*.

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* The heat treatment of the SAE 4340 sheet and bar stock specimens used for this study was performed by Lindberg Steel Treating Co., Melrose Park, Illinois.

IV. COATING SYSTEMS

Candidate coating materials for the program were sought by contacting manufacturers of various type coatings. Letters were sent to approximately 200 manufacturers or applicators of chlorinated rubber, epoxy resin, polyurethane, and alkyd coatings, requesting detailed technical information and samples of coatings. On the basis of the information obtained, coating selections were made in collaboration with the Project Monitor.

A. Coating Materials and Applicable Specifications

Various military specifications cover the technical details of the several pretreatments, primer and topcoat preparations used, and the processes by which they are applied. The specifications which were followed on the program are given in Table III.

Table III

COATING APPLICATION SPECIFICATIONS

Preparation	Specification Number
1. Pretreatments	
a. Sand blast	TT-C-490
b. Phosphoric acid etch	TT-C-490
2. Primer Coatings	
a. Wash primer	MIL-C-8514
b. Zinc chromate primer-alkyd	MIL-P-8585A
c. Epoxy primer	MIL-P-27316
3. Enamel	
a. Alkyd enamel	MIL-E-7729 Type I
b. Polyurethane enamel	MIL-C-27227
c. Chlorinated rubber	None
d. Epoxy enamel	None
e. Fluidized bed applied epoxy enamel	None

B. Identification of Coating Systems

In this study specimens were utilized which had been variously treated and coated. In addition to investigating a total of sixteen complete coating systems, certain specimens subjected to pretreatments only and partial coatings were also studied. The object of investigating these pretreatments and partial coatings was to obtain information concerning the effect metal preparation and coating practices have on either base material performance or on coating performance in service. In Table IV all of the complete coating systems and the various pretreatment and partial coating systems investigated are listed. Complete coating systems studied are identified by numbers 1 through 16 inclusive. Specimens which were machined but not subjected to any treatment prior to testing are identified by the letter "O". Specimens subjected to pretreatment only or partial coating are identified by Roman numerals I through IX inclusive.

C. Application Processes

A total of sixteen complete coating systems were selected for evaluation on the program. A flow chart showing the pretreatments, and specific primer and topcoat enamel types selected is presented in Fig. 5. A summary of the application of the coatings is presented in Table V in which the various coatings and thinners used, proportions of paint to thinner, spray gun operating pressure, distance from the work, dry film thickness per pass, and traverse speed are listed. Details of pretreatments and of primer and topcoat applications are discussed in the following sections.

1. Pretreatment

The cleaning and preparation of steel specimens prior to the application of organic coatings is specified in TT-C-490. Two preconditioning methods were studied. Both preconditioning methods can be classified under Grade II of this specification, i.e. cleaning treatments which leave the metal surface substantially bare. These two methods were types 1 and 4, sand blast and phosphoric acid etch cleaning, respectively.

The requirements of the above specification are extremely open regarding the process of surface cleaning by exposure to abrasive blasting. The specification permits sand, shot, grit or seed blasting, and does not mention any method of measuring the intensity of the blasting action which could serve as a basis for control of the process. Also, the specification imposes no limitation on the relative coarseness or fineness of the abrasive cleaning media, although there is a considerable range in size and character within the individual classes of material which can be used, and an even larger range between the various types permitted. Further, the volume of abrasive flowing, the velocity at which it strikes the work and exposure time are not stipulated.

Table IV

COMPLETE COATING SYSTEMS AND PRETREATMENT
AND PARTIAL COATING SYSTEMS EVALUATED

Complete Coating Systems	Pretreatment and Partial Coating Systems
1. Sand blast, Zinc chromate - Alkyd primer, Alkyd enamel.	O Machined specimen - No treatment.
2. Sand blast, Zinc chromate - Alkyd primer, Polyurethane enamel.	I Sand blast only.
3. Sand blast, Zinc chromate - Alkyd primer, Chlorinated rubber enamel.	II Phosphoric acid etch only.
4. Sand blast, Epoxy primer, Polyurethane enamel.	III Phosphoric acid etch, Wash primer.
5. Sand blast, Epoxy primer, Epoxy enamel.	IV Sand blast, Epoxy primer.
6. Sand blast, Epoxy primer, Alkyd enamel.	V Sand blast, Zinc chromate primer.
7. Phosphoric acid etch, Zinc chromate - Alkyd primer, Alkyd enamel.	VI Phosphoric acid etch, Epoxy primer.
8. Phosphoric acid etch, Zinc chromate - Alkyd primer, Chlorinated rubber enamel.	VII Phosphoric acid etch, Zinc chromate primer.
9. Phosphoric acid etch, Zinc chromate - Alkyd primer, Polyurethane enamel.	VIII Phosphoric acid etch, Wash primer, Epoxy primer.
10. Phosphoric acid etch, Epoxy primer, Polyurethane enamel.	IX Phosphoric acid etch, Wash primer, Zinc chromate primer.
11. Phosphoric acid etch, Epoxy primer, Epoxy enamel.	
12. Phosphoric acid etch, Epoxy primer, Alkyd enamel.	
13. Sand blast, Wash primer, Zinc chromate - Alkyd primer, Polyurethane enamel.	
14. Sand blast, Wash primer, Zinc chromate - Alkyd primer, Chlorinated rubber enamel.	
15. Sand blast, Wash primer, Zinc chromate - Alkyd primer, Alkyd enamel.	
16. Sand blast, fluidized bed applied Epoxy enamel.	

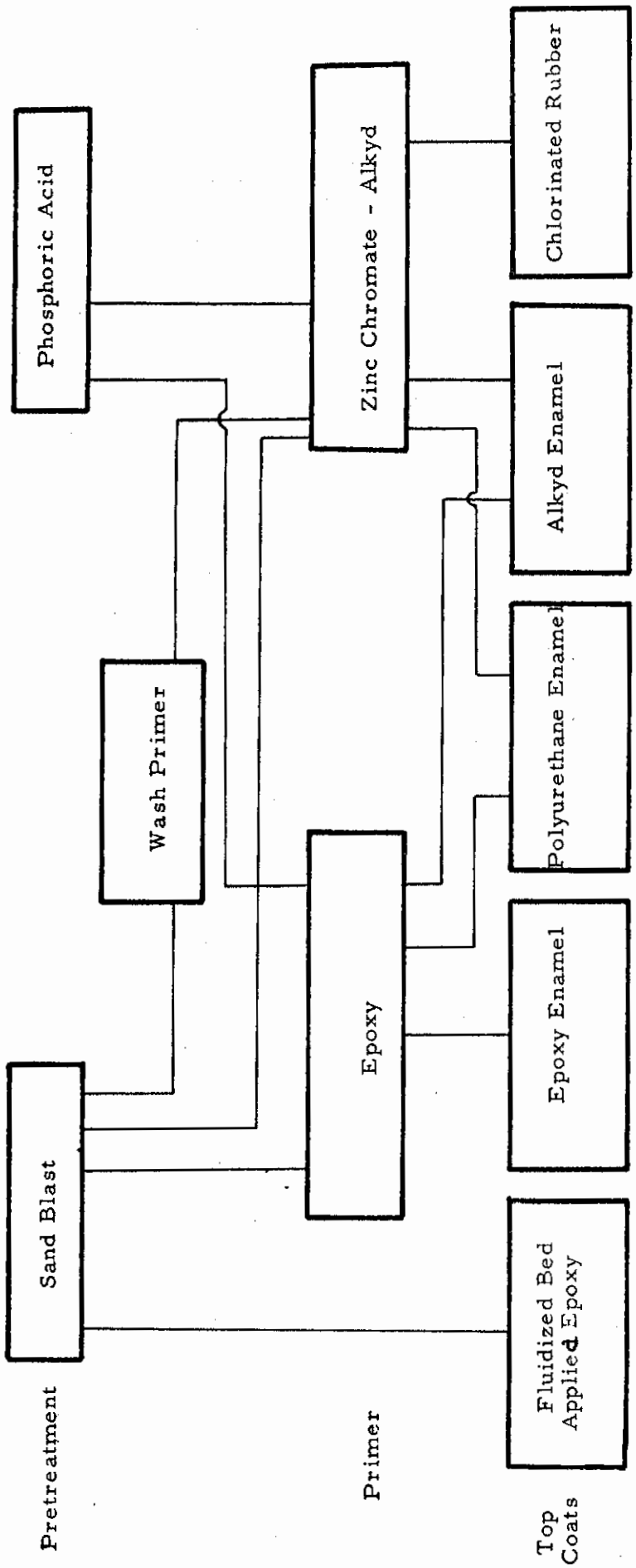


Fig. 5 FLOW CHART FOR COMPLETE COATING SYSTEMS

Table V

APPLICATION DETAILS FOR PRIMER AND ENAMEL COATINGS

Coating	Thinner	Paint: Thinner Ratio (by Vol)	Traversing Speed (in./sec)	Number of Passes	Dry Film Thickness (in.)	Gun to Specimen Distance (in.)	Gun Operating Pressure (psi)
Wash Primer	Isopropyl Alcohol	4:1	2.6	1	0.00025 ±0.00005	9.0	35
Zinc Chromate and Alkyd Primers	Toluene	1:2	3.0	1	0.0003 ±0.0002	7	35
Epoxy Primer	Toluene	6:1	2.6	1	0.0005 ±0.0001	8.75	35
Alkyd Enamel	Mineral Spirits	4:1	2.6	1	0.001 ±0.0002	9.25	50
Polyurethane Enamel	Xylol	8:1	2.6	1	0.0015* ±0.0001	13.25	35
Chlorinated Rubber Enamel	Inertol No. 2000	1:1	2.6	1	0.001	9.5	50
Epoxy Enamel	45% MIBK 5% Butyl Cellosolve 50% Toluene	4:1	2.6	1	0.001	9.5	50

* Two coats were applied here to reach the total thickness of 0.0030 in. ± 0.0003 in.

Note: Total thickness of coatings applied was in accordance with the appropriate specification as shown in Table III.

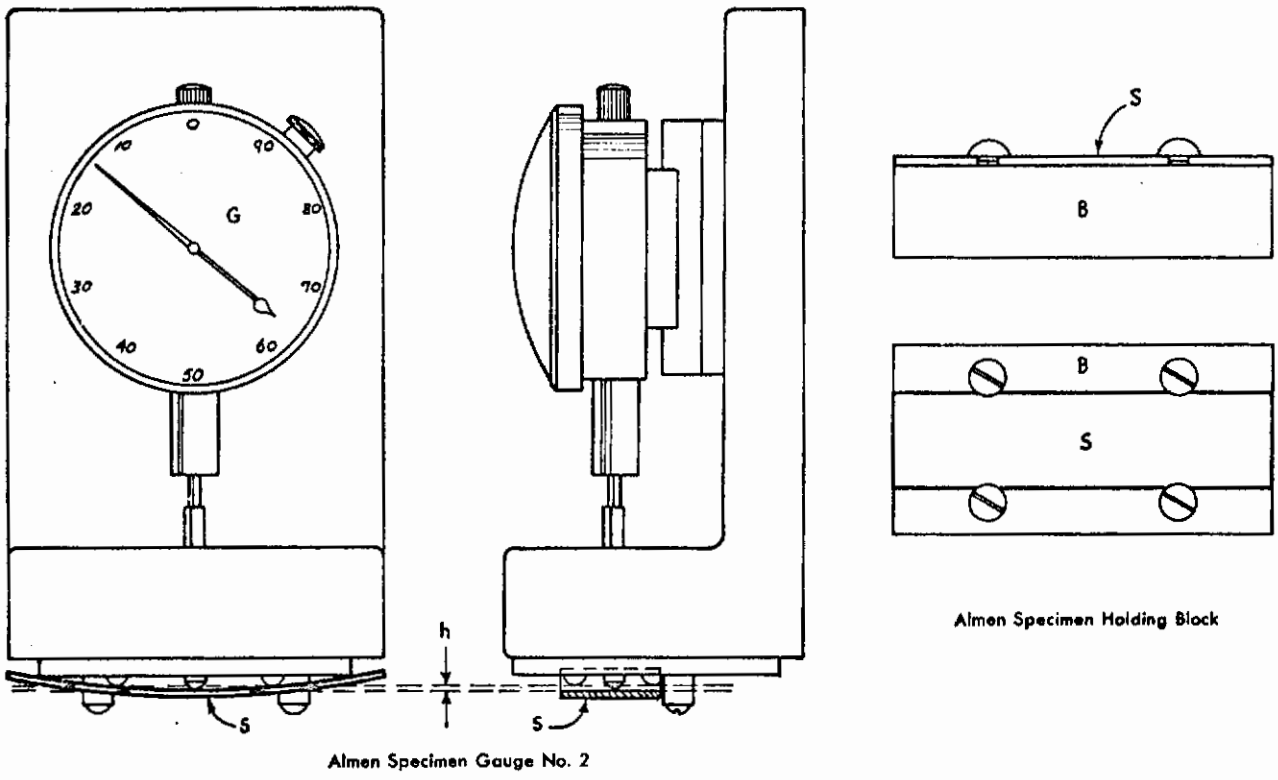
The mechanical cleaning by grit blasting of specimens on the program was accomplished in a Ruemelin No. 12262 sand blasting machine [1/] using The Carborundum Co. No. 20 RA grit silicon carbide. The grit ranged from 0.026 in. to 0.053 in. diameter with an average of 0.037 in. The abrasive was aspirated from a hopper into a high velocity air stream, supplied from a 100 psi air line, which discharged through a 1/2 in. diameter cast steel orifice onto the work. This orifice was mounted in a No. R555 Ruemelin nozzle. Each specimen was moved in a horizontal plane under the grit blast and all were similarly exposed to abrasive blasting from a hand held nozzle. Because of the physical difference in size of the various types of specimens, it was not possible to subject all specimens to the same number of passes of the nozzle blast to achieve a cleaned surface. Rather, specimens were individually exposed to sufficient passes to achieve a clean, uniform appearing surface. Then the specimen was turned over and the process repeated on the opposite surface. Although the grit blast process used met all of the applicable specification requirements, the uniformity of specimen exposure was thought to be somewhat variable.

To resolve this, some experimental work was performed utilizing Almen blocks and Type "A" Almen test strips. A number of type "A" steel test strips were individually mounted on test blocks and were exposed to the same blast cleaning process as accorded specimen samples prior to coating. Upon removal from the blocks, the test strips assumed the characteristic curvature resulting from metal working and compressive stressing of the grit blasted surface. The resulting arc height, measured with the use of an Almen Gage (see Fig. 6), is a convenient means of indicating the grit blasting or peening intensity imposed, although it cannot be directly related to the level of compressive stresses developed in the strip, nor the depth to which these stresses extend below the surface.

Measurement of these grit blasted strips gave arc heights ranging from 0.0035 to 0.005 in. From these data it appeared that satisfactory control was obtained through the process of exposing specimen samples to grit blast cleaning until a uniformly clean appearing surface is produced.

The second pretreatment used prior to the coating of specimens followed Federal Test Method Standard No. 141 Method 2011. This pretreatment consisted of immersing specimens in a 1 to 1 phosphoric acid-distilled water mixture at a temperature from 24° to 29°C for one minute. Subsequently, specimens were sprayed with distilled water for 15 seconds or until each specimen maintained a continuous water film on it. The specimens were then sprayed with 95 percent ethanol to which had been added 1 percent (by volume) reagent grade ammonium hydroxide. The specimens were dried at 125°F in an oven and then were placed in protective paper wrappers and stored until they were removed for coating. The specimens were subsequently handled using appropriate tongs to avoid contaminating the clean surface.

[1/] Manufactured by Ruemelin Mfg. Co., Engineers Mfrs., Milwaukee, Wisconsin.



Almen Specimen Gauge No. 2

Almen Specimen Holding Block

Fig. 6 ALMEN TEST EQUIPMENT FOR INTENSITY OF PEENING

Some specimens tested in the "as received" condition were not given any pretreatment. These included sets of tension, fatigue, and notch embrittlement specimens.

2. Primer Coatings

Primer coatings were applied to specimens following preconditioning treatment. Three different primer coating systems were employed: (1) wash primer, (2) zinc chromate-alkyd primer, and (3) epoxy primer. The cognizant specification covering these materials and operations are found in Table III. The composition of the primer coatings is also contained in the designated specification. A summary of the application data for these primer coatings is presented in Table V.

Initial experimentation on coating application was performed with an apparatus consisting of a double-acting pneumatic cylinder having an 18-in. stroke on which the spray gun was mounted. This device was designed to move the spray gun past stationary specimens at a constant rate, thus applying a uniform coating thickness. Coating thicknesses, however, as indicated by Aminco Magna [1/] gage measurements, were not consistently maintained within the tolerances prescribed by the specifications. The use of this apparatus was therefore discontinued in favor of a conveyor belt type apparatus which was used to apply coatings to all spray coated specimens.

The conveyor belt apparatus constructed for this purpose is shown in Figs. 7 and 8. Specimens were placed horizontally on the conveyor belt apparatus and were thus moved past the stationary spray gun. The conveyor belt was driven by a variable speed motor, permitting various specimen traversing rates to be used. With this unit, other physical parameters could also be varied including distance of gun from the work, width of spray pattern, and operating air pressures in the gun. The spray gun used was a Sprayit Gun ER-1-150 [2/]. The thickness of the coatings were controlled by varying the above parameters to develop the prescribed film thickness. The previously mentioned Aminco gage was used for measuring the film thickness.

