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Report

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ABCA/3/USN/F1/73

NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20034

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THE INTERACTION OF DISTILLATE FUELS WITH INORGANIC ZINC COATINGS IN SIMULATED NAVY FUEL TANKS

by
E. W. White and K. V. Nagy

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Naval Ship Research and Development Center
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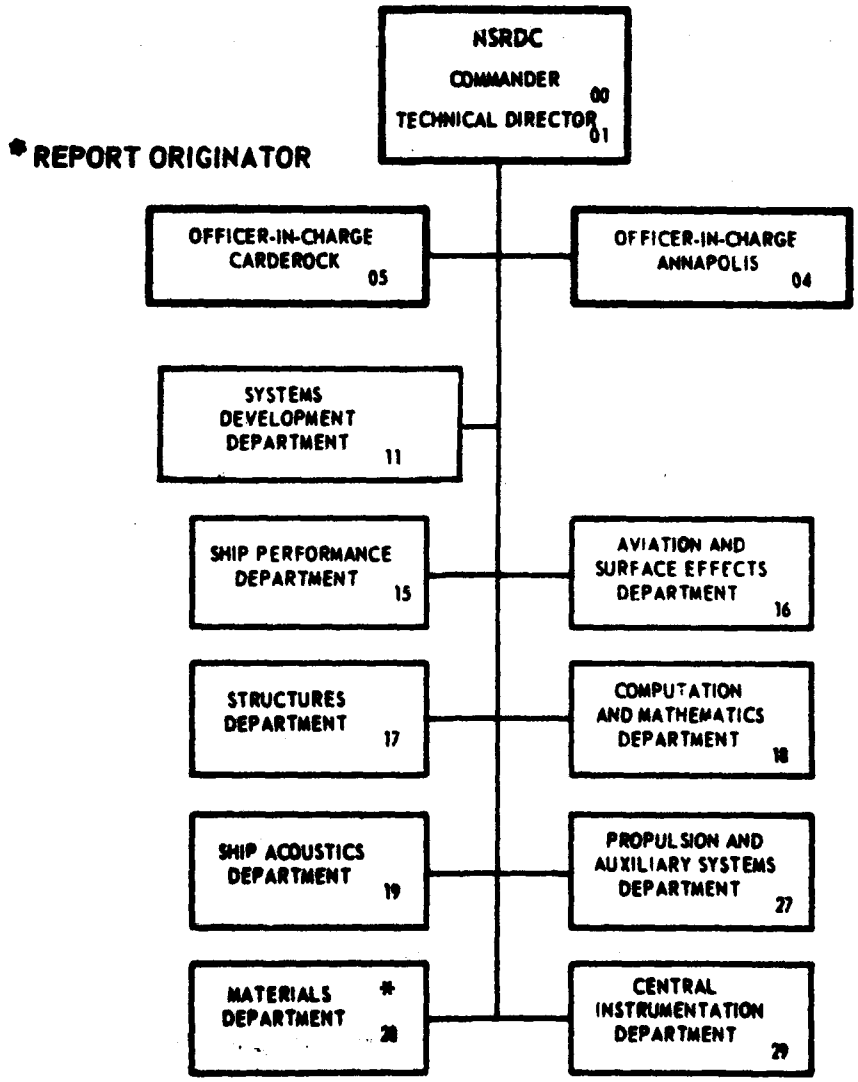

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DEPARTMENT OF THE NAVY

NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

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July 1973 28-509 Report 3928

ABSTRACT

The results of an investigation into the compatibility of the new Navy Distillate-type fuel with inorganic zinc fuel-tank coatings are reported. Interaction between Navy Distillate fuel and the representative coatings used in the investigation was indicated by visible change in the coatings and by increased levels of zinc in the fuels. The concentration of zinc in a fuel was found to depend upon the acidity of the fuel and upon the length of contact between fuel and coating. Coatings which had been contacted by many batches of fuel were found to release less zinc to a fuel than did newly applied coatings. On the basis of the data obtained in this investigation, the maximum concentration of zinc that might be found in a fuel stored for a long time in a typical tank protected with an inorganic zinc coating is in the order of magnitude of 20 milligrams per 100 milliliters (about 230 parts per million). It was concluded that the use of inorganic zinc coatings should be prohibited in Navy Distillate service.

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ADMINISTRATIVE INFORMATION

This report is milestone C-1 (for fiscal year 1973) of the Multipurpose Fuel Program (SF54 543 303, Task 12295). This program is described in reference (a). A preliminary report, reference (b), was previously issued.

The Multipurpose Fuel Program is sponsored by the Naval Ship Systems Command. Mr. E. A. Bukzin, NAVSHIPS (SHIPS 03421), of the Ship Research and Technology Division, is the Program Manager. Mr. E. C. Davis, NAVSEC (SEC 6101F), of the Fuels and Lubricants Section, is the Technical Agent for the program.

At this laboratory, the Multipurpose Fuel Program falls under the cognizance of the Applied Chemistry Division (Dr. G. Bosmajian) of the Materials Department (Mr. R. J. Wolfe). The work is performed by the Fuels and Lubricants Branch (Mr. N. Glassman), with Dr. E. W. White as principal investigator. The laboratory work unit number is 1-2831-155.

ACKNOWLEDGMENTS

The assistance of the following is gratefully acknowledged:

- Messrs. E. Morgenstern and R. Kramer of the Coatings and Environmental Control Section, NAVSEC (SEC 6101C), for suggesting methods and representative post- and self-cured coatings from the products qualified under military specification MIL-P-23236.