Edges of specimens were not coated using the spray gun but were hand painted using a fine camel hair brush. Primer and enamel coating of specimen edges were handled in this manner.

3. Enamel Coatings

Following pretreatment and primer coating operations, enamel coatings were applied to the specimens. Four different enamel coatings were evaluated: (1) alkyd, (2) polyurethane, (3) chlorinated rubber, and (4) epoxy. The specifications describing these enamels and their application were listed

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[1/] Manufactured by the American Instrument Co., Silver Spring, Md.

[2/] Manufactured by the Sprayit Company, Sheboygan, Wisconsin.

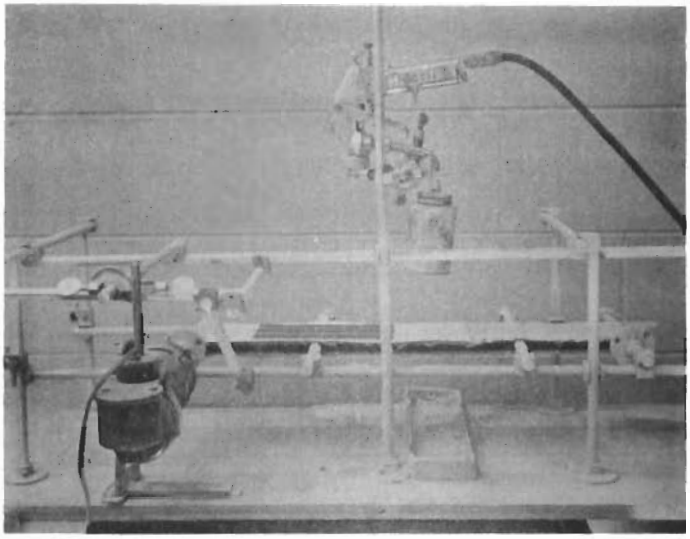


Fig. 7 SPRAY GUN APPARATUS FOR COATING APPLICATION - SIDE VIEW

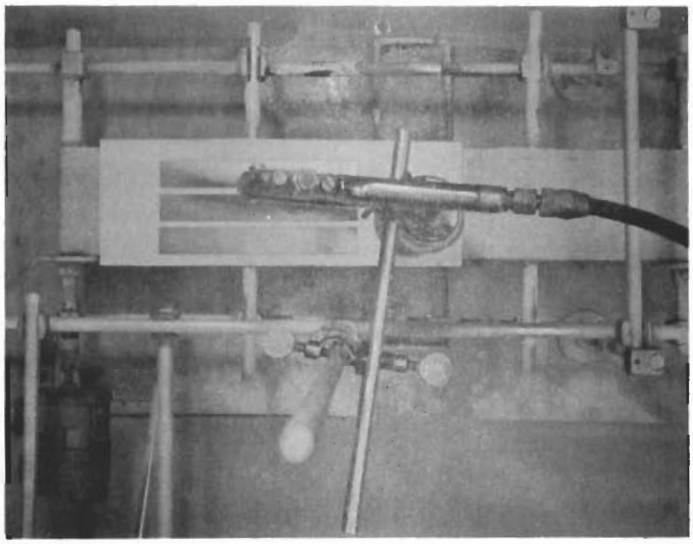


Fig. 8 TOP VIEW OF SPRAY GUN AND CONVEYOR APPARATUS

earlier (see Table III). The techniques employed to apply the sprayed enamel coatings to specimens are summarized in Table V.

Two methods were used to apply enamel coatings to the specimens. With the first method, coatings were applied using the spray gun and the conveyor apparatus described earlier. The second method was that used for application of a single epoxy enamel coating by fluidized bed techniques. No primer coating was used on specimens to which the fluidized bed epoxy coating was applied.

To coat specimens to a uniform thickness by the fluidized bed process, specimens were first preheated in an oven to a temperature above the melting point of the coating material. In this investigation, wherein an epoxy coating was used, the specimens were preheated to 350°F. After preheating, the specimens were dipped vertically into a bed of the finely-divided epoxy resin powder and were moved slowly by hand in a horizontal plane. Fluidization of the bed was accomplished by forcing air through the porous bottom of the container and upward through the bed. At the same time the bed was vibrated. The combination of vibratory movement and air flow caused the finely divided particle bed to behave as a fluid.

As the individual resin particles contacted the heated specimen they melted and adhered to the specimen surface. The thickness of the coating applied is a function of the temperature of the specimen, the thermal properties of the resin, and the length of time that the specimen is exposed to the bed. Specimens coated for this study were exposed to the fluidized bed until the coating had attained the proper thickness.

In this investigation, the epoxy used was a thermo-setting resin and therefore required a subsequent curing cycle. To accomplish this curing, specimens were returned to the oven at 350°F for a period of one hour after being coated.

The fluidized bed coating process can be summarized as follows: sand blast cleaning of metal followed by vapor degreasing, clamping the specimen in a holding fixture used during subsequent preheating, exposure to the fluidized bed coating material, post heating and cooling. After cooling, specimens were removed from the holding fixture.

The fluidized bed epoxy coating was applied to a full set of specimens at Rock Island Arsenal through the courtesy of Mr. Lloyd Gilbert. A complete set of specimens was given the required sand blast and phosphoric acid etch treatments, coated with petrolatum and forwarded to Mr. Gilbert, who arranged to have the specimens degreased, fluidized bed coated as previously described, and then returned for subsequent evaluation.

V. EXPERIMENTAL EVALUATION

A. General Procedure

Each of the sixteen coating systems described earlier was subjected to the same evaluation program. Basically the series of evaluation studies consisted of two important subgroups. These were the control series and the subsequent environmental and mechanical test series.

The control series consisted of three individual types of tests which included tension, fatigue and embrittlement studies. These tests were designed to evaluate coating performance at various stages of the program. Consequently the control tests were performed on untreated, pretreated, primer coated, and enamel coated specimens as well as on such specimens after thermal change and humidity, and corrosion environmental conditioning.

The environmental-mechanical test series included thermal change and humidity, salt spray corrosion, accelerated weathering, flexibility, abrasion resistance, adhesion, and stress-corrosion studies. The first four of these were to be used to eliminate those coatings from further study on the program which failed to pass those tests. However, in actuality all coatings performed fairly well in those tests, hence none was eliminated from further evaluation on the program.

A flow chart listing the tests imposed on untreated machined specimens, and on specimens subjected to pretreatment, partial and complete coating system application is shown in Fig. 9. This flow chart clearly illustrates the progression of specimens through successive environmental exposures prior to final evaluation by means of tension, fatigue, embrittlement, flexibility and adhesion tests.

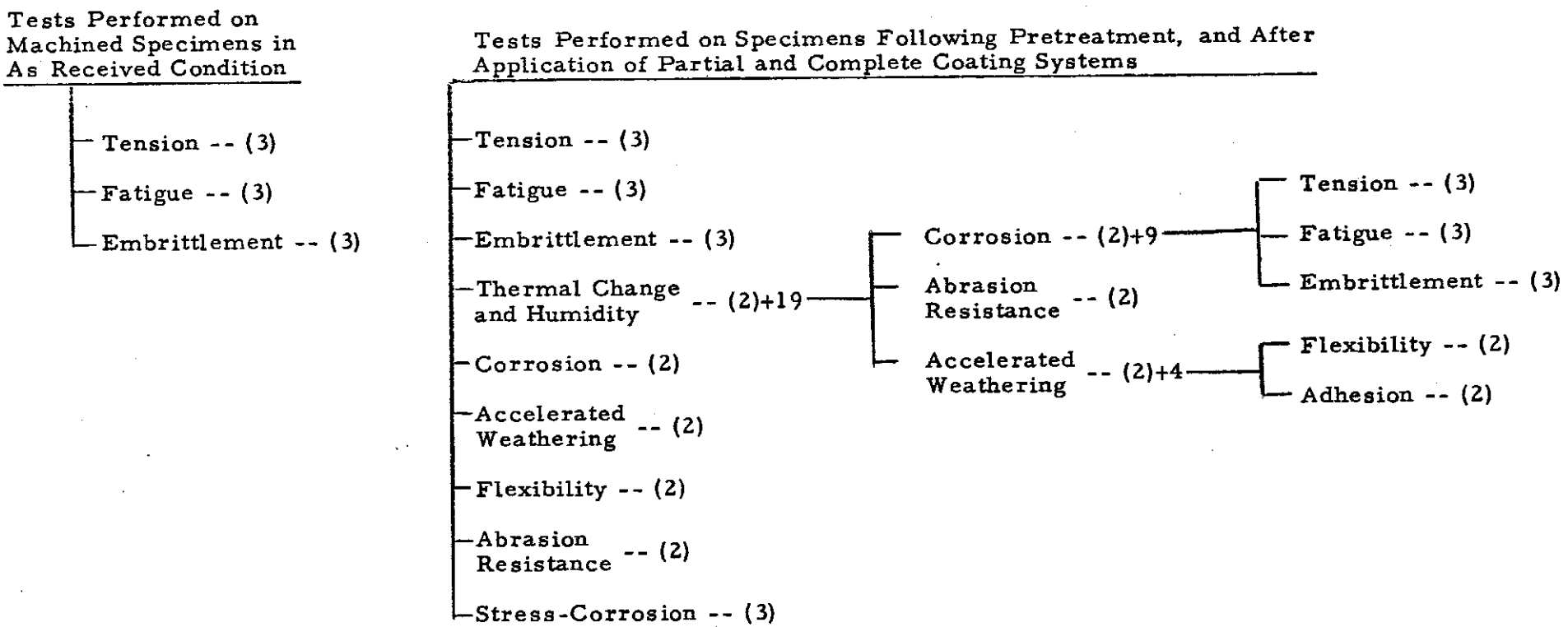
B. Description of Tests

1. Tension

Tension specimens shown in Fig. 1 were mounted in a Riehle Universal Testing machine Model No. MA-SP-No. 30. The specimens were loaded at a constant rate of crosshead travel of approximately 2 in./min. The ultimate load was recorded to the nearest 25 lbs increment. Initially three untreated specimens were tested to failure. These specimens failed at stresses calculated to be 279,000, 285,000, and 282,000 psi respectively for an average ultimate tensile strength of 282,000 psi.

2. Fatigue

Fatigue studies were performed on Tatnall-Krouse Sheet Fatigue machines using specimens as shown in Fig. 2. The shape of the specimen is designed to produce a uniform outer fiber stress throughout the entire



Note: The number in parenthesis following test identification is the number of specimens evaluated for the indicated condition. Subsequent numbers indicate the number of specimens exposed to the environmental conditioning preparatory to further environmental exposure and testing.

Fig. 9 SPECIMEN FLOW CHART FOR ALL COATING SYSTEMS

tapered length of the specimen. A cantilever mounted triangular plate, as shown in Fig. 10, is subject to a load P at the apex. The outer fiber stress is given by the expression,

$$\sigma = \frac{P \times h}{21}$$

Where

P = load at the apex, lb

x = distance from the apex along centerline of plate, in.

h = thickness of plate, in. and

$I = \frac{xh^3 \tan \theta}{6}$, the moment of inertia of plate cross section a distance x from the apex, and

θ = semi angle at the apex.

Preliminary experimental results from a series of tests performed on untreated specimens using the Tatnall-Krouse Sheet Fatigue Machine indicated that an outer fiber stress of 100,000 psi would produce failure in a reasonable time and in a relatively small number of cycles. At the same time this stress level was thought to be low enough so that recognition of the possible deteriorating effect of various coatings could be observed by a reduction in the specimen life. To maintain a constant stress level of 100,000 psi throughout the tapered beam, as calculated using the above formula, it was necessary to apply a 58.85 lb load at the apex.

To develop the required 100,000 psi outer fiber stress the fatigue specimen was inserted into the mounting block of the Tatnall-Krouse machine. The clamp, containing the pin for attachment to the end of the eccentric arm, was then fixed in place at the apex of the plate. A dead load of 58.85 lbs was placed on the plate and an electrical contact made near the apex of the deflected specimen using a standard machine fixture. The load was then removed and the eccentric arm connected to the clamp at the pin joint. The eccentric arm was then adjusted until the maximum displacement of the eccentric was just sufficient to energize the preset electrical contact described earlier. The electrical contact device was then removed. With this setting the machine would produce a specimen deflection corresponding to a 100,000 psi outer fiber stress in the material. For each revolution of the driving eccentric the specimen outer fiber stress would alternate from 100,000 psi tension to 100,000 psi compression and return. (See Fig. 11.)

Difficulties were encountered initially in obtaining consistent fatigue results. The problem of inconsistent data for some coated specimens was attributed to pin wear at the connecting rod clamp. This wear resulted in some reduced displacement and in generation of a lower than anticipated stress in the specimen. The pin wear problem was eliminated by rigidly clamping the pin and providing for the necessary rotation between the pin

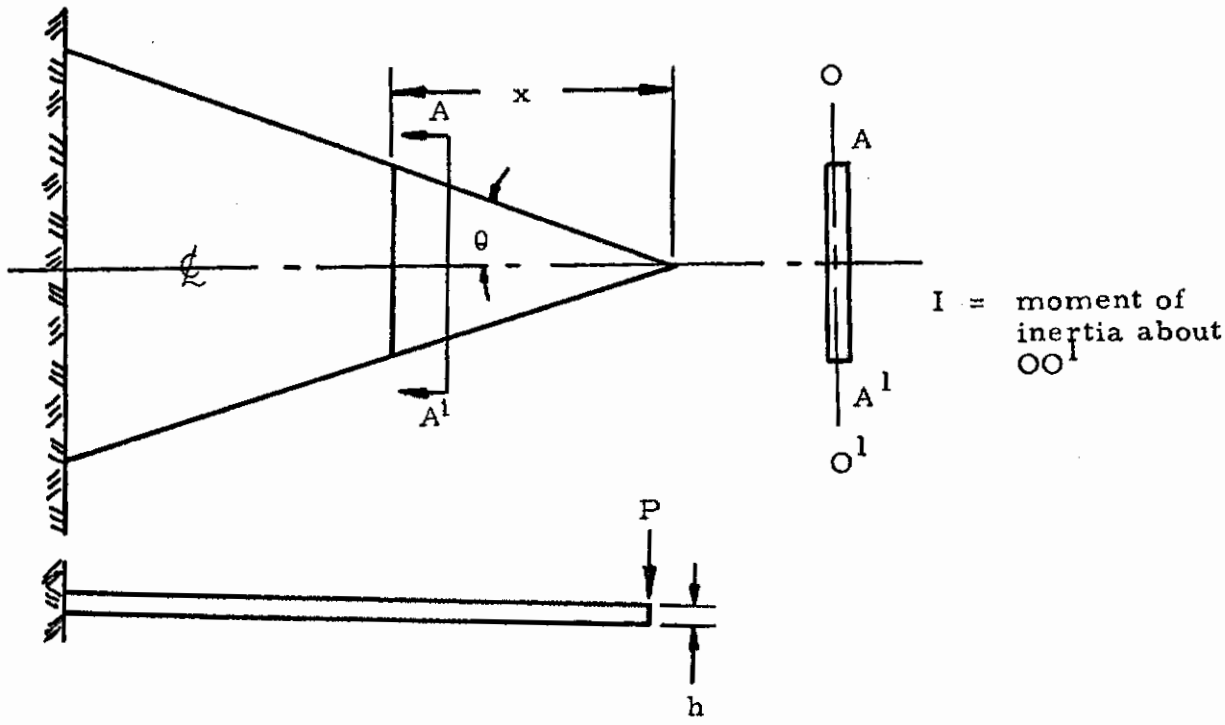


Fig. 10 TRIANGULAR CANTILEVER PLATE WITH CONCENTRATED LOAD AT APEX

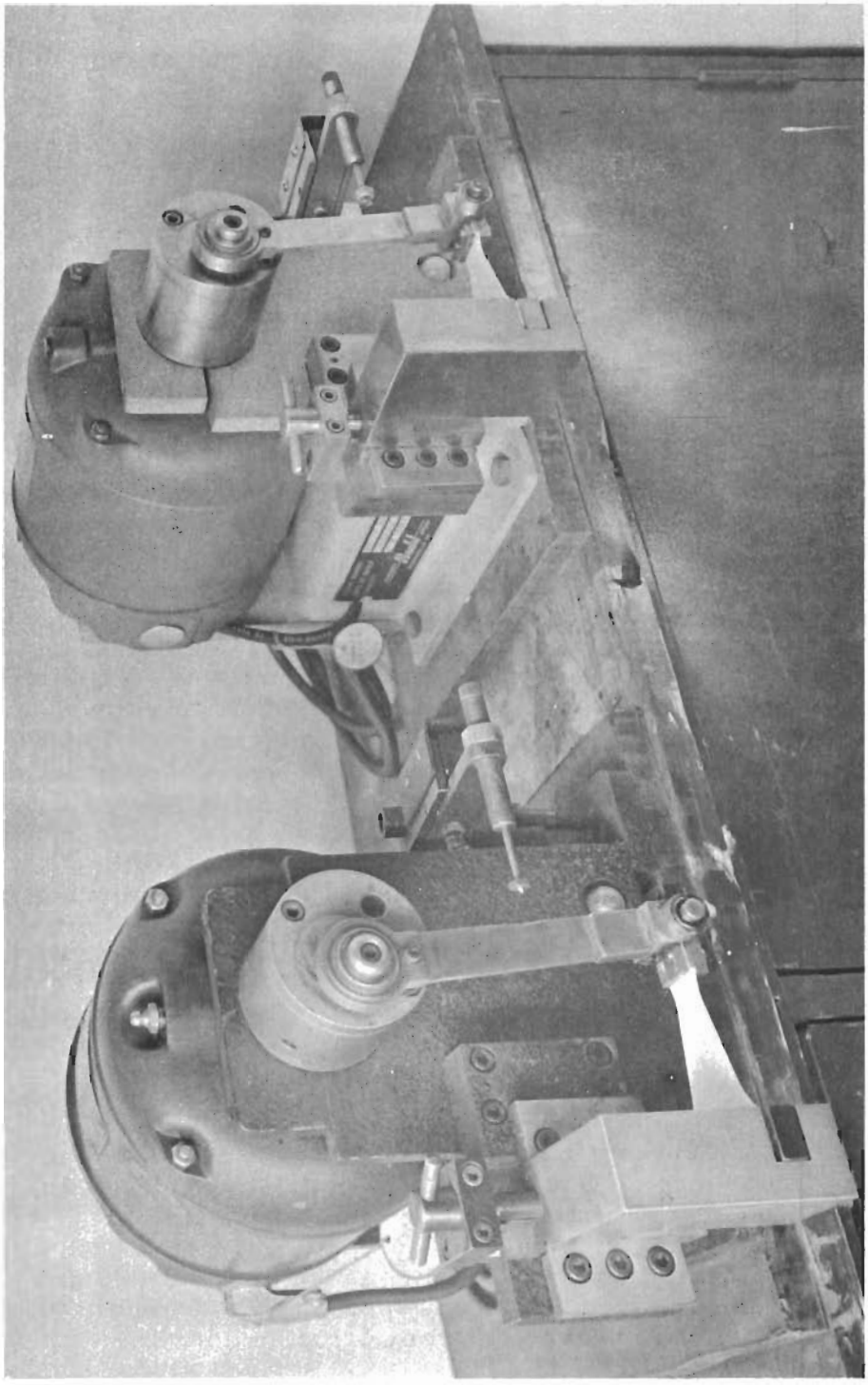


Fig. 11 MOUNTING OF SPECIMENS IN SHEET FATIGUE MACHINE

and reciprocating arm at a needle bearing connection. Following this modification consistent fatigue test results were obtained.

Initially three untreated specimens were run at the 100,000 psi stress level and failed after 85,600, 71,800 and 72,000 cycles respectively.

3. Embrittlement

Embrittlement studies were conducted in accordance with the methods described in WADC Technical Report 58-481 1/. Embrittlement specimens as shown in Fig. 3 were loaded in conventional creep machines utilizing standard calibrated weights and a lever system to develop a stress level at the notch of 300,000 psi. Specimens were maintained at this stress level for a period of 200 hours unless failure occurred prior to that time. In Fig. 12 the experimental setup used for loading the embrittlement specimens is shown. Embrittlement specimens are shown mounted in the two machines in the foreground of the illustration.

4. Thermal Change and Humidity

Thermal change and humidity studies were performed in accordance with Federal Test Method Standard Number 141, Method 6201 using specimens shown in Fig. 4a. All specimens were aged for a minimum of 168 hours after coating under ambient conditions prior to subjecting them to temperature and humidity cycling. The temperature and humidity cycling was performed for a 14 day period using a Weber Environmental Chamber Model No. WF 10-125-300H. The daily cycle consisted of 3 hours at -40°F and 0 percent humidity, 3 hours at 180°F and 0 percent humidity, and 18 hours at 120°F and 100 percent relative humidity. Reflectivity readings of the coatings were made prior to testing and after the specimens were removed from the environmental chamber. The equipment employed in taking reflectivity readings was a Photovolt Corporation Reflectometer Model 610.

5. Corrosion

Corrosion studies were conducted in accordance with Federal Test Standard 141 Method 6061 on specimens as shown in Fig. 4a. All specimens were subjected to 300 hours exposure in a twenty percent sodium chloride salt spray atmosphere. The specimens were suspended from rods by means of clips in a closed corrosion chamber maintained at 88°F. Figure 13 shows a view of the corrosion chamber. The specimens were spaced in such a manner that no contact between specimens was permitted, and that there was free settling of the sprayed fog on all specimens. In addition, the condensate from one specimen was prevented from dripping onto any other specimen.

1/ A New Look at the Hydrogen Embrittlement of Cadmium Coated High Strength Steels, by N. M. Geyer, G. W. Lawless and B. Cohen, Dec. 1958.

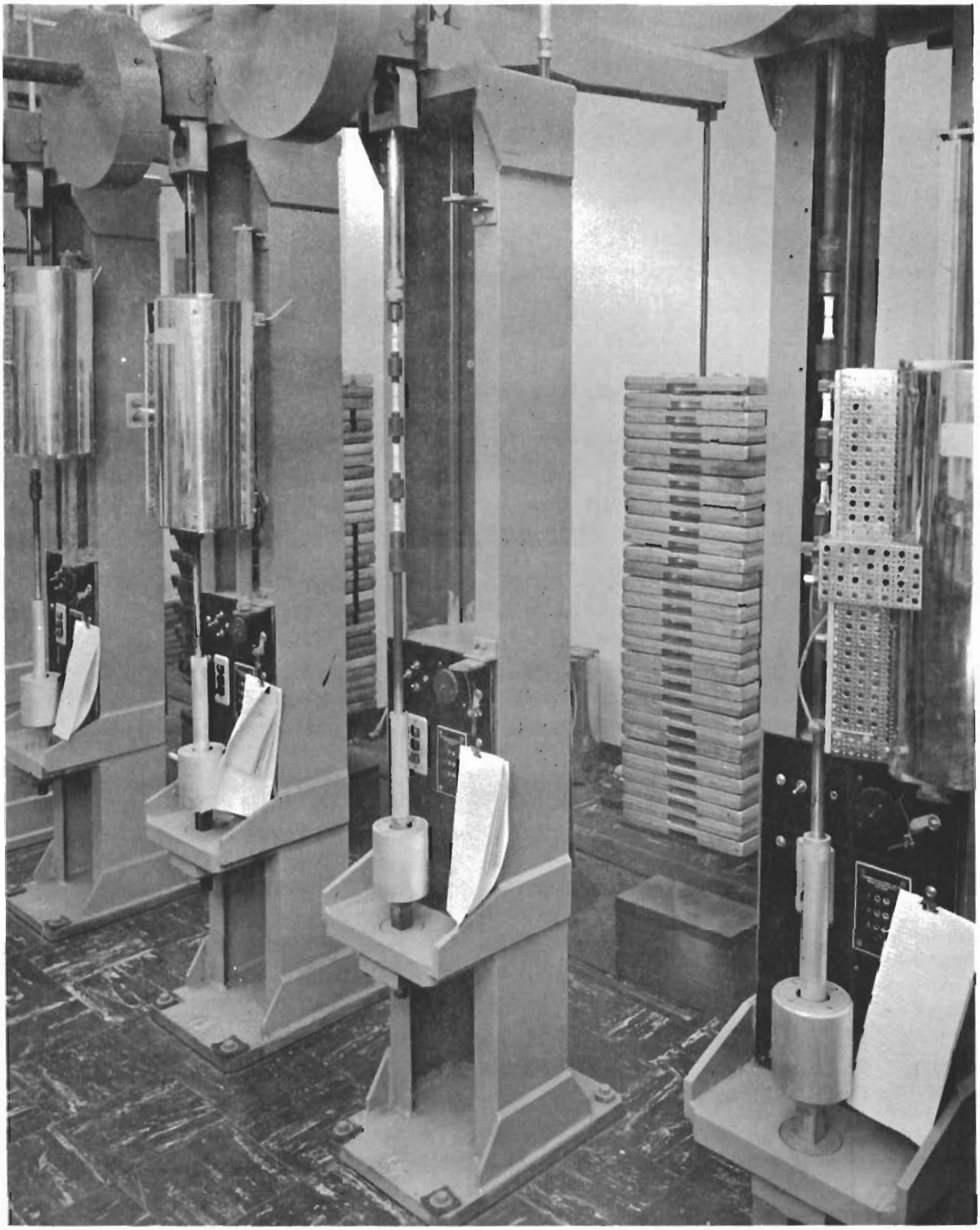


Fig. 12 SETUP FOR EMBRITTLEMENT STUDIES

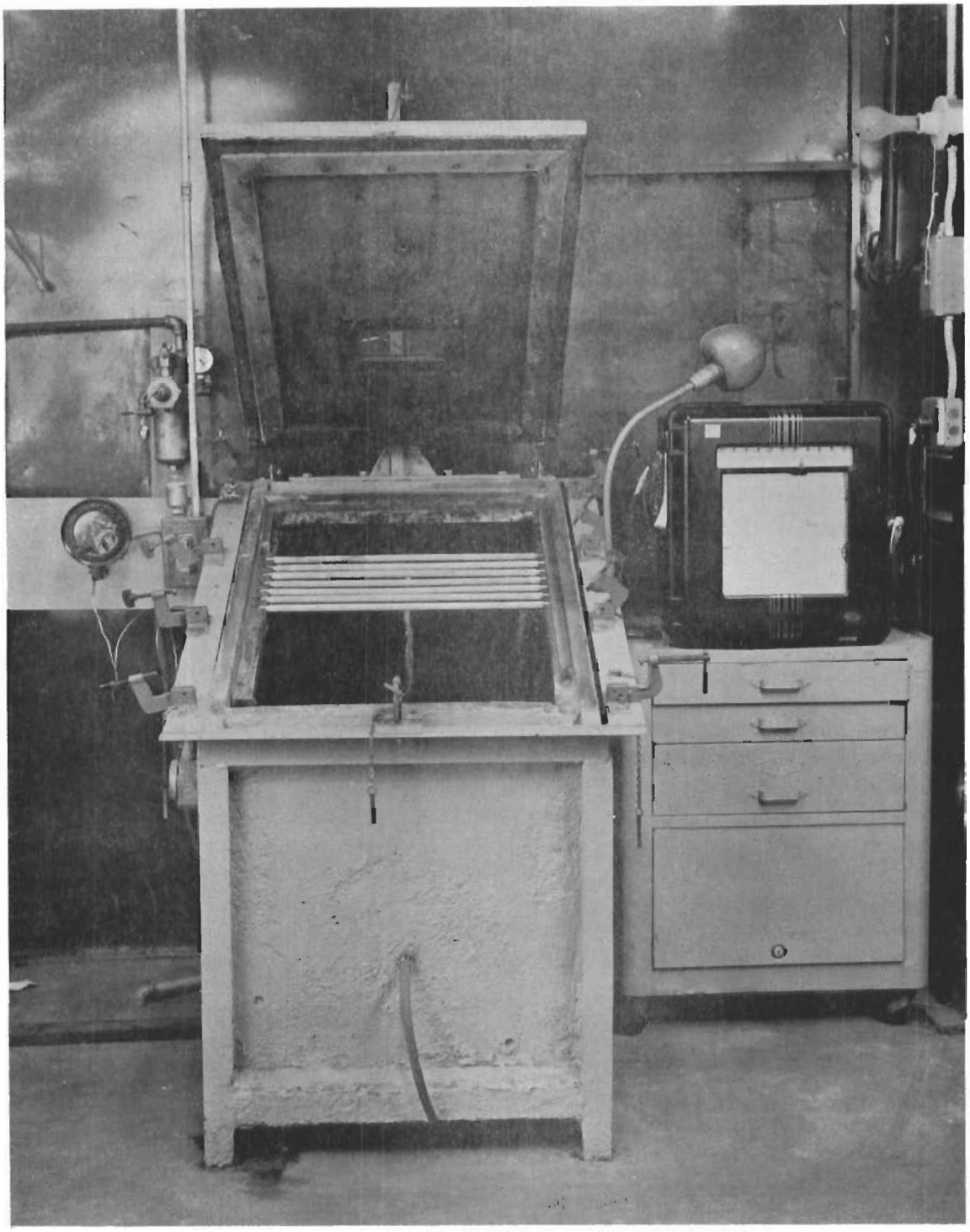


Fig. 13 CHAMBER USED IN CORROSION STUDIES

At the end of 300 hours the specimens were removed from the corrosion chamber and were visually examined for deterioration. Reflectivity readings were taken prior to exposure and immediately after the specimens were removed from the chamber as a means of observing the effect of corrosion exposure on specimen coatings.

6. Accelerated Weathering Tests

Accelerated weathering studies were performed in accordance with Federal Test Method Standard 141 Method 6152 on specimens shown in Fig. 4a. Specimens were exposed to accelerated weathering with the use of an Atlas Twin Arc Weatherometer illustrated in Fig. 14. The test was conducted over a period of 7 days and consisted of 5 days of exposure divided into consecutive 2 hour conditioning cycles followed by two days of undisturbed rest in the chamber. Each two-hour conditioning cycle consisted of 102 minutes of carbon arc light without water followed by 18 minutes of combined light with water spray. The black panel temperature used was $145^{\circ} \pm 5^{\circ}F$. To observe the effect of this exposure on coatings, reflectivity readings were made on all specimens before and after accelerated weathering cycling.

7. Flexibility

During the course of the program it was determined that the flexibility test described in Federal Test Method Standard 141 could not meet the requirements of this evaluation program. The heat treated SAE 4340 steel base material does not exhibit appreciable plastic deformation before fracturing. As a practical objection it is quite impossible to bend the specimens around a 1/4 in. diameter mandrel as prescribed in the above specification without fracture. Since it is the flexibility of the coating which is in question, it was decided to test specimens as simply supported beams loaded at mid-span using 1/4 in. diameter rods on the loading member contacting the specimen. After some experimentation the span length was increased to 3 in. to produce increased specimen deflection for a given load. At this span a 1000 lb load produced a mid-span deflection of approximately one quarter in. with some slight permanent set remaining upon removal of load. The loading rate used was 0.2 in./min. Loads were applied to obtain incremental specimen deflections. Specimens were removed from the loading fixture and were examined for cracks after being subjected to deflections of 0.250 in., 0.375 in., 0.500 in., 0.700 in., 0.800 in., 0.850 in., and 1.000 in. The examination for cracks was made with a microscope with a 20X magnification. Using this approach, cracking was observed in some of the specimen coatings. For those specimens where the loading imposed did not crack the coating, loading was continued and evaluation was based on the maximum allowable deflection achieved without coating failure.

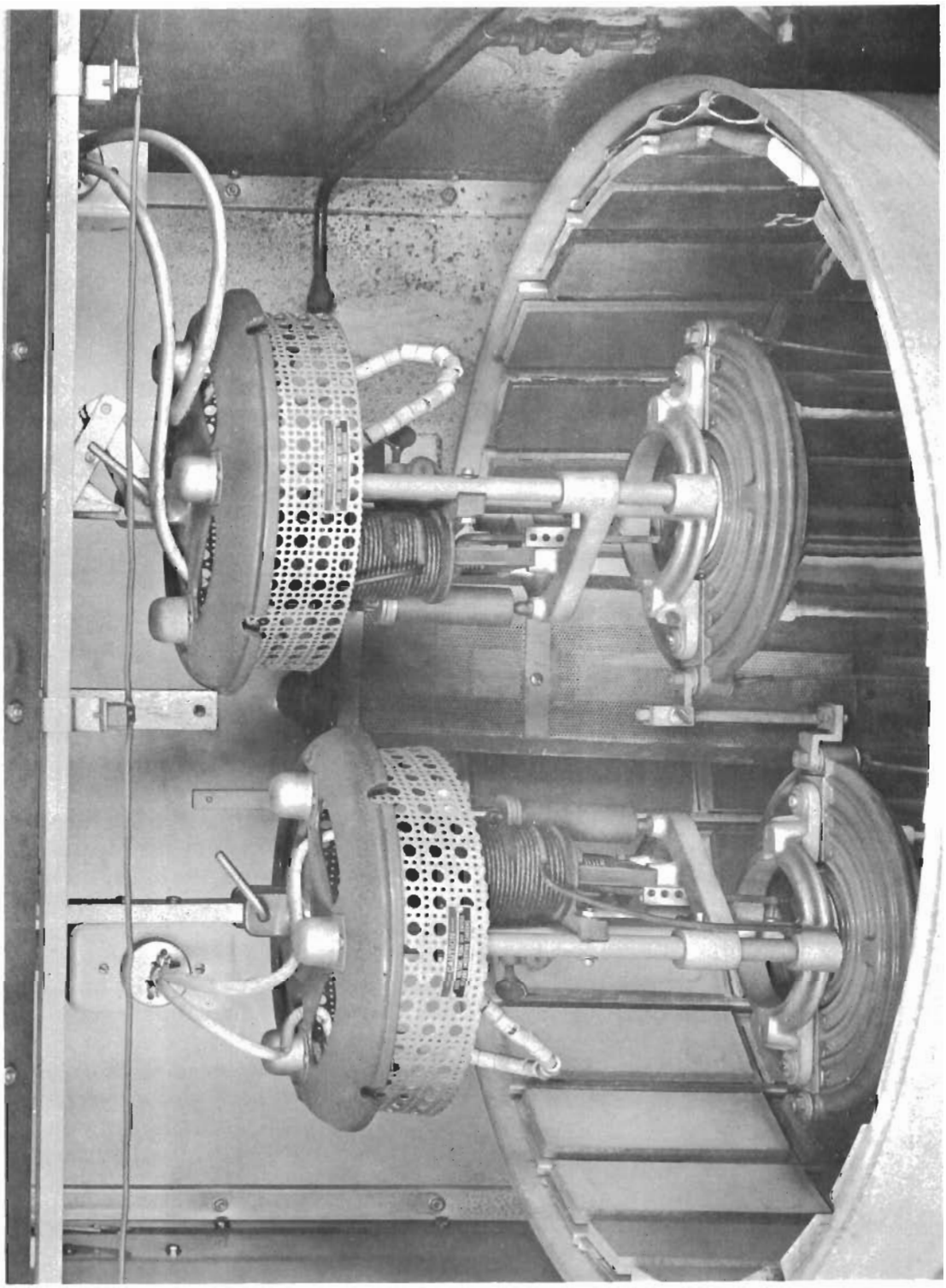


Fig. 14 TYPICAL VIEW OF ATLAS TWIN ARC WEATHEROMETER USED IN ACCELERATED WEATHERING STUDIES

8. Abrasion

Abrasion resistance studies were conducted in accordance with Federal Test Method Standard 141 Method 6192 on specimens shown in Fig. 4b. The specimens were fastened to the rotating table of the Taber Abraser apparatus shown in Fig. 15, and subjected to abrasion using CS-10 Calibrase wheels. The 250 gram load on the wheel was obtained using standard machine weights.