- The personnel of Shop 71 of NAVSHIPYD PHILA for the preparation and coating of the panels used in this investigation. (Special appreciation is due to Mr. M. Di Tullio, who coordinated and expedited the preparation and transfer of the panels.)

- Mr. R. Field of NSRDC/A (Code 2733) for the application of statistical evaluation techniques to the experimental data.

ADMINISTRATIVE REFERENCES

(a) NSRDC/A Program Summary SF54 543 303, Task 12295, Work Unit 2831-155 of 1 May 1973
(b) NSRDC/A ltr rept 28-41 of 13 Jan 1972

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INTRODUCTION

The steel fuel tanks of ships that burn Navy Special Fuel Oil (NSFO) (MIL-F-859) under their boilers are protected from corrosion to some extent by the fuel itself. A previous laboratory investigation revealed that some distillate fuels permit corrosion rates from about 1 to 3 times that of a single NSFO used as the basis for comparison.[1] Such results indicated the possible need to protect with corrosion-inhibiting coatings the fuel tanks of ships being converted from the use of NSFO to the use of the new Navy Distillate (ND) (MIL-F-24397) fuel.

Four coating systems for use in steel ship tanks in fuel/salt-water-ballast service are specified in MIL-P-23236. Of these, the inorganic zinc coatings (silicate, phosphate, or silicone zinc) are usually preferred on the basis of cost and ease of application, for example, to epoxy coatings, if the conditions of the proposed service render such zinc coatings suitable. These coatings contain particles of metallic zinc which are thought to act as sacrificial electrodes. That is, the coatings rather than the underlying steel are attacked and corroded.

The zinc lost from such sacrificial electrodes may enter the attacking medium, in this case, the sea water and/or the fuel. Fuel-soluble zinc compounds can deposit in burners and engines. Insoluble zinc compounds can plug filters, strainers, and other restricted openings. In either case, the presence of the zinc compounds necessitates additional maintenance of the fuel system and could even result in operational casualties.

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[1] Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

On the basis of such considerations of the possible undesirable side effects associated with the use of such coatings, an investigation of the compatibility of ND fuels with inorganic zinc coatings has been conducted so that a determination can be made whether or not to use them. Experiments were made to ascertain how much zinc migrates into the fuel phase and how this migration depends on fuel properties and on the general system environment and configuration. This report describes and discusses the results of those experiments.

TECHNICAL BACKGROUND

GENERAL

The protection of iron and steel with a coating of zinc metal is said to date from 1740 when hot dip galvanizing originated.[2] Zinc, being higher in the electromotive series than iron, gives electrochemical sacrifical protection of the steel which it coats by making the steel cathodic even when the base metal is exposed in small areas. If a galvanized steel is submerged in an aqueous solution, the life of the coating is known to depend upon the concentration of hydrogen ions (pH), oxygen, and carbon dioxide and upon the concentrations of the various anions and cations present. The presence of oxygen leads to rapid attack, but this is soon retarded by the deposition of zinc hydroxide which limits the diffusion of oxygen to the metal. The pH is also critical, as protection is afforded only in the range of 6 to 12.5, with the rate of corrosion increasing sharply at pH values above and below this range. This effect seems to be tied into the amphoteric nature of the corrosion product, zinc hydroxide ($Zn(OH)_2$). In general, zinc coatings give good protection to iron and many other metals in sea water and in other solutions high in chlorides. However, zinc can become passive, particularly at a pH of about 10, the concentration at which zinc hydroxide is least soluble. If the zinc is rendered passive by a film formation, it becomes cathodic to the base steel and permits attack.

It was later learned that zinc powder, dispersed in a vehicle liquid and painted onto a steel surface, would provide many of the benefits of the complete zinc coating provided by galvanizing. Gelfer,[3] as early as 1938, reported the use of an inorganic zinc-lead silicate formula, postcured by a phosphate-based curing agent. The early inorganic zinc coatings which require the application of an acidic curing agent to the zinc-rich coating some time after the initial application, were all of the postcured type. About 10 years ago, a series of self-curing, zinc-rich coatings began to find use in place of the postcured type. Both types have been qualified under military specification MIL-P-23236 for paint coating systems applicable to steel ship tanks for fuel and salt-water ballast. MIL-P-23236 includes the zinc-rich paints as class 3, those systems which "shall be composed principally of an inorganic silicate, phosphate or silicone with zinc, which may be both free and combined." One sales brochure covering a commercial line of inorganic zinc paints indicates that the dry applied film contains 89% zinc by weight when either the company's inorganic silicate type of paint or the ethyl silicate type is used.

INORGANIC ZINC COATINGS IN SHIPBOARD FUEL TANKS

In the past, the Fleet has used inorganic zinc coatings in shipboard fuel and ballast water tanks in jet fuel (JP-5) and diesel fuel marine (DFM) service. Fleet experience with these coatings is understood to be generally good on carriers where the coated tanks have been used for JP-5 fuel storage. Some whitish deposit is formed on the surface of the coating during the first few weeks as a result of the curing process, but adhesion to the steel tank walls has been good, and the service life has been about the same as that obtained with epoxy-type coatings.

Problems with the use of the inorganic zinc coatings have already been noted in DFM service. One example of fuel problems related to inorganic zinc-coated tanks occurred several years ago. When fuel sludging and injector problems were encountered on the THOMAS WASHINGTON (AGOR 10), the presence in the fuel of zinc from the tank coatings was thought to be the cause. Garner

and Evans[4] reported zinc levels in samples taken from the ship's fuel system contained from about 6 ppm* zinc in the storage tanks to about 14 to 18 ppm in the service tanks and in the float-and-drain tanks. Another investigator apparently found as much as 50 ppm zinc in a fuel sample taken from a storage tank.