The specimens were weighed to the nearest 0.1 milligram after thermal change and humidity cycling and before being subjected to abrasive wear. After the required number of cycles (1000 cycles), or when the coating had worn through to the substrate, the specimen was reweighed and the change in weight and the number of cycles recorded.

9. Adhesion Tests

Adhesion studies were performed in accordance with Federal Test Method Standard 141 Method 6302 using specimens shown in Fig. 4c. These studies were performed with the Arco Microknife equipment shown in Fig. 16. Eleven parallel lines 1/32 in. apart were cut in each of two perpendicular directions on all specimens except those epoxy coated specimens prepared by fluidized bed, and those top coated with the polyurethane enamel. In the case of the epoxy fluidized bed coating, the coating was extremely thick and brittle which did not permit cutting lines closer than 1/8 in. apart. In the case of the polyurethane enamel it was generally not possible to cut two parallel lines, for the toughness and thickness of the coating induced so much resistance to the cutting action of the knife that the coating tore rather than cut. The polyurethane had enough affinity for the primer that the loss in adhesion for specimens coated with this system occurred between the metal and the primer.

The number of squares which broke completely away from the surface were counted and subtracted from the total number of squares cut into the coating (100 squares). If an entire square did not lose adhesion and break away it was counted as if it were still adhering to the surface.

10. Stress-Corrosion

The specific method to be used for investigating coating performance under stress-corrosion was not defined in advance. Rather, a method was to be suggested by ARF for consideration and approval by the Program Monitor after some preliminary experimentation had been performed on the program. On the basis of such work the following stress-corrosion study was suggested and approved for use on the program.

a. Fixtures accommodating either one or two specimens per fixture could be used.

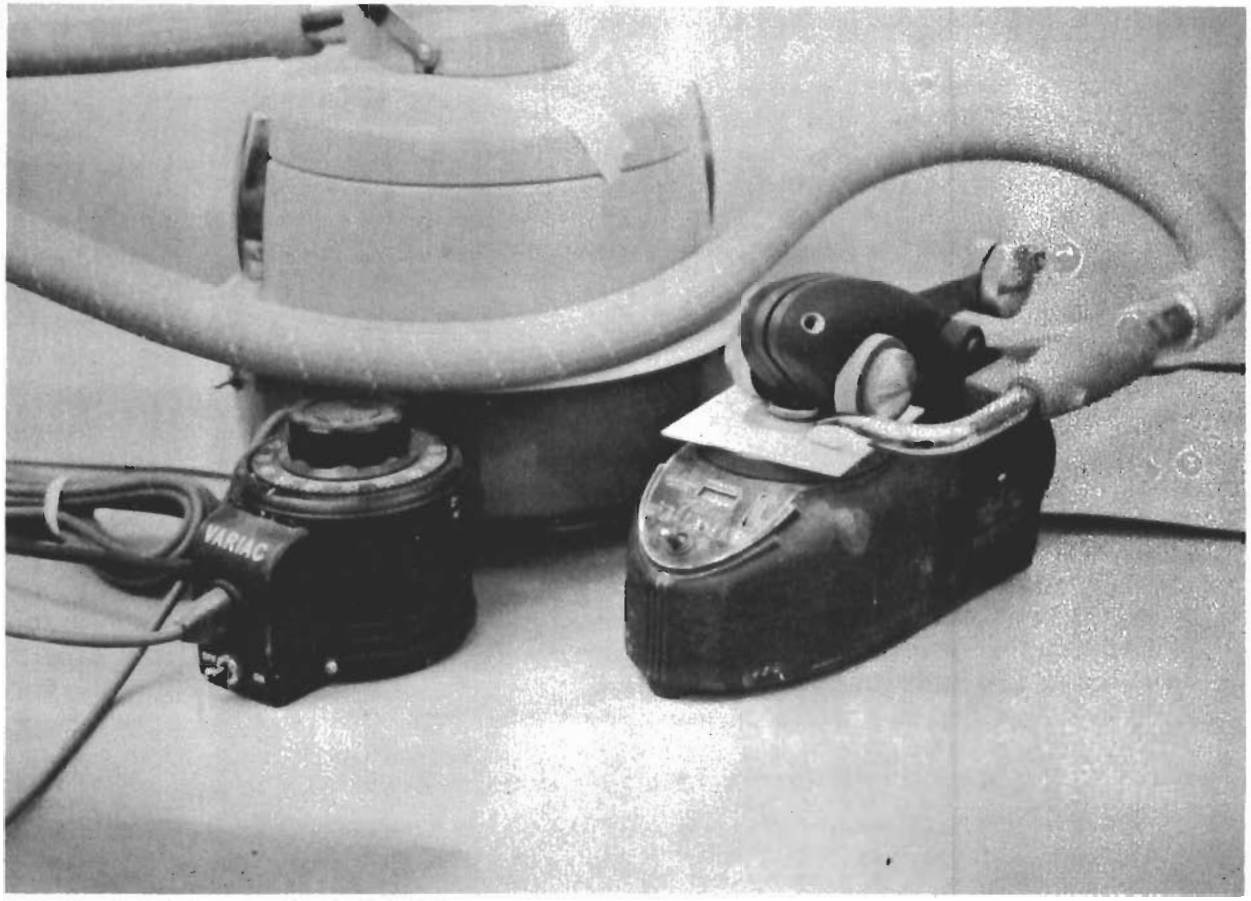


Fig. 15 TABER ABRASER EQUIPMENT USED IN ABRASION STUDIES

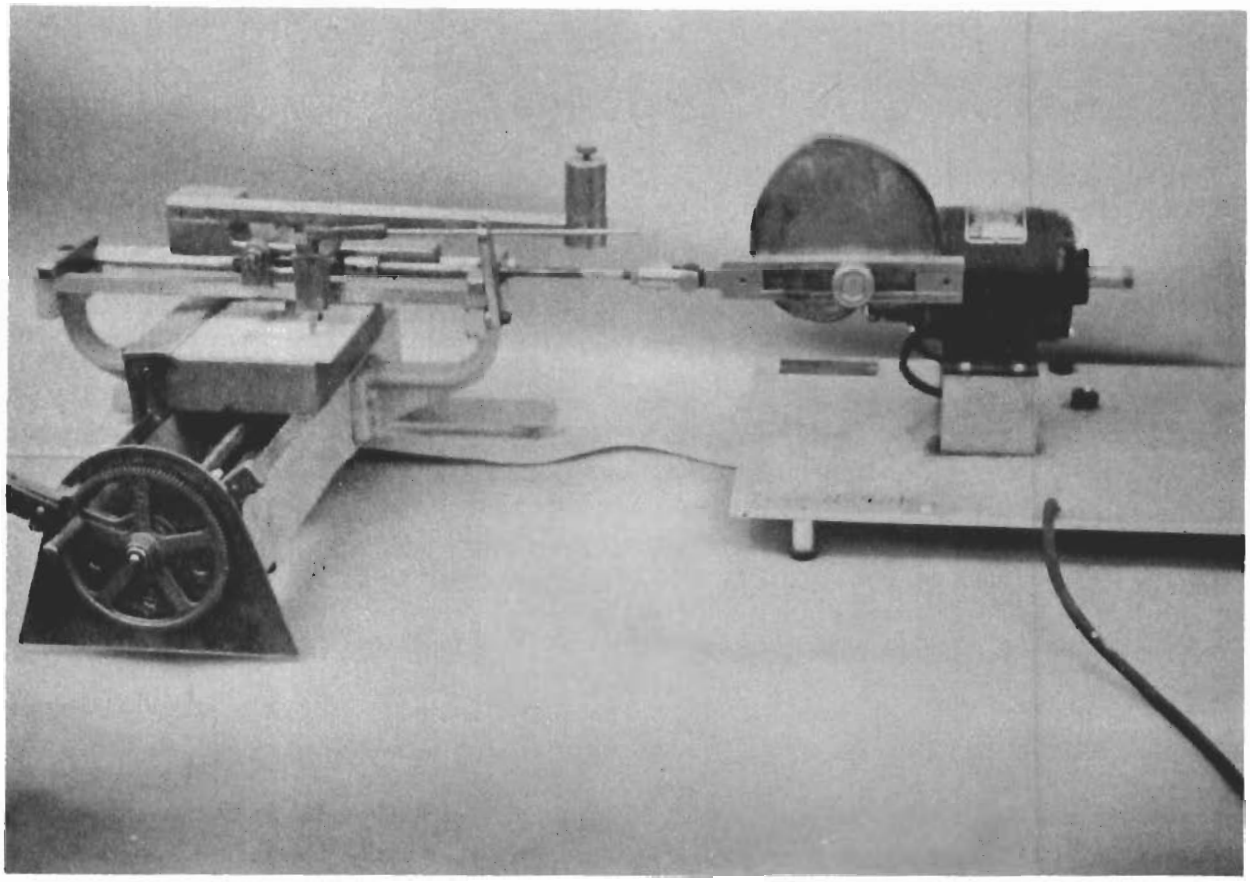


Fig. 16 ARCO MICROKNIFE EQUIPMENT USED IN ADHESION STUDIES

b. Expose specimens to spray of saturated solution of calcium nitrate [1/] while maintaining a chamber temperature of 88°F.

c. Expose specimens to combined stress-corrosion environment for a test period of 7 days (168 hours).

d. Subject all specimens to a stress level of 225,600 psi, 80 percent of the average ultimate tensile strength of the material. (Arc height of 0.091 in. for a 2-in. central chord length.)

e. Monitor specimen life by use of a continuity circuit and a thermocouple recorder to provide print out data for establishing the time of specimen failure.

The stress-corrosion tests were performed with specimens shown in Fig. 4c and with bend fixtures shown in Fig. 17. The same chamber was used for this work which earlier was utilized for the salt spray corrosion study. With both the single and double specimen type fixtures, the adjustment of nuts on threaded rods served to load the specimens as pin-ended columns. With this apparatus it was a simple matter to produce the desired amount of bending in the specimens.

To permit close adjustment of the stress developed in the specimen and thus prevent any overstressing, the fixture shown in Fig. 18 was developed for directly measuring the arc height of deflected specimens over a 2 in. chord length. The arc height, d, was found as follows:

If ρ is the radius of curvature at the beam center, ϵ is the strain in the outer fiber, and h is the thickness of the beam we have

$$\rho = \frac{h}{2\epsilon}$$

Then by Hooke's law, since $\epsilon = \sigma/E$ we have $\rho_{\text{outer fiber}} = h/2\,(1 + \frac{E}{\sigma})$. The height, d, of a circular arc whose radius $\rho_{\text{outer fiber}}$ and whose chord length is L, is given by

$$d = \rho_{\text{outer fiber}} - \sqrt{(\rho_{\text{outer fiber}})^2 - (\frac{L}{2})^2}$$

Table VI gives calculated arc height values from a two inch chord length for various ratios of outer fiber stress to ultimate tensile strength. These ratios are based on an average ultimate tensile strength of 282,000 psi for the base material.

[1/] Calcium Nitrate was selected on the basis of discussions with our metalurgists and because of its known ability to attack low alloy steels; see for example R. A. Davis "Investigation of Susceptibility of High Strength Martensitic Steel Alloys to Stress Corrosion" Q.P.R. No. 11, June 30, 1961, Contract AF 33(616)-7839, page II-20. Calcium Nitrate is also readily available in large quantities at reasonable cost in a form suitable for stress-corrosion work.