The amount of zinc that migrates from the zinc-rich coating into the fuel will depend upon a number of factors. The information presented previously, with regard to galvanized zinc coatings, implies that the acidity of the fuel and water in contact with the inorganic zinc coating, the level of dissolved oxygen in the fluids, and the presence of an electrolyte (saline water) are critical. In addition, the area of contact between the coating and the contacting fluids, the volume of fuel, and the duration of the contact may be pertinent. The net amount of zinc in the fuel at any time will be the result of totaling the amount of zinc that has entered the fuel, minus that which has been removed from the fuel, e.g., by formation of insoluble compounds that settle out.

The one factor that seems most likely to affect the amount of zinc migrating into different fuels is the acidity of the fuel itself. The configuration and size of the tanks, the relative volumes of fuel and sea water, the amount of oxygen dissolved in the fluids, and similar factors would probably be relatively constant for a given ship. The acidity, however, varies from fuel to fuel and even from supplier to supplier of the same type of fuel. The specification for DFM restricts the acidity (neutralization number) of that type of fuel to a maximum of 0.5 mg KOH/g of fuel. The permissible acidity of JP-5 fuel is not directly specified but is always much lower. ND-type fuel must be neutral to methyl orange indicator, but this permits neutralization numbers which have been observed as approaching three times the DFM maximum. Theoretically then, levels of zinc in ND fuels in contact with inorganic zinc coatings could be much greater than that observed in DFM service.

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

MATERIALS AND PROCEDURES

Interactions of seven distillate fuels and five inorganic zinc coatings were investigated by three basic procedures. Interactions of each fuel with each coating were not investigated by each method. The three procedures are the "static," the "replenishment," and the "dynamic." In the static procedure, a steel panel coated with one of the five inorganic zinc formulations was placed in a jar containing equal volumes of synthetic sea water and one of the seven fuels; the jar was held in a 110° F oven for a selected period, and the amount of zinc lost to the fuel/sea-water system was then determined. The same physical arrangement was used in the replenishment procedure except that the fuel was drained and replaced weekly. In the dynamic procedure, the same arrangement of panels in fuel and sea water was used, but ship's motion was simulated by placing the jar in a shaking apparatus. Details of the materials used and of the individual test procedures are given below.

MATERIALS

Fuels

Seven distillate fuels were used. Two of them were Standard Distillate Reference (SDR) fuels covered by MIL-F-24376A, three were classified as ND (MIL-F-24397) fuels, one was a DFM (MIL-F-16884) and the seventh was a JP-5 fuel (MIL-T-5624). Pertinent properties and inspection data for these fuels are listed in table 1.

Panels and Coatings

Dimensions of panels used in these experiments were roughly 4 1/2 x 2 x 1/8 inch. The coated panels, which should be representative of actual shipboard coatings, were prepared by Shop 71, NAVSHIPYD PHILA, whose personnel were experienced in applying inorganic zinc coatings to ships. The panels were to be prepared according to paragraph 4.3.1.6 of MIL-P-23236(SHIPS) except for their reduced size. Consequently, they consisted of a basic panel of blasted hot-rolled mild steel coated with an inorganic zinc formulation. Galvanized panels without other coating were used in a few experiments.

TABLE 1
PROPERTIES AND INSPECTION DATA OF THE FUELS

Properties	Type of Fuel						
	SDR		ND			DFM	JP-5
	Fuel Code						
	A	B	C	D	E	F	G
Gravity, °API, 60°/60° F	28.9	30.6	32.2	34.2	36.7	37.7	42.8
Viscosity, cSt, at 100° F	6.1	6.0	4.8	3.6	2.4	3.2	1.4
Neutralization number, mg KOH/g	1.38	0.81	0.09	0.02	0.02	0.03	0.01
Sulfur, %	1.2	1.1	0.1	1.2	0.2	0.1	0.0

API - American Petroleum Institute
cSt - centistokes

Five inorganic zinc formulations, qualified by their manufacturers under MIL-P-23236(SHIPS), were used. Two of the formulations were postcured and three were self-cured types. Panels as received from NAVSHIPYD PHILA were covered with a whitish haze of salts which migrated to the surface. They were therefore scrubbed gently with foam rubber under warm running water and then dried before being used.

Synthetic Sea Water

The synthetic sea water used in the experiments was prepared according to procedure B of ASTM procedure D 665-60, "Rust-Preventing Characteristics of Steam-Turbine Oil in the Presence of Water."

STATIC PROCEDURE

In the static procedure, a panel was placed in a pint Mason jar containing 200 ml of synthetic sea water. A 200-ml volume of fuel was poured gently into the jar. This left about 1/8 inch of the panel exposed to air above the surface of the fuel. The jar was covered and placed in an oven, regulated at 110° F, for a selected period of time ranging from 1 day to 24 weeks. At the end of the selected period, the jar was removed from the oven. The contents of the jar were separated into solids, water, and fuel fractions. First, the liquids were decanted from the jar through a weighed filter paper (5-micrometer pore size). The jar and panel were rinsed with naphtha followed by distilled water, and the rinsings after passing through the same filter paper were discarded. The filter paper was dried in an oven and weighed to determine the weight of the solids. The solids were converted into a sulfated ash, dissolved in hydrochloric acid, diluted, and analyzed for zinc by the atomic absorption technique.

The filtrate from the solids separation step was allowed to form into water and fuel layers in a separatory funnel and split into the respective phases. The aqueous phase was acidified with hydrochloric acid, and its zinc content was determined by atomic absorption. The fuel layer was sampled, and the sample was converted into sulfated ash. Following solution of the ash in hydrochloric acid and dilution with distilled water to obtain a suitable concentration, the zinc content was determined by atomic absorption. Sometimes the iron and silicon contents were also measured.

In some instances, the static procedure was modified by substituting either 400 ml of fuel or 400 ml of sea water for the 200-ml fuel/200-ml sea water normally employed.

The effect of area of coating on the interaction between fuel and coating was determined by a modified static procedure. In one case, instead of one panel being placed in the Mason jar, two panels were used, thus doubling the area for a fixed volume of fuel. In other procedures, one panel was used, but larger diameter containers were used so that the same depth of fuel represented a larger fuel volume and hence a reduced area of coating per unit volume of fuel. The separation procedure following removal of the vessel from the oven and the subsequent analytical techniques remained the same.

REPLENISHMENT PROCEDURE

The replenishment procedure started in the same manner as the static procedure. The Mason jar containing panel, sea water, and fuel was prepared in the same way and placed in the same 110° F oven. However, after 1 week the fuel and sea water were decanted from the jar and replaced with fresh materials. This procedure was intended to simulate the periodic refuelings which tanks aboard ship experience. Two slightly different procedures were used in replacing the fuel and sea water. In one, the sea water and fuel were gently poured into the jar in that sequence, and the jar was returned to the oven. In the other procedure, the panel, while still covered by the old liquids, was scrubbed gently with a soft rubber device to remove adherent deposits, thus simulating the scrubbing action of entering fuel or ballast water aboard ship. The fluids were then decanted and replaced before returning the jar to the oven. This replenishment procedure was repeated weekly for up to 30 weeks. Only the zinc content of the replaced fuel was determined. The procedure was similar to that for the static experiment samples.

DYNAMIC PROCEDURE

A jar containing fuel, sea water, and a coated panel was prepared in the same way as in the static and replenishment procedures. However, rather than being placed in an oven at 110° F, the jar was placed in a shaking apparatus which imparted a reciprocating motion to the contents of the jar in a manner simulating the effects of ship motion. The shaker had an amplitude of motion of 1.1 to 1.2 centimeters. The reciprocating frequency was set at about 70 cpm. A heater in the shaker kept the contents of the jar at about 110° F. The jars were left in the shaker for a period of a day or a week. When the jar was removed from the shaker, the contents were treated in a manner similar to that in the static experiment.

REPEATABILITY OF PROCEDURES

To establish an estimate of the repeatability of the static procedures, three fuel/coating combinations were run in duplicate for periods of 1 day and 1, 4, and 24 weeks. Average deviations ranged from 0.1 to 4.0 mg/100 ml and tended to increase as the level of zinc being measured increased. Converted to a percentage of the zinc level in the fuel sample, these become a range of 2% to 11%, with the percentage deviation decreasing with an increase in the zinc concentration.

Similar duplicate determinations were not run with the other procedures, but the similarities among all the procedures used in this investigation led to the conclusion that similar levels of repeatability were obtained.

RESULTS AND DISCUSSION

STATIC EXPERIMENTS

A total of 144 standard static experiments involving seven fuels and five inorganic zinc coatings were made. Experiment durations ran from 1 day to 24 weeks, although all fuel/coating combinations were not examined for the full 24 weeks. The largest number of experiment duration times for any fuel/coating pair was associated with the fuel A/coating 1 (A/1) pair with which experiments of 1 day and 1, 2, 4, 8, 16, 20, and 24 weeks were made. In contrast, a single experiment duration of 4 weeks was employed with the F/2, F/3, G/2, G/3, and G/4 pairs. In addition to these 144 experiments with both water and fuel in the jar, 18 experiments were run with only fuel in the jar, and 3 experiments were run with only synthetic sea water in the jar with the coated panel. Specifically, fuels A and C were used in combination with coatings 1, 4, and 5 in experiments lasting 4, 8, and 16 weeks; sea water was used in combination with the same three coatings in experiments lasting 4 weeks.

Interaction between the coated panels and the fluids in the static system was evident by visual inspection a few weeks after the start of an experiment. Figures 1 and 2 show the appearance of two types of coated panels after 24 weeks of contact with each of four fuels. The appearance of a fresh panel is also shown for each of the two coatings. The sea-water/fuel interface level is evident on each panel, and the fuel/air interface level is evident on several of the panels.

Zinc from the coatings was found in both the fuel and the sea water at the end of an experiment; a solid precipitate also collected at the bottom of the water phase. Zinc in the fuel phase is a major concern because this zinc is carried by the fuel to filters and burners or engines. Figure 3 shows the zinc concentration in the fuel as a function of contact duration for several of the fuel/coating pairs. Three things are noted. First, the fuel appears to be a major factor in determining the level of zinc in the fuel at the end of the experiment. Second, for a given fuel, there is a scatter of points perhaps dependent upon the particular coating on the panel. Third, the zinc content of the more acidic fuels reaches a maximum in about 4 to 5 weeks and then declines slightly in a manner similar to the classic sequential reaction curves found in the literature of physical chemistry.