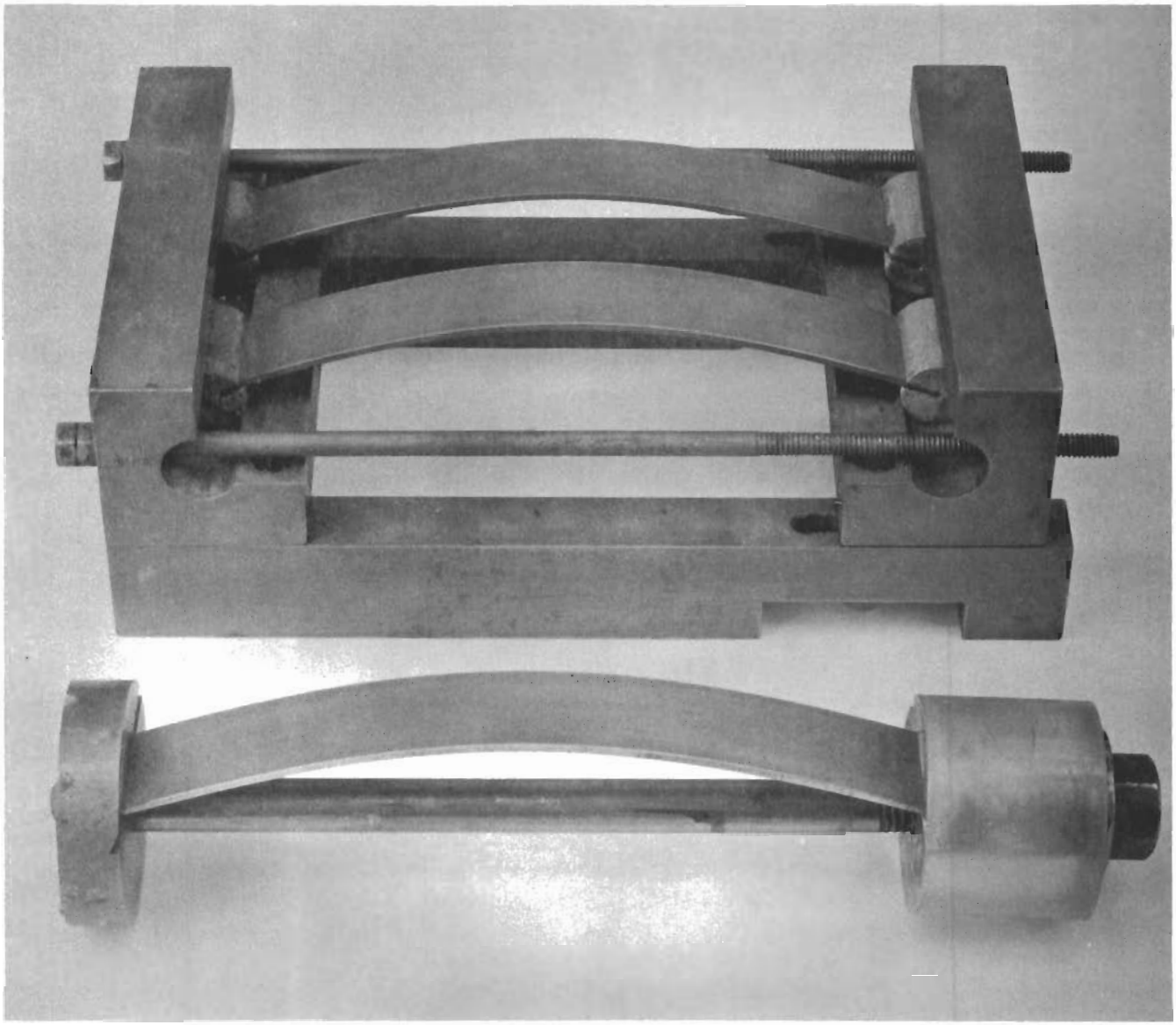


Fig. 17 STRESS CORROSION BEND TEST FIXTURES

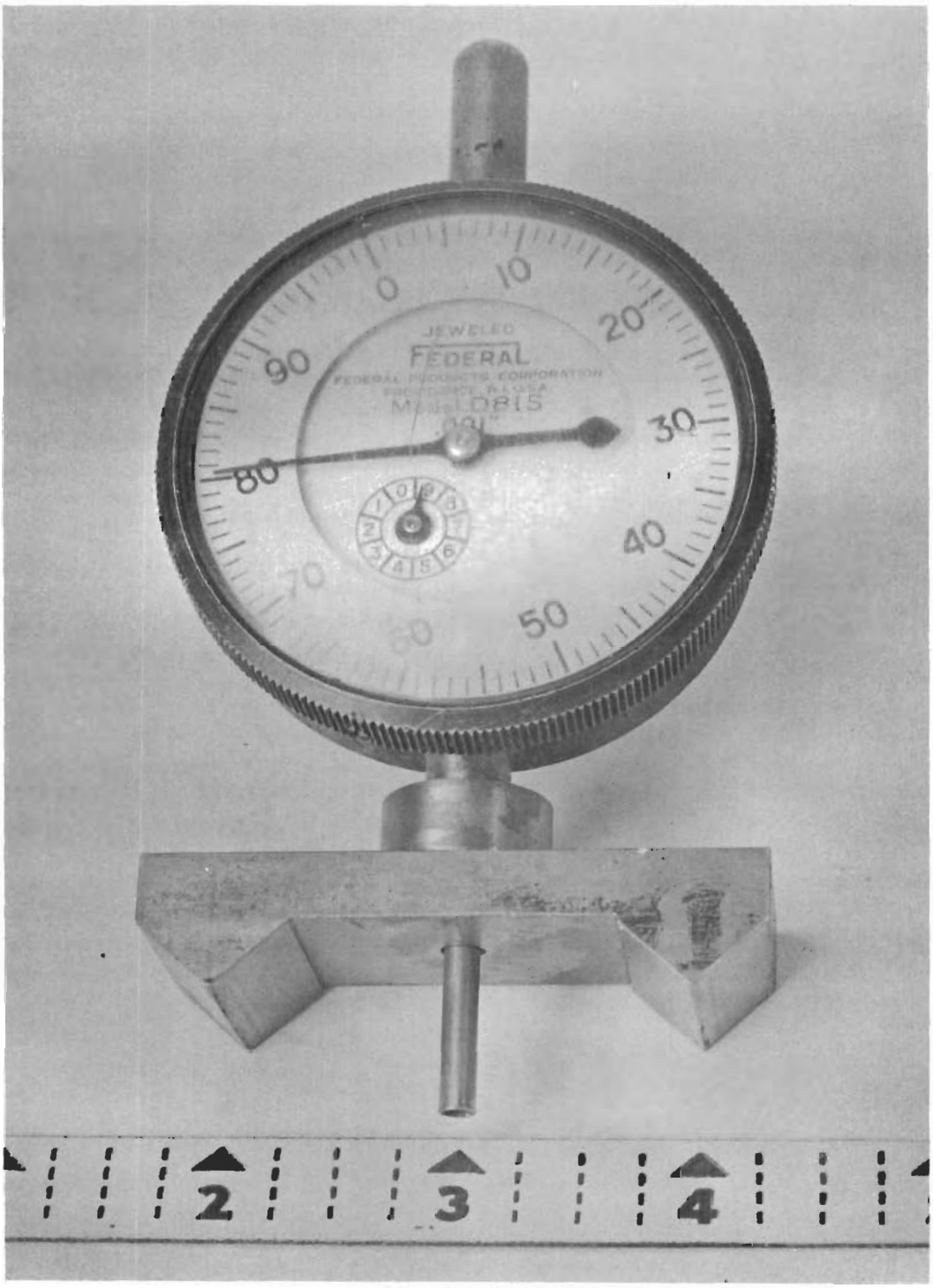


Fig. 18 GAGE FOR MEASURING SPECIMEN ARC HEIGHT

Table VI

STRESS-CORROSION SPECIMEN
ARC HEIGHT FOR VARIOUS STRESS RATIOS

σ/σ_{ult}	d (in.)
0.65	0.073
0.70	0.078
0.75	0.085
0.80	0.091
0.90	0.102

For the stress-corrosion study it was necessary to maintain a stress level high enough to produce failure of unprotected specimens in a relatively short time period. However, it was also necessary to keep the stress level low enough so that large strains in the outer fibers of the specimen would not cause cracking of the coatings applied. Such cracking would permit the corrosive media to freely attack the specimen and result in premature failure.

The exact conditions under which subsequent stress-corrosion work was to be performed was the subject of preliminary experimentation. Uncoated specimens were stressed to various levels and exposed to the calcium nitrate spray environment. The various stress levels used for that preliminary work, the arc height observed, and the time period to failure are presented in Table VII. This preliminary study was undertaken primarily to obtain rough estimates of the time to failure and consequently the results should be interpreted with this understanding. Since only one datum was available at each stress level, the results shown can only represent approximate values. Note, for example, that the time to failure for the 80 percent stress level is less than the time to failure for the 90 percent stress level. For more accurate times to failure a statistical approach would have to be undertaken. This was felt to be unnecessary and a stress level of 80 percent of ultimate tensile strength was selected for all subsequent stress-corrosion work.

After loading the specimens to the desired curvature, the fixtures were placed in the stress-corrosion chamber and a saturated calcium nitrate solution mist was continuously sprayed over the specimens. The chamber temperature was maintained at 88°F by means of resistance heaters. The specimens were retained in this state until they had either failed or a period of 7 days (168 hours) had elapsed.

Table VII

TIME TO FAILURE FOR
UNCOATED STRESS-CORROSION SPECIMENS
FOR VARIOUS STRESS INTENSITIES

σ/σ_{ult}	Arc height (in.)	Time to Failure (hrs)
0.65	0.073	89
0.70	0.078	88
0.80	0.091	37
0.90	0.102	52

The following technique was devised to permit observation of the exact exposure time at specimen failure. Using a twelve channel Leeds and Northrup Micro-Max Temperature Recorder, 12 electrical circuits were set up incorporating a stress-corrosion specimen in each. This was accomplished by scraping off a small area of coating near the two ends of the specimen and welding leads to the specimens in those low stress areas. One end of the stress-corrosion specimen was mounted on an insulating plastic base to prevent grounding of the specimen through the fixture frame. Such grounding would prevent an open circuit from developing upon specimen failure which is necessary to the successful operation of this inspection technique. The areas where the thermocouple leads were affixed to the specimen and the entire fixture base was coated with wax to prevent deterioration of the welded leads and the fixture in the corrosive atmosphere. Figure 19 shows both single and double specimen fixtures in the chamber with thermocouple leads attached.

During stress-corrosion testing the Micro-Max Recorder was operated and cycled continuously, thereby recording the continuity of each of the twelve circuits. When failure of a specimen occurred, the resulting open circuit caused the printer head to move to one end of the scale where it would print. If this happened when unattended, the printed record of failure permitted the time of failure to be accurately determined from the test starting time, the length of chart exposed, and the chart speed.

The recorder used to monitor failures was a twelve channel type. Since there were a total of forty-eight stress-corrosion specimens to be tested, it was necessary to repeat the test a total of four times. This was done by testing only one sample at a time of a particular coating type and testing the three samples each of the sixteen coating systems in four successive test runs.

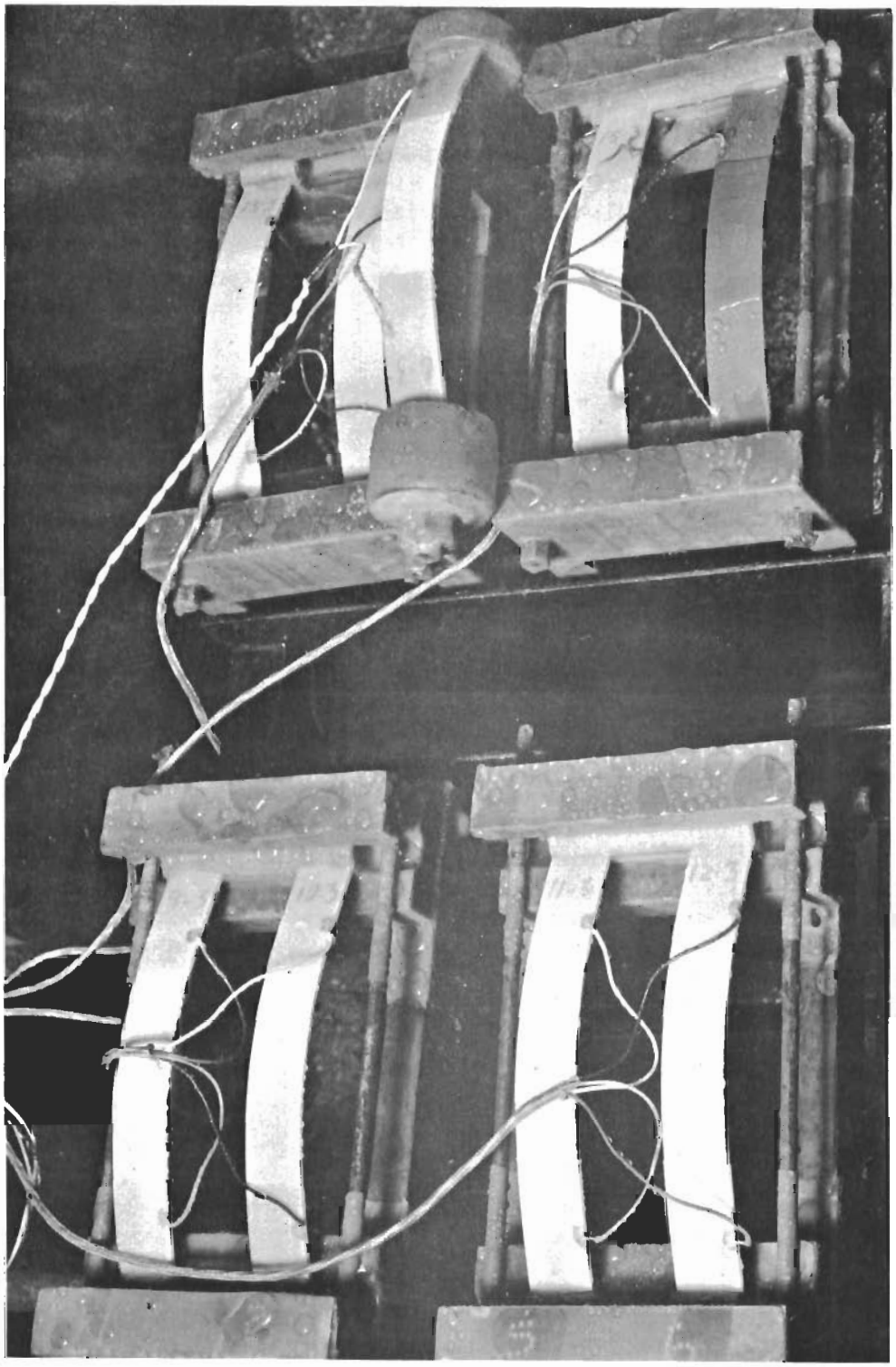


Fig. 19 VIEW OF STRESS-CORROSION SPECIMENS UNDER TEST SHOWING SINGLE AND DOUBLE SPECIMEN FIXTURES

VI. EXPERIMENTAL RESULTS, SUMMARY AND DISCUSSION

The results obtained from the experimental studies described in the previous chapter are summarized and presented here in tabular form. This presentation is made to facilitate comparison of protective coating systems on the basis of (1) mechanical property determinations of the substrate and (2) environmental-mechanical tests of the coatings.

A. Control Tests

The control test series included tension, fatigue and embrittlement studies and were performed on untreated, pretreated, primer coated and enamel coated specimens. Control tests also were performed on coated specimens subjected to thermal change and humidity followed by corrosion. Average test results obtained from untreated specimens evaluated in the as received condition, were considered as the datum to which other results were referred for comparison.

1. Tension

The three untreated specimens tested to determine the ultimate tensile strengths of the substrate gave values of 279,000, 285,000 and 282,000 psi respectively for an average tensile strength of 282,000 psi. In Table VIII this average value is identified as system "O", no pretreatment. The average tensile strength values determined for specimens with pretreatments or partial coatings applied are identified I through IX in that table. Tensile strengths of specimens with complete coating systems applied are identified by coating system numbers 1 through 16. The range of tensile strengths for all specimens not environmentally conditioned was from a minimum of 278,000 to a maximum of 297,000 psi for a percent variation of -1.47 to +5.3 related to the 282,000 psi datum value. However, the average percent variation was -0.57 to +1.5 with respect to the 282,000 psi stress level.

Results obtained from tension specimens tested after thermal change and humidity exposure followed by corrosion are also presented in Table VIII. Values of tensile strength of such specimens ranged from 279,000 psi to 294,000 psi for a percent variation of -1.06 to +4.25 compared to the untreated specimen results. Again, the average percent variation of -0.89 to +1.47 was considerably less than the maximum variation reported.

It is apparent from observation of the values reported that tensile strength data does not provide a satisfactory basis for evaluating performance of the coating systems investigated. The variations in tensile strength observed are of the order to be expected cumulatively as a result of material and heat treat variations between specimens and experimental error. While this is a negative result, it permits us to conclude that none of the coating system pretreatments, primers or enamel topcoats investigated has any significant effect on the ultimate tensile strength of SAE 4340 steel.

Table VIII

SUMMARY OF TENSION, FATIGUE AND EMBRITTLEMENT RESULTS

Reported values are averages of three tests unless otherwise noted

Environmental Conditioning	Tensile Strength lb/sq in.		Fatigue Life Cycles to Failure		Embrittlement Hours at 300,000 psi Tensile Stress	
	None	Thermal Change - Humidity and Corrosion	None	Thermal Change - Humidity and Corrosion	None	Thermal Change - Humidity and Corrosion
O	282,000	-	76,500	-	200	-
I	291,000	-	102,000	-	220	-
II	289,000	-	87,400	-	220	-
III	281,000	-	72,100	-	240	-
IV	286,000	-	139,100	-	210	-
V	281,000	-	97,200	-	360 1/*	-
VI	283,000	-	83,000	-	210	-
VII	283,000	-	65,400	-	300	-
VIII	290,000	-	82,600	-	210	-
IX	288,500	-	73,400	-	210	-
1	283,500	288,000	152,500	103,500*	220	210
2	284,000	289,000	376,000*	111,600	210	210
3	284,000	284,000	137,900	144,100*	220	210
4	290,000	283,000	204,900	108,800*	210	210*
5	290,000	279,000	145,500	227,100*	270	240
6	281,000	284,000	243,350	82,670	300	230
7	278,000	286,000	74,700	57,350*	260	240
8	289,000	285,000	95,900	62,650*	260	260
9	286,000	294,000	92,400	56,950*	260	240
10	285,000	287,000	86,900	63,300*	210	240
11	286,000	286,000	96,300	96,600*	220	240
12	286,000	284,000	96,100	72,700*	210	240
13	281,000	288,000	136,000*	164,500	210	240
14	291,000	285,000	156,400	160,500*	210	240
15	297,000	283,000	170,200	99,300*	210	220
16	284,000	280,000	170,200	123,400*	210	220 2/*

* Average of two specimens.

1/ One failure after 369.6 hours.

2/ One failure after 33.9 hours.

2. Fatigue

The results of fatigue tests are also summarized in Table VIII. Results are presented as the average number of cycles to failure for three specimens tested per condition. This includes various pretreatments, application of partial or complete coatings, and fatigue results for coating systems 1 through 16 after environmental conditioning by thermal change and humidity followed by corrosion exposure. The average number of cycles to failure for untreated specimens tested in the as received condition was 76,500 and served as the datum from which fatigue performance of all other specimens was judged. Because of the inherent spread of fatigue test results, it is not appropriate to draw positive conclusions regarding performance of individual coating systems. In this regard one can observe the apparent large drop in fatigue performance for systems 2, 4, 6 and 15 after environmental conditioning. It is more realistic to assume that these performances can be attributed to normal fatigue data scatter. However, conclusions can be drawn from the general performance of groups of specimens similarly treated.

The bar graph shown in Fig. 20 provides a visual representation of specimen fatigue life for all coating systems. For coatings 1 through 16 the shaded portion presents fatigue life of specimens after thermal change and humidity followed by corrosion exposure.

It can be readily noted from this graph that, in general, the fatigue performance of the substrate appears to depend on the pretreatment which it has received. Examining the performance of specimens with pretreatments and partial coatings (systems I through IX) it is evident that systems I, IV and V which have been sand blasted have a higher fatigue life than those systems which incorporate phosphoric acid etch in their preparation. Average cycles to failure for all sand blast specimens in these three groups is approximately 112,800. For the six pretreatment systems employing phosphoric acid etch, the average number of cycles to failure is approximately 77,300.

For coating systems 1 through 16 a similar effect can be noted, although here the number of cycles to failure for sand blast treated specimens is greatly increased over those of systems I, IV and V. This is most likely a result of slight differences in the sand blast exposure of specimens. In this regard it should be remembered that a slight difference in surface compressive stress induced by sand blasting can have a rather strong influence on specimen fatigue life.