The significance of the scatter of points was determined by an analysis of variance for all points obtained after 4, 8, 20, and 24 weeks of investigating the five different coatings. Such an investigation assumes either, after the maximum value is obtained, the subsequent values remain the same, i.e., an asymptotic value is reached and maintained, or the decrease is minor relative to the general scatter of data. The analysis of variance uses the F-statistic[5] which is based upon the probability distribution of the ratios of two sample variances. By convention $F_{0.95}$ and $F_{0.99}$ signify the F-statistic value such that 95% and 99%, respectively, of all F-statistic values will be smaller; i.e., only 5% and 1%, respectively, will be higher. The F-statistic for five panel coatings at each of the four experiment duration periods was calculated as 1.46 for fuel A and as 2.53 for fuel B. In both cases, the $F_{0.95}$ and $F_{0.99}$ values were 3.06 and 4.89, respectively. Since the calculated F-statistic value was smaller than either the $F_{0.95}$ or the $F_{0.99}$ value from the table, the null hypothesis that there is no statistical difference among the coatings cannot be rejected.

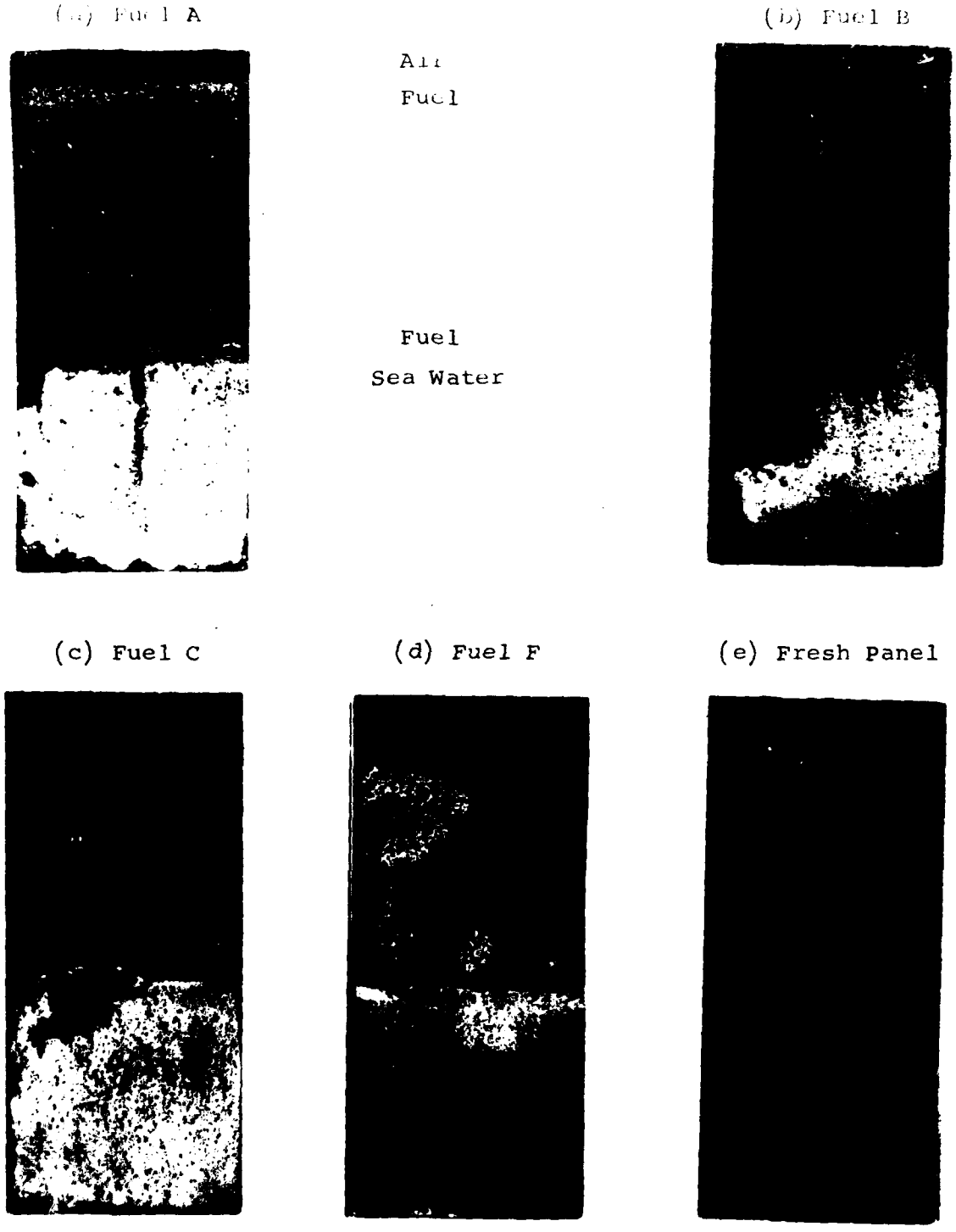

Figure 1 - Appearance of Panels Coated with Coating 1 After 24 Weeks of Contact With Each of Four Fuels Compared With the Appearance of a Freshly Prepared Panel