Comparing sand blast treated specimens of coating systems 1 through 6 and 13 through 16, with the phosphoric acid etch treated specimens of coating systems 7 through 12, the higher fatigue performance of sand blast treated specimens is very clear. This is a demonstration of a side benefit to be gained from sand blast cleaning, and is another manifestation of the well

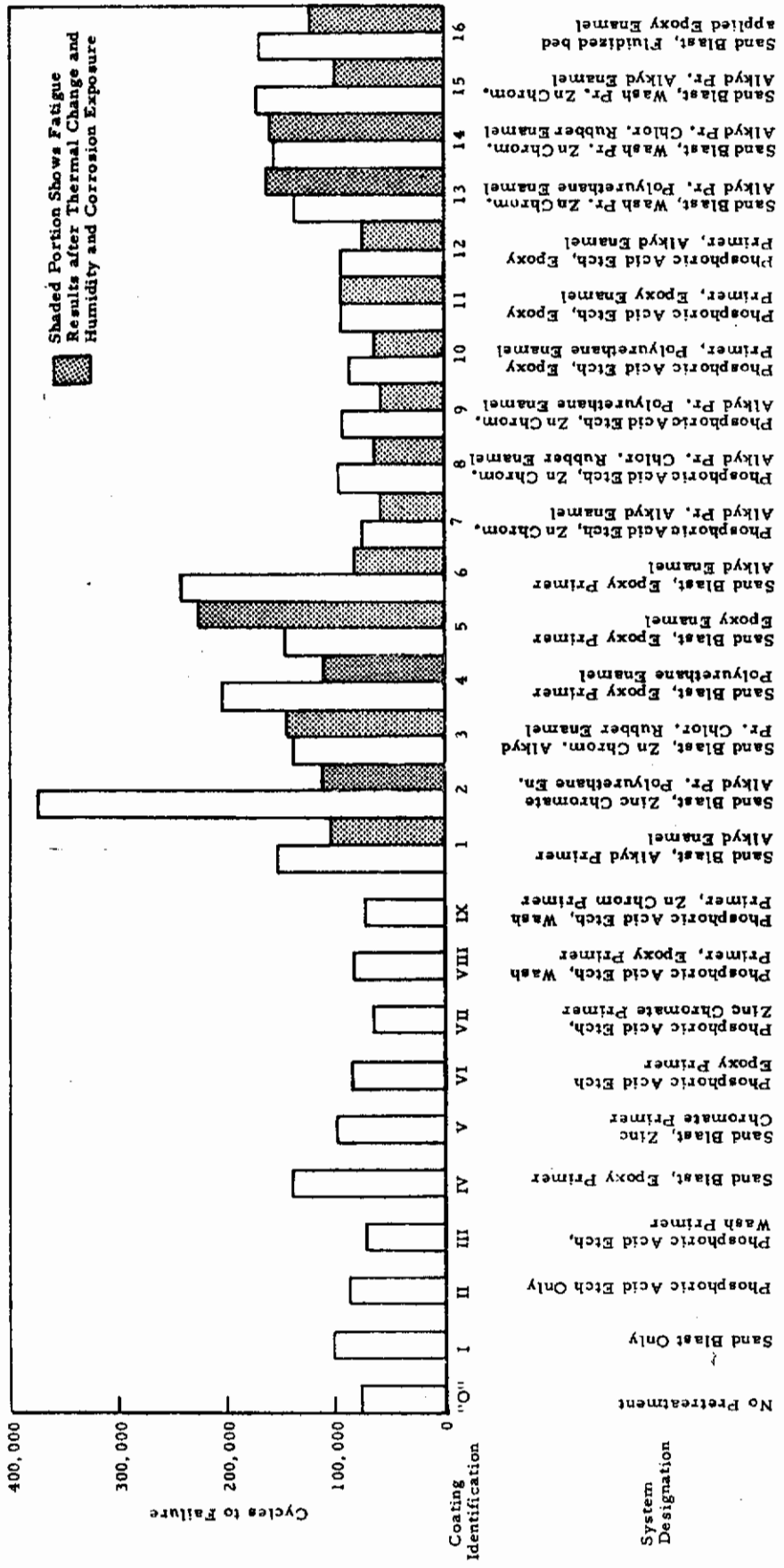


Fig. 20 GRAPHICAL REPRESENTATION OF ALL FATIGUE RESULTS

known effect which sand blasting and shot peening of metal has on fatigue performance [1].

It should not be inferred from the above that phosphoric acid etch is not a satisfactory method of metal treating prior to application of coatings. Comparing the fatigue life of untreated specimens "O" with the life determined for specimens coated using systems 7 through 12, (which incorporate phosphoric acid etch pretreatment) reveals no general reduction in performance with acid etch treatment. In fact, the average fatigue life of unconditioned specimens for coating systems 7 through 12 is 90,400 cycles compared to 76,500 for untreated specimens (system O).

The average fatigue life of specimens protected by complete coating systems 1 through 16 subjected to thermal change and humidity conditioning and corrosion exposure prior to testing is shown in Table VIII and Fig. 20. These results are generally difficult to interpret with regard to specific coating performance. If the coating system provides complete protection against the environmental exposures imposed it would be reasonable to expect that fatigue life would be approximately the same as for the same specimen tested without conditioning. A reduction in specimen fatigue life after environmental exposure may indicate a possible deficiency of the coating and may suggest some porosity of the system permitting admission of the exposure elements that may have an adverse effect on specimen performance. While there are a considerable number of such instances with the coatings studied, the significance of the effect observed is difficult to assess in view of the various pretreatments, primers, and enamel topcoats making up the coating systems. We are unable to advance any reason for the appreciable improvement in fatigue life of environmentally conditioned specimens of coating system 5. The slight improvements shown in Fig. 20 with systems 3, 11, 13 and 14 are not thought to be significant and are associated with the normal scatter of such experimental results.

3. Embrittlement

Embrittlement specimens prepared without pretreatment, with pretreatment and partial coating systems identified I through IX, and with complete coating systems 1 through 16 were tested at a notch tensile stress of 300,000 psi for a minimum 200 hour period. In addition, embrittlement specimens were prepared with complete coating systems 1 through 16 applied and subsequently exposed to thermal change and humidity followed by corrosion before testing. The results of this work is also summarized in Table VIII.

As indicated above the required duration of embrittlement tests was 200 hours. However, in Table VIII periods longer than 200 hours are reported. This results from the fact that test termination at 200 hours frequently occurred during non-working hours, such as at night or during week

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[1] See for example H. F. Moore, "Shot Peening and the Fatigue of Metals", published by American Foundry Equipment Co., Mishawaka, Ind., 1944.

end periods, consequently specimens were not removed until later and the actual test duration period is reported.

The results of the embrittlement tests performed do not reveal any tendency of the treatments or coatings systems to induce detrimental metal embrittlement. During the 200 hour test period only one specimen failure occurred. That failure occurred for one specimen to which coating number 16 had been applied and which had been subjected to thermal change and humidity followed by corrosion exposure. The remaining two specimens of that group both withstood the 300,000 psi notch tensile stress for 220 hours without failure. The only other failure experienced was with one specimen of partial coating system V, prepared with sand blast pretreatment and a zinc chromate primer coating. Continued testing of that system had reached almost 370 hours before failure was obtained, almost twice the minimum required test period.

The embrittlement studies permit one to conclude that, for the tests performed, no tendency was observed for any of the pretreatments, partial or complete coating systems investigated to induce embrittlement in SAE 4340 steel.

B. Environmental-Mechanical Studies

The environmental-mechanical test series was performed in its entirety on the 16 complete coating systems, as shown in the flow chart of Fig. 9. Of this test group a number are environmental tests which were performed to determine the effect of a specific environment on coating performance. The results of such tests must frequently be assessed by visual observation and inspection. Consequently such results are frequently highly subjective and are not precisely defined. Wherever possible, definitive measuring systems were utilized for evaluating environmental effects in an attempt to overcome the subjective character of coating inspection. Where mechanical type tests are involved, usually the test results are in a form which can generally be compared without difficulty. In the environmental-mechanical studies both types of evaluation are involved.

1. Thermal Change and Humidity, Corrosion and Accelerated Weathering

The 16 coating systems under study were each subjected to an investigation of the effect of (a) thermal change and humidity, (b) corrosion, and (c) accelerated weathering. For each of these three tests a set of specimens from each coating system was exposed to the required environment as described earlier.

Visual inspection served as the means of assessing the effects of such exposure on the ability of the coating to afford protection to the substrate.

In addition, the combined environmental effect of specimens subjected to thermal change and humidity followed by corrosion, and to thermal

change and humidity followed by accelerated weathering was investigated. The effect of such combined exposure on coatings was also studied by means of visual examination of the specimens.

Visual specimen inspection results are not tabulated for individual coating systems exposed to various environments. Rather, observations are made regarding the visible effects of a particular environment on coatings generally. Thermal change and humidity conditioning causes some darkening of coatings because of the heating involved. This darkening is considerably greater for certain coating systems than others. The fluidized bed applied epoxy coating appeared relatively unaffected by the thermal change and humidity environment.

The corrosion environment resulted in some attack on the coating and produced a certain dullness of the coating surface. On the specimen edges, where coatings were applied by brush, some rusting was evident. Whether this was from coating porosity stemming from brush application, or from the effect on paint film thickness of the sharp edge corner was not determined. The only coating system which did not permit any edge rusting was the fluidized bed applied epoxy enamel.

The accelerated weathering exposure appears to be generally somewhat less severe than either thermal change and humidity or corrosion on coating performance. The general result is to cause some loss of color and loss of gloss from the combined ultra-violet light and water spray environment. For virtually all of the coatings some edge rusting occurred although it was less than that experienced as a result of corrosion. Again the fluidized bed coated specimens did not exhibit any edge rusting.

As observed above, slight edge discoloration and rusting occurred on nearly all the specimens. Except for this none of the coatings broke down sufficiently to cause damage to the substrate. This is taken as an indication that all of the coatings afford protection to the substrate against all of the various environments studied on this program.

In addition to the visual observations of the effects of both single and combined environment exposure on coating system performance, reflectivity measurements were also made for each specimen. Since these measurements do not adequately describe the relative protection afforded the substrate by the coating, the results are not presented as part of the main text. The presentation and analysis of the reflectivity data is found in Appendix I to this report.

2. Flexibility

The sixteen coating systems were subjected to flexibility or bend tests to determine their relative capability for resisting cracking when subjected to tensile strain. The test performed does not permit reporting of the strain developed. Instead, a capability comparison for the various coatings was made and is presented in Table IX in which the flexibility performance of individual coatings systems is reported without conditioning,

Table IX

FLEXIBILITY PERFORMANCE OF COATINGS

Coatings on 2 in. x 4 in. specimens inspected for cracking using 20X magnification after imposing scheduled incremental deflections.

Enamel Coating Type	Coating No.	System Score Unconditioned Specimens	Coating Type Score Unconditioned Specimens	System Score After Thermal Change and Humidity and Accelerated Weathering	Coating Type Score After Thermal Change and Humidity and Accelerated Weathering
			Average		Average
Alkyd	1	1	0.6	3	2.2
	6	2		2	
	7	0		0	
	12	0		4	
	15	0		2	
Polyurethane	2	1	1.6	7	6.8
	4	2		6	
	9	4		7	
	10	0		7	
	13	1		7	
Chlorinated Rubber	3	0	2.3	6	5.7
	8	2		5	
	14	5		6	
Epoxy	5	0	0	4	5.0
	11	0		6	
Epoxy (Fluidized Bed Applied)	16	6	6	7	7

Note: High scores indicate poor performance.

Scoring: 0 - Coating was not observed to crack prior to substrate fracture.
1 - Coating cracked after 1.00 in. specimen deflection; 2 after 0.850 in.; 3 after 0.800 in.; 4 after 0.700 in.; 5 after 0.500 in.; 6 after 0.375 in.; and a score of 7 if cracked by a deflection of 0.250 in.

and following exposure to thermal change and humidity and accelerated weathering.

Scoring of flexibility performance was made as follows: those coatings which did not crack up to fracture of the specimen are scored zero (0). Those coatings which failed before the specimen fractured are scored from one (1) to seven (7) on the basis of the specific incremental deflection (of the seven imposed) at which cracking occurred. If coating failure occurred at the first incremental deflection the coating received a score of 7. Hence high rating numbers are associated with poor flexibility performance. In Table IX the performance of individual coating systems are grouped as to their basic coating type and from arithmetic averages of the individual system scores, a score is obtained for the various coating types.

Reference to Table IX shows that the alkyd coatings exhibit the best overall flexibility performance considering both the unconditioned and environmentally exposed specimens. The fluidized bed applied epoxy coating exhibits the poorest flexibility performance for both types of specimens. The unconditioned polyurethane coatings generally perform quite well but lose a considerable portion of this ability as a result of the imposed environmental conditioning. On the average the chlorinated rubber coatings perform about the same as the polyurethanes. While the unconditioned epoxy specimens perform perfectly, there is a considerable effect associated with thermal change and humidity and accelerated weathering exposure.

A more suitable method to test for flexibility, would be to deflect a coated specimen around a suitably shaped mandrel to develop known strains in the specimen along its length. The limit of cracking of the coating along the specimen length would then define the strain at which the coating fails. The higher the strain value at coating failure the higher would be the coating flexibility rating. If necessary to develop higher strains to produce coating fracture than can conveniently be obtained with steel, a lower modulus material such as aluminum could be used.

3. Abrasion

Investigation of abrasion resistance of coatings was performed for all sixteen complete coating systems described earlier. These studies were also performed for coated specimens after environmental conditioning by thermal change and humidity exposure. The wear resulting from testing in the Taber Abraser apparatus was reported as a wear index computed from the following relation:

$$\text{Wear Index} = \frac{(A - B)\,1000}{C}$$

where

A = specimen weight before abrasion,

B = specimen weight after abrasion, and

C = the number of abrasion cycles recorded.

The average of wear indices determined from the sixteen individual coating systems are reported in Table X in which specimens are grouped as to their coating type. As a means of comparing the four coating types, individual coating system wear indices within a single group were arithmetically averaged and are also listed for comparison.

The abrasion resistance performance within each of the four types of topcoat enamels used was quite consistent. On the basis of this observation it is apparent that pretreatment and primer coatings have little effect on abrasion performance of various coating systems. This is logical since ability to resist abrasion is principally a function of the topcoat and its capacity to resist initiation of removal of surface material.

Reference to Table X shows that the one fluidized bed applied epoxy, coating 16, exhibited best abrasion resistance and had the lowest wear index of any system for both unconditioned specimens and specimens subjected to thermal change and humidity exposure. Next best in performance was the polyurethane group, the average performance of which was essentially the same for unconditioned and conditioned specimens. The spray applied epoxy coatings, which performed next in order, exhibited a considerable improvement in abrasion resistance as an apparent result of thermal change and humidity exposure. From the average wear index values presented, the unconditioned chlorinated rubber coatings exhibit abrasion resistance about midway between the best and worst performing coatings. From the wear index values reported it appears that abrasion resistance of chlorinated rubber is unaffected by thermal change and humidity performance. The most severely abraded coatings are of the alkyd type which perform noticeably worse than any of the other systems based on unconditioned specimen performance. Specimen exposure to thermal change and humidity reduces the effect of abrasion for alkyd type materials to where they perform about the same as chlorinated rubber coatings. Apparently the effect of thermal change and humidity exposure on alkyd coatings results in some hardening of the coating which is reflected in reduced abrasive wear.

4. Adhesion

The adhesion performance of the sixteen coating systems was investigated utilizing the Arco Microknife technique. Adhesion studies were conducted on both specimens which had no environmental conditioning and upon those which were exposed to conditioning by thermal change and humidity cycling followed by accelerated weathering.

Coating adhesion performance is a composite of the adhesion of the various primer combinations to the pretreated metal substrate, and the adhesion of the topcoat to the primer. Consequently, the coating systems were grouped by various primer combinations to facilitate comparison of overall adhesion performance. The results of the adhesion study are summarized and presented in Table XI. Figures 21 through 24 illustrate adhesion of coating systems 1 through 16 after Arco-Microknife testing.

Table X

WEAR INDEX OF COATINGS*

Enamel Coating Type	Coating No.	Wear Index Unconditioned Specimens	Coating Type Wear Index Unconditioned Specimens	Wear Index After Thermal Change and Humidity Exposure	Coating Type Wear Index After Thermal Change and Humidity Exposure
Alkyd	1	38.0	33.2	17.9	12.6
	6	30.6		11.0	
	7	34.9		11.6	
	12	36.3		9.1	
	15	26.1		13.4	
Polyurethane	2	3.5	3.3	4.2	3.4
	4	2.2		2.7	
	9	3.2		3.3	
	10	3.2		3.7	
	13	4.5		2.9	
Chlorinated Rubber	3	16.1	14.6	16.4	13.6
	8	12.7		13.4	
	14	15.0		10.9	
Epoxy	5	7.7	8.1	2.8	2.6
	11	8.5		2.5	
Epoxy (Fluidized Bed Applied)	16	2.1	2.1	2.0	2.0

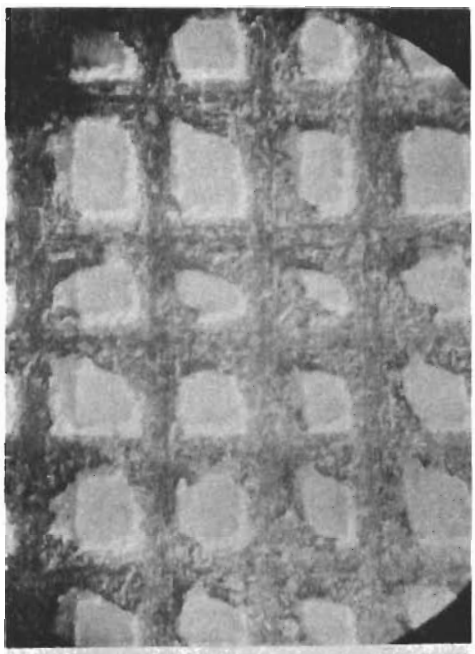
* Calibrase CS-10 wheels with a weight of 250 grams were used in these tests.