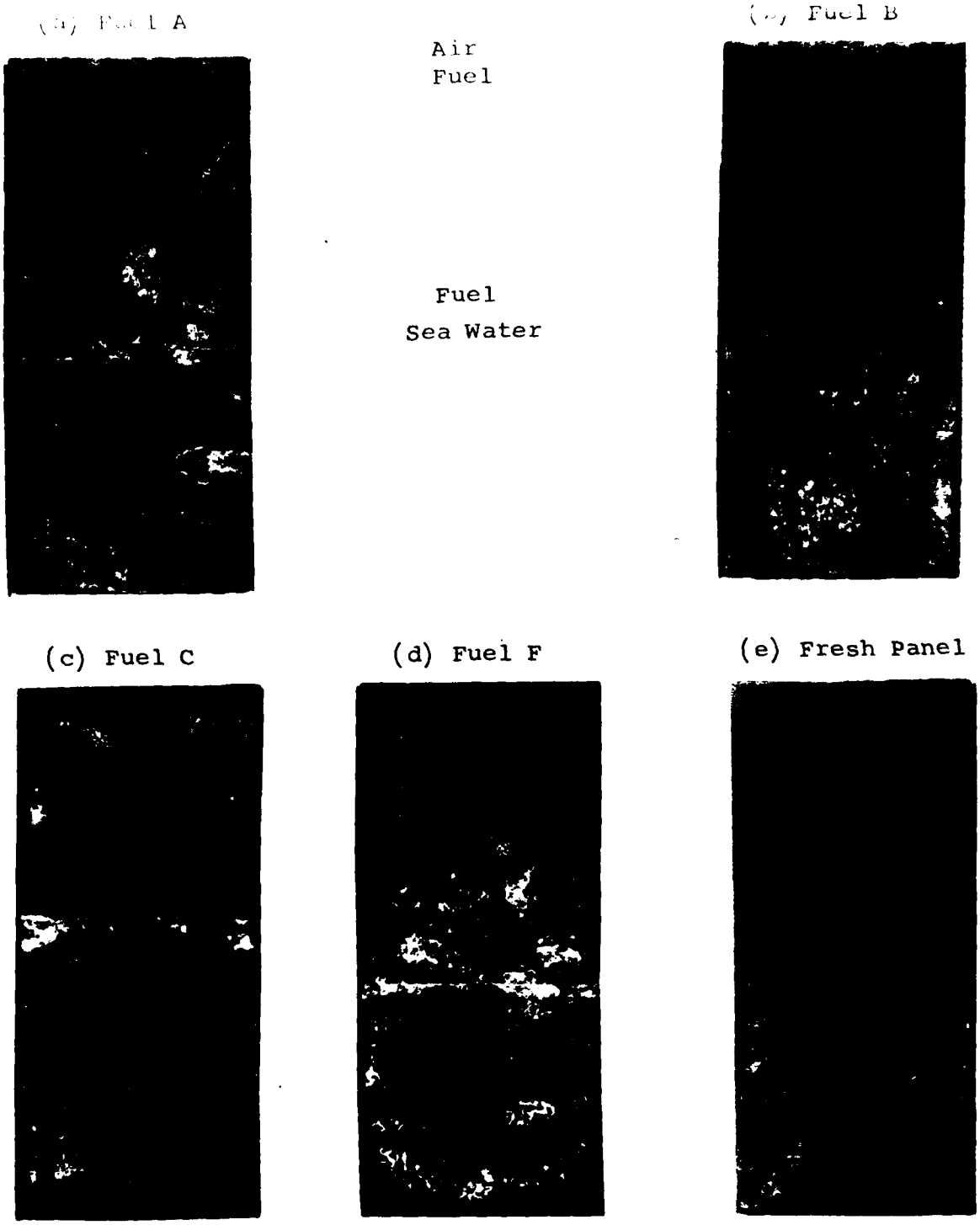

Figure 2 - Appearance of Panels Coated with Coating 5 After 24 Weeks of Contact With Each of Four Fuels Compared With the Appearance of a Freshly Prepared Panel

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We therefore conclude that differences among the five coatings used in the experiments are not statistically significant, insofar as the amount of zinc found in the fuel is concerned, although the visual inspections and the time-versus-zinc content curves of figure 3 do indicate some minor differences among the coatings.

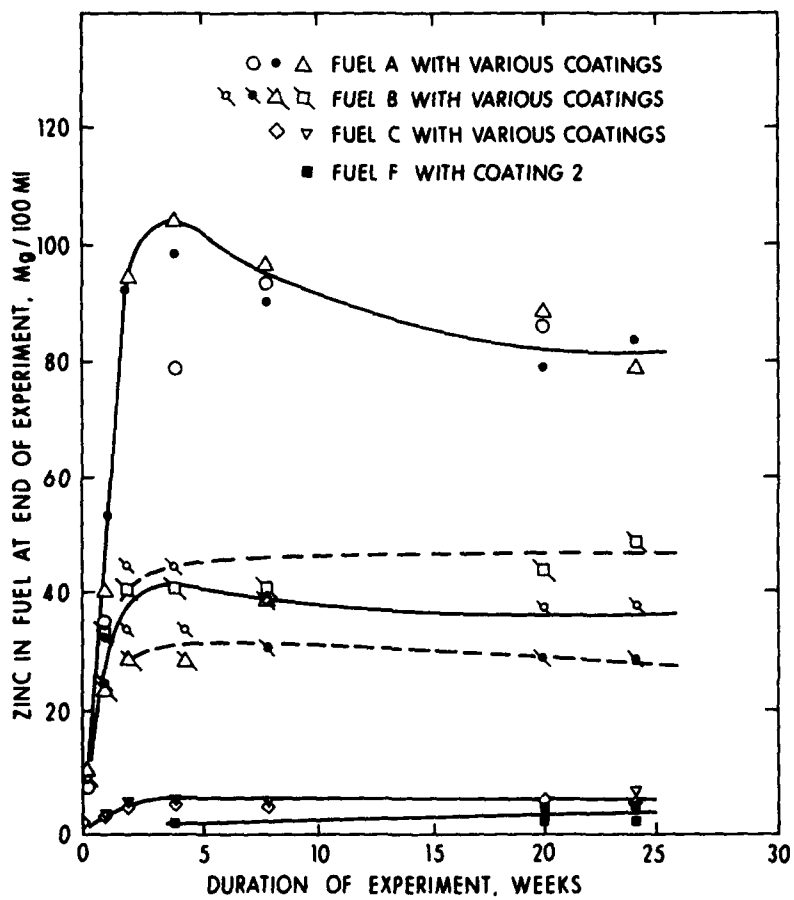

Figure 3
Effect of the Duration
of Contact Between Fuel and Panels
Coated with Inorganic Zinc Coatings
on the Amount of Zinc in the Fuel