Table XI

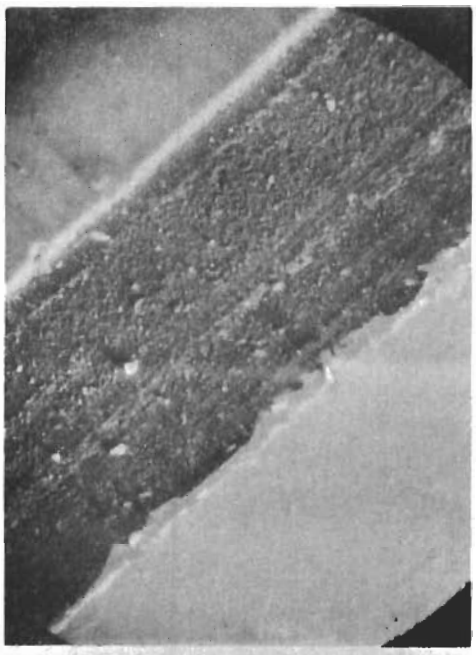
RESULTS OF ARCO MICROKNIFE ADHESION STUDIES

Coating System No.	Pretreatment	Primer Combination	Topcoat Enamel	Coatings Without Environmental Conditioning: Average No. of Squares Intact After Test	Coatings Without Environmental Conditioning: Comments	Coatings Exposed to Thermal Change and Humidity and Accelerated Weathering: Average No. of Squares Intact After Test	Coatings Exposed to Thermal Change and Humidity and Accelerated Weathering: Comments
1	Sand Blast	Alkyd	Alkyd	100	Every square has portions missing.	100	Portions of squares missing.
2	Sand Blast	Zn Chr-Alkyd	Polyurethane	0	Primer and topcoat completely out. Could not cut two parallel lines.	0	Primer and topcoat off completely.
9	Phosp. Acid	Zn Chr-Alkyd	Polyurethane	0	Primer remains intact. These specimens exhibited better adhesion than treated specimens in that it was possible to cut parallel lines in one direction.	0	Primer and topcoat flakes off between parallel cuts.
3	Sand Blast	Zn Chr-Alkyd	Chlorinated Rubber	100	Not every square has portions out. Missing portions at corners only.	99	Portions of squares missing.
8	Phosp. Acid	Zn Chr-Alkyd	Chlorinated Rubber	100	Clean cut squares and lines.	100	Portions of squares missing.
7	Phosp. Acid	Zn Chr-Alkyd	Alkyd	100	Every square has portions missing. Parallel lines are ragged edged.	0	Primer intact, portions of topcoat flakes off between parallel cuts.
4	Sand Blast	Epoxy	Polyurethane	92	Remaining squares have portions out. Adhesion lost between primer and metal.	89	Portions of remaining squares missing. Adhesion lost between metal and primer.
10	Phosp. Acid	Epoxy	Polyurethane	73	Adhesion lost between primer and metal. Remaining squares have portions missing.	0	Coating flaked off between parallel cuts. Adhesion lost between metal and primer.
5	Sand Blast	Epoxy	Epoxy	100	Clean cut squares	100	Portions of squares missing.
11	Phosp. Acid	Epoxy	Epoxy	100	Portions missing in every square.	100	Portions of squares missing.
6	Sand Blast	Epoxy	Alkyd	100	Clean cut squares. Improvement over treated specimens.	100	Portions of squares missing.
12	Phosp. Acid	Epoxy	Alkyd	100	Portions of some squares missing.	77	Portions of remaining squares missing. Adhesion lost between metal and primer.
13	Sand Blast	Wash-Zn-Chr-Alkyd	Polyurethane	0	Adhesion lost between topcoat and primer.	0	Primer and topcoat flakes off between parallel cuts.
14	Sand Blast	Wash-Zn-Chr-Alkyd	Chlorinated Rubber	100	Clean cut squares. Best appearing.	100	Best appearing specimens. Clean cut squares.
15	Sand Blast	Wash-Zn-Chr-Alkyd	Alkyd	100	Portions of every square missing. Parallel lines jagged.	100	Primer intact. Portions of topcoat squares missing.
16*	Sand Blast	None	Epoxy-Fl. Bed Applied	100	Lines cut 1/8 in. apart. Portions every square missing.	100	Portions of squares missing formed by lines cut 1/8 in. apart.

* For the fluidized bed applied epoxy a thicker than normal coating was applied. Arco microknife lines 1/32 in. apart could not satisfactorily be cut in specimen. Lines 1/8 in. apart were cut instead.



System 1



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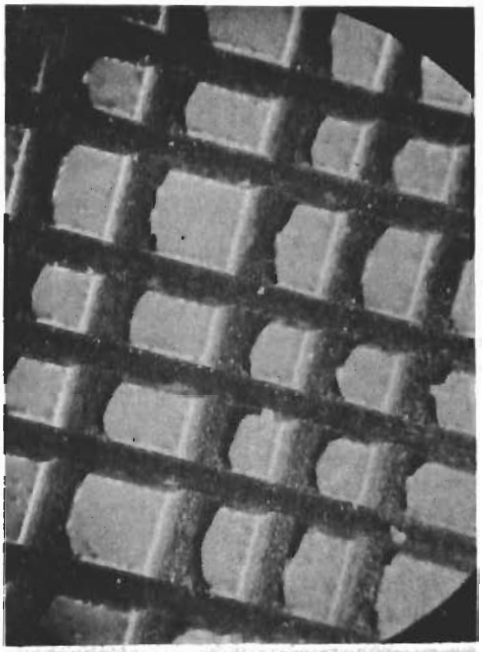
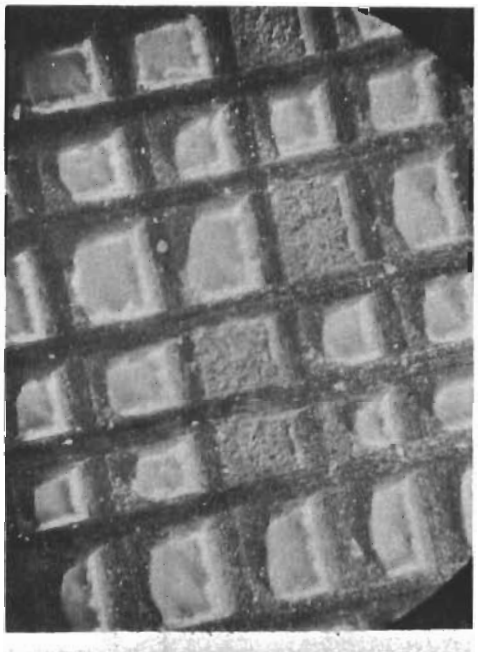
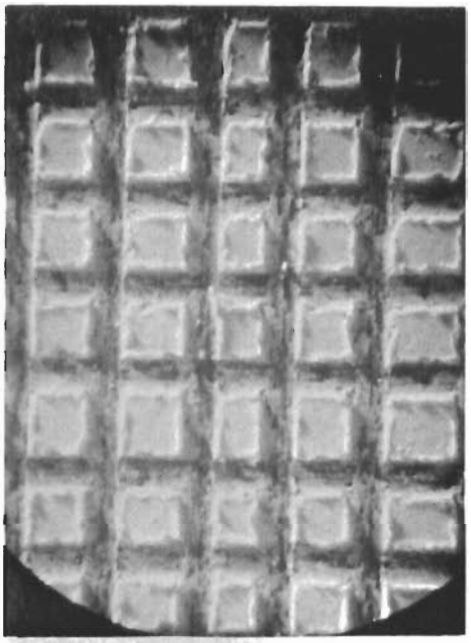


System 3

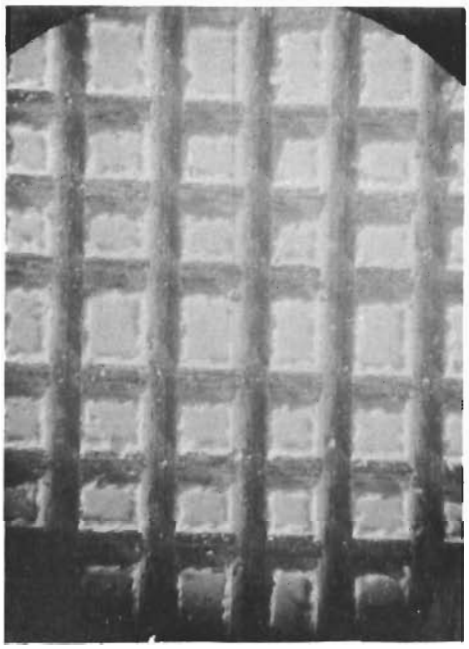


System 4

Fig. 21 ILLUSTRATIONS OF ADHESION PERFORMANCE OF COATING SYSTEMS 1 THROUGH 4

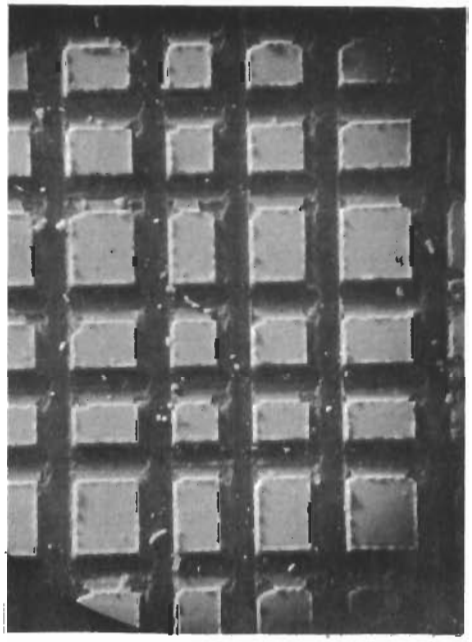


System 5



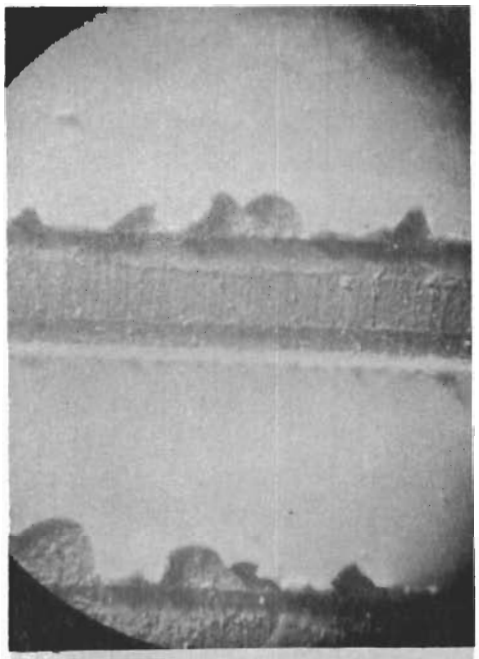
System 6

System 7

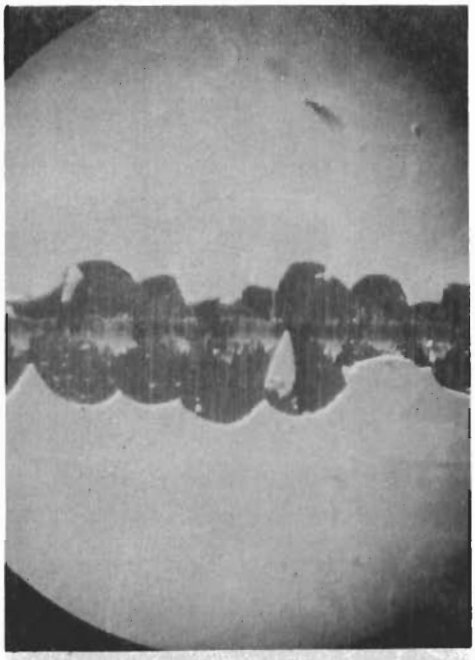


System 8

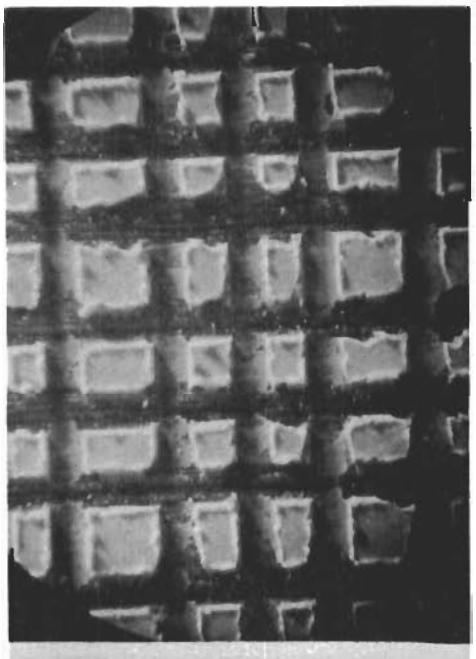
Fig. 22 ILLUSTRATIONS OF ADHESION PERFORMANCE OF COATING SYSTEMS 5 THROUGH 8



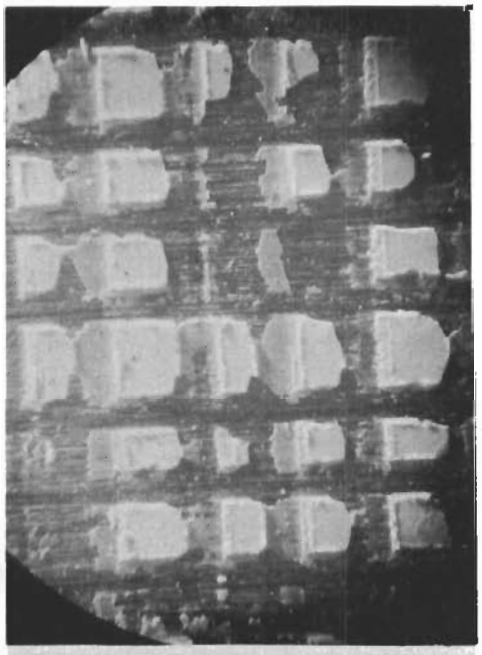
System 9



System 10



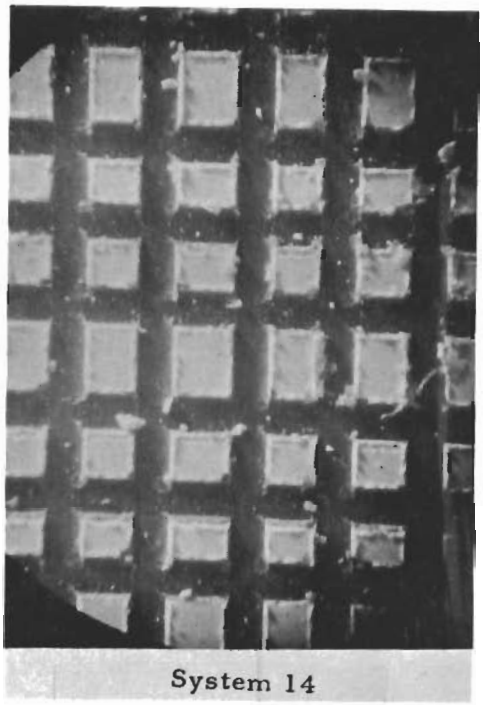
System 11



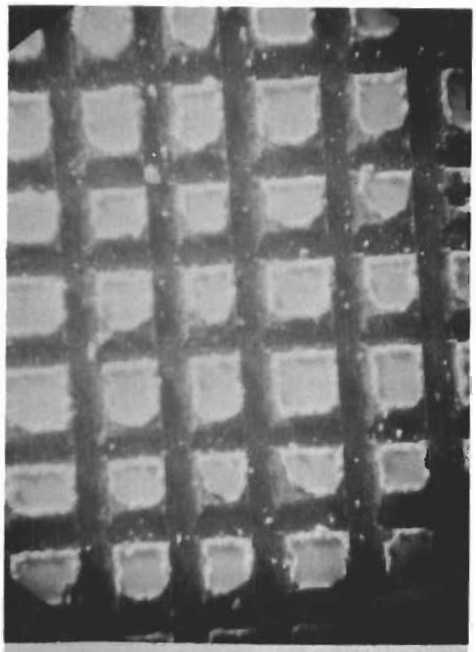
System 12

Fig. 23 ILLUSTRATIONS OF ADHESION PERFORMANCE OF COATING SYSTEMS 9 THROUGH 12

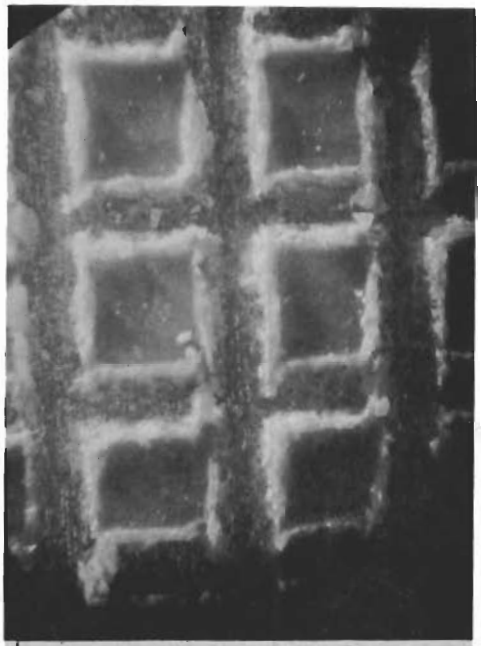
System 13



System 14



System 15



System 16

Fig. 24 ILLUSTRATIONS OF ADHESION PERFORMANCE OF COATING SYSTEMS 13 THROUGH 16

From those results a number of general observations can be made regarding relative adhesion performance of various coating systems. With the single exception of the alkyd enamel coating system 7, all other alkyd topcoats performed rather well when applied over alkyd, epoxy, and wash-zinc chromate-alkyd primer systems. The single exception was for phosphoric acid etch pretreated specimens to which a zinc chromate-alkyd primer had been applied. For that system portions of the alkyd topcoat enamel flaked off leaving the primer intact.

The epoxy enamel and the chlorinated rubber enamel both performed quite well. The chlorinated rubber enamel of system 14, applied over the wash-zinc chromate-alkyd primer coatings, appeared to perform the best of all systems permitting sharp squares to be cut in the coating without flaking. The chlorinated rubber enamel of coating systems 3 and 8, applied over zinc chromate-alkyd primer with sand blast and phosphoric acid etch specimen pretreatment, also performed satisfactorily although portions of all squares were missing. Epoxy enamel of systems 5 and 11, applied over epoxy primers with sand blast and phosphoric acid specimen pretreatments respectively, both performed well although some portion of remaining squares were missing. The coating system showing poorest performance with respect to adhesion as indicated by this test was polyurethane applied over the zinc chromate-alkyd primer system. For this combination, systems 2 and 9, the polyurethane topcoat enamel tore off completely taking the primer with it. For polyurethane over epoxy primer the topcoat again tore the primer off in many cases.

5. Stress Corrosion

The effectiveness of coatings for protecting missile substrate materials from a corrosive atmosphere was investigated for each of the sixteen coating systems. The coated specimens were deflected until a maximum stress level 80 percent of ultimate was developed in the substrate material (225,600 psi) and the specimens subjected to 7 days (168 hours) of saturated calcium nitrate spray as described earlier. The data from this investigation consists of the exposure time required to produce specimen failure. These data are presented in Table XII.

Examination of the stress-corrosion results indicates that in general all of the topcoat enamels provide satisfactory protection of the substrate against admission of the saturated calcium nitrate spray solution. A total of eight stress-corrosion failures occurred and were distributed among seven different coating systems. Of that number only one coating system 5, was a system incorporating sand blast pretreatment. Seven of the failures occurred with specimens which had received phosphoric acid etch pretreatment and were distributed among six different coating systems, with two failures occurring for coating system 9. From this it appears quite clear that the phosphoric acid etch is a principal factor in the development of stress-corrosion failure. However, the exact role of the phosphoric acid etch in producing such failures is not known. It may be speculated that minute damage may be done at the grain boundaries of the material during the etching process. This may create a susceptibility to a stress-corrosion

Table XII

RESULTS OF STRESS-CORROSION TESTS

Coated specimens stressed to 80 percent of ultimate strength and exposed to concentrated calcium nitrate solution spray.

Coating System Number	Pretreatment	Enamel Type	Time to Failure (hr) Specimen No. 1	Specimen No. 2	Specimen No. 3
1	Sand Blast	Alkyd	*	*	*
2	Sand Blast	Polyurethane	*	*	*
3	Sand Blast	Chlorinated Rubber	*	*	*
4	Sand Blast	Polyurethane	*	*	*
5	Sand Blast	Epoxy	*	*	43.25
6	Sand Blast	Alkyd	*	*	*
7	Phosphoric Acid	Alkyd	*	*	63.25
8	Phosphoric Acid	Chlorinated Rubber	*	*	139.25
9	Phosphoric Acid	Polyurethane	*	141	59.25
10	Phosphoric Acid	Polyurethane	120.7	*	*
11	Phosphoric Acid	Epoxy	*	47	*
12	Phosphoric Acid	Alkyd	88.5	*	*
13	Sand Blast	Polyurethane	*	*	*
14	Sand Blast	Chlorinated Rubber	*	*	*
15	Sand Blast	Alkyd	*	*	*
16	Sand Blast	Epoxy	*	*	*

* No failure after 168 hours continuous exposure.

condition simply as a result of subsequent stressing, even if all acids were effectively removed by washing prior to coating. If, however, the acid is not completely removed by washing, a corrosive environment may be present beneath the coating to precipitate early failure of the type experienced on the program. From these results a further investigation of the role of phosphoric acid etch in stress-corrosion failure appears warranted.

It might be pointed out that hydrogen embrittlement due to the original etch treatment alone is not a very probable cause of the stress-corrosion failures observed. First of all, the times to failure were relatively short (of the order of 50 to 100 hours). If hydrogen embrittlement was of some importance, then this should also have been observed in the embrittlement tests where the specimens were under load for much greater periods of time (of the order of 200 to 400 hours). Such was not the case. No failures were observed for the specimens under the longer exposure times. Perhaps if the specimens were exposed for a much longer period of time, failures might possibly have occurred. Under the time limitations such lengthy exposure times were unwarranted. The stress levels in the stress corrosion tests were 80 percent of ultimate and the stress level in the embrittlement tests were of the order of 300,000 psi. This value, in excess of the uniaxial tensile ultimate of 270,000 psi, was possible due to the complex three-dimensional state of stress present at the root of the notch in the embrittlement specimens. Thus the magnitude of the stresses was higher in the embrittlement tests than in the stress-corrosion tests. Last it might be surmised that traces of the phosphoric acid etch might remain after the original etch treatment. However, it seems likely that if this were the solution to the problem, then almost certainly these traces would be present at the root of the embrittlement specimen notches since this would be the more difficult place to clean away.

VII. CONCLUSIONS

From the investigations performed a number of conclusions can be drawn. Because of the wide diversity of coating performance studied it is not possible, nor is it appropriate, to seek to establish an overall ranking of the various coating systems. Examination of coating performance data presented will provide needed information on the relative capability of the coatings studied within individual test categories.

The following conclusions are not listed in the order of their relative importance, but rather follow the general report chronology.

1. Based on tensile strength results, coating systems 1 through 16 all provide satisfactory protection of the substrate material from degradation effects of exposure to thermal change and humidity followed by corrosion.
2. The tensile strength of SAE 4340 steel is not adversely affected by the pretreatments, partial coatings, and complete coating systems investigated on the program.
3. Fatigue test results demonstrate the increase in fatigue life resulting from sand blast pretreatment of metals prior to coating.
4. Although sand blast metal preparation increases fatigue life, it introduces a variable factor which clouds interpretation of various partial and complete coating system performance.
5. Insofar as fatigue investigation results are concerned phosphoric acid etch is a satisfactory metal preparation treatment. No reduction in fatigue life is experienced from use of phosphoric acid etch pretreatment.
6. By providing a more consistent datum reference, the effects of coatings on substrate fatigue performance will be more readily discerned using phosphoric acid etch pretreated specimens.
7. None of the coatings systems studied was observed to induce detrimental metal embrittlement.
8. Alkyd coatings exhibit the best flexibility performance, considering both unconditioned and environmentally exposed specimens, and the fluidized bed applied epoxy exhibits worst performance in both categories.
9. The flexibility tests performed, in which coatings were inspected for cracking at selected incremental deflections, are difficult to interpret with regard to individual coating capability. Scoring the performance of various coating types permits some comparison. The results of the flexibility tests indicate, however, that no cracking problem exists up to the strain limit of the steel substrate used. Thus all the coatings show appreciable flexibility and will probably be able to follow the strains of the substrate in the prototype without serious consequences.

10. The abrasion resistance of coatings defined by wear index is a reasonable coating evaluation method. Coatings of similar type exhibit consistent abrasion resistance performance.

11. Fluidized bed applied epoxy coating provides the best abrasion resistance performance for unconditioned and environmentally conditioned specimens. Alkyd coatings exhibit very poor abrasion resistance for unconditioned specimens; however environmental exposure significantly improves their abrasion resistance.

12. The effect of primer coatings on overall coating performance is most readily seen in adhesion tests. Capabilities of coating systems are demonstrated not only by Arco Microknife score, but by the location of adhesion failure in the coating system.

13. Apart from the pretreatments used the sixteen coating systems studied provide satisfactory protection against the admission of saturated calcium nitrate during stress-corrosion testing.

14. Phosphoric acid etch pretreatment appears to be the principal factor in initiating stress-corrosion fracture in the SAE 4340 substrate material tested. In view of the serious implication of this finding, the role of phosphoric acid etch pretreatment should be further investigated.

15. The test categories which exhibit the best potential for evaluating effects of pretreatments or coatings on substrate performance include fatigue and stress-corrosion studies.

VIII. RECOMMENDATIONS

The following recommendations covering further coating-substrate investigations are made on the basis of the information generated and results obtained on the subject program. The first recommendation is one which we feel should be given prompt attention.

1. Investigate the effect of phosphoric acid etch on stress-corrosion performance of SAE 4340 steel. In view of the serious implications of the adverse effect of phosphoric acid etch on stress-corrosion performance, this study should be initiated immediately.
2. Slight differences in the sand blasting of individual specimens cloud any interpretation of the results of the tests to determine the effect of coatings on fatigue performance. We therefore recommend performance of additional fatigue tests of uncoated and coated specimens, simultaneously pretreated by various levels of closely controlled sand blasting, to establish effect of this process on substrate fatigue performance.

APPENDIX I

RESULTS OF LIGHT REFLECTIVITY MEASUREMENTS FOR THE ENVIRONMENTAL STUDIES

INTRODUCTION

The effect of single and combined environment exposure on coating system performance is estimated on the basis of the recorded daylight reflectivity measurements summarized in Table XIII. Reflectivity measurements are used for this purpose in the absence of any better measurable quantity associated with environmental effects on coatings. Their use assumes that changes in daylight reflectivity are an evidence of coating "degradation". However, one type of degradation, chalking, will appear as increased reflectivity so that the ultimate effect of degradation produced by environmental exposure is not known from this test.

On the basis of reflectivity data the effect of thermal change and humidity on pretreatments and primer coatings is not apparent. This is not surprising since reflectivity is primarily a function of topcoat performance.

The results of reflectivity inspection of specimens from the environmental studies are summarized and presented in Table XIII. All reflectivity measurements are expressed as a percent of the reflectivity from a standard white color sample, the reflectivity of which is 100 percent measured with the reflectometer. All of the complete coating systems studied utilized white enamel coatings except for system 16, the fluidized bed applied epoxy, which was a dark green color. Consequently, the reflectivity measurements for that system should not be directly compared with those for the other systems. Coating systems 1 through 15, though not of identical whiteness, are close enough to permit direct comparison.

A. Alkyd Coatings

The strong effect of thermal change and humidity on alkyd coating reflectivity is clearly seen from reference to reflectivity measurements for individual coatings summarized in Table XIII and for the four basic coating systems compared in Table XIV. Coating systems 1, 6, 7, 12 and 15 all have alkyd topcoats and exhibit reflectivity changes greater than any of the other eleven coatings. Actually the average reflectivity change of 17 points for the five alkyd topcoat systems identified above are approximately four times greater than the average for all of the other systems. Further, it is interesting to note that of the five alkyd coating systems, coatings 1, 7 and 12, which had both alkyd primer and alkyd topcoats, exhibited the highest reflectivity changes.

Table XIII

AVERAGE REFLECTIVITY OF SPECIMENS EXPOSED TO VARIOUS ENVIRONMENTS

Coating System No.	Initial Reflectivity of Coating %	After Thermal Change and Humidity		After Corrosion		After Accelerated Weathering		After Thermal Change-Humidity and Corrosion		After Thermal Change-Humidity and Accelerated Weathering	
		Reflectivity %	Change %	Reflectivity %	Change %	Reflectivity %	Change %	Reflectivity %	Change %	Reflectivity %	Change %
1	80.7	60.6	-20.1	72.1	- 8.6	82.7	+ 2.0	58.5	-22.2	78.9	-1.8
2	84.1	78.1	- 6.0	75.0	- 9.1	72.9	-11.2	78.5	- 5.6	74.6	-9.5
3	82.9	74.6	- 8.3	72.1	-10.8	82.2	- 0.7	74.9	- 8.0	78.8	-4.1
4	82.5	77.4	- 5.1	77.2	- 5.3	73.9	- 8.6	77.3	- 5.2	74.4	-8.1
5	83.5	78.6	- 4.9	73.8	- 9.7	78.8	- 4.7	82.1	- 1.4	78.0	-5.5
6	77.7	65.8	-11.9	69.0	- 8.7	77.7	0.0	61.5	-16.2	77.0	-0.7
7	82.2	62.3	-19.9	72.3	- 9.9	82.5	+ 0.3	54.3	-27.9	79.2	-3.0
8	76.6	73.7	- 2.9	70.3	- 6.3	76.6	0.0	71.9	- 4.7	77.2	+0.6
9	82.8	77.4	- 5.4	77.0	- 5.8	74.1	- 8.7	77.4	- 5.4	75.1	-7.7
10	81.2	76.5	- 4.7	75.5	- 5.7	73.4	- 7.8	76.0	- 5.2	73.6	-7.6
11	83.6	81.4	- 2.2	75.6	- 8.0	80.2	- 3.4	81.0	- 2.6	76.5	-7.1
12	80.2	64.9	-15.3	70.0	-10.2	79.8	- 0.4	59.7	-20.5	75.8	-4.4
13	81.3	77.2	- 4.6	76.6	- 5.2	73.4	- 8.4	78.0	- 3.8	73.8	-8.0
14	79.6	74.8	- 4.8	73.4	- 6.2	81.4	+ 1.8	75.3	- 4.3	77.9	-1.7
15	80.9	62.9	-18.0	74.7	- 6.2	80.2	- 0.7	61.0	-19.9	80.5	-0.4
16	5.1	5.0	- 0.1	7.0	+ 1.9	5.5	+ 0.4	6.1	+ 1.0	6.8	+1.7

Table XIV

COMPARISON OF EFFECT OF ENVIRONMENTAL CONDITIONING ON REFLECTIVITY PERFORMANCE OF ALKYD, POLYURETHANE, CHLORINATED RUBBER AND EPOXY ENAMELS

	Average Reflectivity Loss after Environmental Exposure Indicated				
	Thermal Change and Humidity	Corrosion	Accelerated Weathering	Thermal Change-Humidity, and Corrosion	Thermal Change-Humidity, and Accelerated Weathering
Alkyd Coating Systems 1, 6, 7, 12 and 15	17.0	8.7	0.1	21.3	2.06
Polyurethane Coating Systems 2, 4, 9, 10 and 13	5.2	6.2	8.9	5.0	8.2
Chlorinated Rubber Coating Systems 3, 8 and 14	5.3	7.7	-0.3	5.4	2.1
Epoxy Coating Systems 5 and 11*	3.6	8.9	4.1	2.0	6.3

* Epoxy System 16, the fluidized bed applied coating, is not appropriate for comparison because of the great difference in reflectivity readings resulting from the dark color.

The influence of corrosion on alkyd coatings is quite significant with respect to reflectivity measurements. An average reflectivity change of 8.7 points was observed for alkyd systems 1, 6, 7, 12 and 15. Table XIV shows that the alkyd coatings perform slightly less satisfactorily than the polyurethane and the chlorinated rubber, and about the same as the epoxy coatings of systems 5 and 11.

Exposure to accelerated weathering has an insignificant effect on all of the alkyd coatings based on reflectivity measurements. In this respect its performance is similar to that of chlorinated rubber which is also unaffected by accelerated weathering.

For alkyd coatings the combination of thermal change and humidity followed by corrosion exposure produces the greatest reduction in reflectivity. Corrosion following thermal change and humidity causes an approximate 25 percent further change in reflectivity. However, accelerated weathering exposure following thermal change and humidity has a marked reverse effect on alkyd coatings as shown in Table XIV. That exposure combination results in an average reflectivity reduction of 2 points from that of unexposed specimens. However, more startling is the fact that on the basis of reflectivity, the accelerated weathering cycling appears to counteract the effect of thermal change and humidity. One possible explanation for this phenomena is to associate such a reflectivity change to a bleaching out of the thermal change and humidity effects by the action of the accelerated weathering ultra-violet light exposure. While reflectivity measurements indicate this "healing" effect, we seriously doubt that the capability of the coating to provide protection to the substrate is generally enhanced by accelerated weathering cycling following thermal change and humidity exposure.

B. Polyurethane Coatings

Coating systems 2, 4, 9, 10 and 13 all utilize polyurethane enamels. The general performance of polyurethane coatings exposed to various environments compared to other systems can be seen from Table XIV. From this comparison it is evident that, based on reflectivity, only epoxy coatings perform better than polyurethanes after thermal change and humidity, and thermal change and humidity followed by corrosion exposure. For corrosion exposure alone polyurethanes perform best. The effect of accelerated weathering, and thermal change and humidity followed by accelerated weathering on the polyurethanes is greater than for any other coating system.

C. Chlorinated Rubber Coatings

The chlorinated rubber enamel coatings are utilized in systems 3, 8 and 14. Reference to Table XIV shows that for thermal change and humidity, and thermal change and humidity followed by corrosion exposure the chlorinated rubber performs about the same as polyurethane and is surpassed only by epoxy. For corrosion resistance alone, the chlorinated rubber performance is only surpassed by that of the polyurethane systems.

The performance of chlorinated rubber exposed to the combination of thermal change and humidity followed by accelerated weathering ameliorates the effect of thermal change and humidity alone. However the amount of reflectivity recovery is not as great. The overall effect of the combined environment on the resulting reflectivity change is essentially the same as for the alkyd system.

D. Epoxy

The effect of environmental exposure on coating system reflectivity summarized in Table XIV includes the epoxy systems 5 and 11. The fluidized bed epoxy system is not included because the dark color of the coating applied make comparisons based on reflectivity inappropriate. The spray applied epoxies performed best in two exposure categories, namely after thermal change and humidity, and thermal change and humidity followed by corrosion. In this the epoxy coatings demonstrated overall superiority since each of the other coatings only performed best for one environment. Reflectivity of epoxy coatings were most affected from corrosion exposure alone. For both accelerated weathering, and thermal change and humidity followed by accelerated weathering, the epoxy performance was about midway between the alkyd and chlorinated rubbers (which were best) and the polyurethane coating.

The fluidized bed applied epoxy coating exhibited generally good performance under environmental exposure. While reflectivity measurements of the system are not meaningful for comparison with other coatings, the small changes noted indicate its good performance. The reflectivity measurements made show a slight increase in reflectivity while for all other systems environmental exposure resulted in a reflectivity loss. For the fluidized bed epoxy coating this increase in reflectivity was associated with a slight lightening or bleaching of the basic dark color of the coating.