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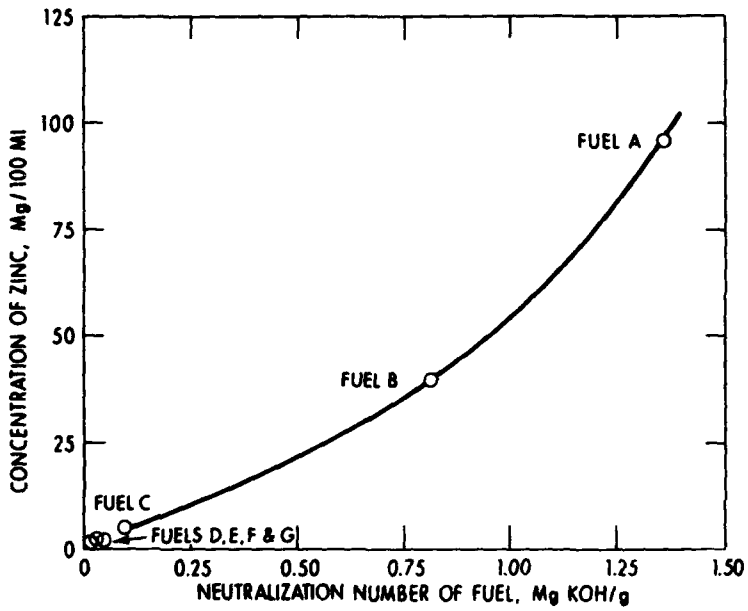
As noted earlier, a few experiments were conducted with galvanized rather than painted coatings on the panels. When duplicate experiments of galvanized panels in fuels A and B are compared with the averages of the five coatings in the same fuels, the difference in zinc pickup by the fuels is found to be highly significant. Pertinent data are shown in table 2.

TABLE 2
COMPARISON OF ZINC CONTENTS OF FUELS
GALVANIZED VERSUS INORGANIC ZINC COATINGS

Type of Zinc Coating	Zinc	
	Inorganic	Galvanized
Fuel A		
Mean zinc content, mg/100 ml	95	64
Number of items in mean	5	2
Standard deviation, mg/100 ml	4.3	4.0
Fuel B		
Mean zinc content, mg/100 ml	39	28
Number of items in mean	5	2
Standard deviation, mg/100 ml	3.6	3.0

From these data the Student's-t values are found to be 8.8 for fuel A and 3.87, for fuel B, both of which are greater than the t-score of 3.36 as determined from tables for a one-tailed test at the 0.01 level of significance. We thus conclude that significantly more zinc is picked up by the fuel from the painted inorganic zinc coatings that from a galvanized zinc coating.

Figure 3 shows differences in the level of zinc dissolved in fuel as a function of the time of contact, with the particular fuel as a parameter. Different levels of dissolved zinc are noted with the different fuels. Solution of a metal usually involves the conversion of the metal into an ionic state by the removal of electrons. In many cases the electron acceptor is ionic hydrogen from an acid already in solution. Figure 4 shows that there is a relationship between the initial acidity of the fuel, as measured by the neutralization number (ASTM procedure D 664-58), and the zinc found in the fuel after 8 weeks of contact between fuel and coated panel.



Note: Neutralization number is a measure of fuel acidity.

Figure 4 - Relationship Between the Initial Acidity of a Distillate Fuel and the Zinc Found in the Fuel after 8 Weeks of Contact Between the Fuel and the Coated Panel

If hydrogen ions from an acid in solution do react with the metallic zinc to effect solution, the hydrogen discharges from the system as gaseous hydrogen, and the measured acidity should decrease. Neutralization numbers were determined on fuels A, B, C, F, and G both at the beginning of an experiment and after 24 weeks of contact with panels coated with coating 1, 4, or 5. Fuels F and G were found to have acid numbers of 0.03 and 0.01, respectively. These values are so low that any measured change occurring during the experiments could only fall within the reproducibility/repeatability limits of the neutralization number procedure. Fuel C, with an initial value of 0.09 mg KOH/g and a final value averaging 0.04 for the three panels, falls on the borderline of reproducibility but does tend to indicate a decrease in the acidity of the fuel. However, fuel A, with an initial neutralization number of 1.36, had a final value after the 24 weeks averaging 0.90 mg KOH/g; fuel B, with

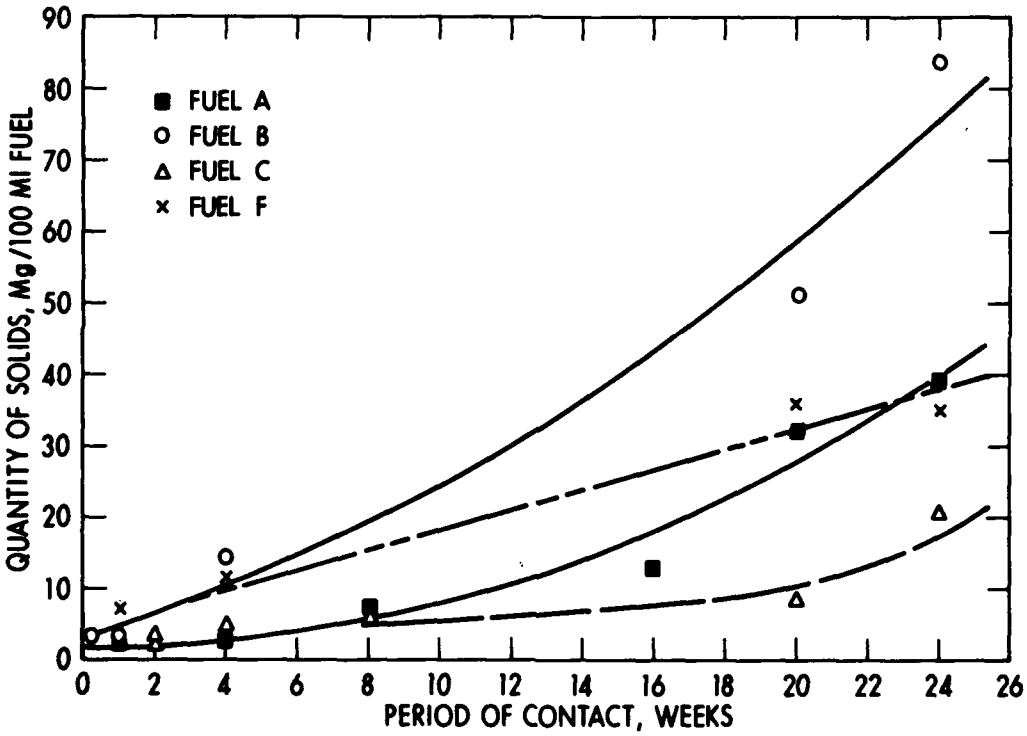
an initial neutralization number of 0.81, had a final value averaging 0.54 mg KOH/g. Thus, both fuels A and B showed strong evidence of acid consumption during the 24 weeks of contact with inorganic zinc-coated panels. This supports the hypothesis that the amount of zinc that dissolves in a fuel is related to the acidity of that fuel.

As noted previously, a few experiments were run with only fuel or only synthetic sea water in the jar with a coated panel. The results of those experiments are shown in table 3, together with results obtained over the same period of time with the usual fuel plus sea water in the jar. It is evident that neither fuel alone nor sea water alone is as reactive as the combination of the two in contact with the coated panel. It is postulated that both the acidity present in the fuel and the ionization provided by the water must be present for the greater attack on the coating.

Coating	Zinc in Fluid, mg/100 ml		
	4 Weeks	8 Weeks	16 Weeks
Fuel A Alone			
Coating 1	30	32	-
Coating 4	50	-	58
Coating 5	46	-	59
Average	42	32	58
Fuel A + Sea Water			
Coating 1	100	92	60
Coating 4	106	98	-
Coating 5	101	94	-
Average	102	95	60
Fuel C Alone			
Coating 1	1	-	-
Coating 4	1	2	-
Coating 5	1	-	-
Average	1	2	-
Fuel C + Sea Water			
Coating 1	<7	6	-
Coating 4	<5	5	-
Coating 5	<6	5	<5
Average	<6	5	<5
Sea Water Alone			
Coating 1	<0.1	-	<0.1
Coating 4	<0.1	-	<0.1
Coating 5	<0.1	-	<0.1
Average	<0.1	-	<0.1

TABLE 3
REACTIVITY OF FUEL
OR SEA WATER ALONE VERSUS
FUEL/SEA-WATER COMBINATION

Solids were found to form in the static systems jars, presumably either as a by-product of the reaction of fuel with the inorganic zinc coating or as a result of the flaking and pealing of the coating. Figure 5 shows that the amount of solids formed increased with the duration of the contact between fuel and coating and, in fact, increased more and more rapidly as time passed. However, although the amount of solids formed appears to be related to the nature of the fuel, it is apparently unlike the zinc found in the fuel since the acidity is not the controlling fuel property. For example, fuel A, which possesses the highest neutralization number, does not produce the most solids.



Note: Data points represent averages of the amount of solids formed by three coatings in contact with each of four fuels.

Figure 5 - Effect of the Duration of Contact Between a Fuel and an Inorganic Zinc Coating on the Formation of Solids

Table 4 shows that all the coatings are not affected equally by a fuel in regard to the level of solids formation. Fuel A, for example, formed much more solid with coatings 2 and 3 after 4 weeks that it did with the other three coatings, whereas fuels C, F, and G produced more solids with coatings 3 and 5. In general, coatings 3 and 5 produced two to three times as much solids as coatings 1, 2, and 4 during a 4-week period.

TABLE 4 - LEVEL OF SOLIDS
FORMED WITH DIFFERENT COATINGS

Fuel	Period of Contact Weeks	Solids Formed, mg/100 ml fuel Coating Number				
		1	2	3	4	5
A	4	3	15	23	2	3
	24	24	-	-	40	54
B	4	18	3	17	9	17
	24	55	-	-	68	128
C	4	3	1	13	3	9
	24	4	-	-	6	51
F	4	4	7	12	3	27
	24	6	-	-	12	85
G	4	5	5	21	6	10
	24	93	-	-	-	-
Average	4	6	6	17	5	13
	24	36	-	-	32	80

When the amount of solids formed by fuel alone, by both fuel and sea water, and by sea water alone are compared (table 5), a general lack of consistency is noted. Thus, comparison of fuel A alone versus A plus sea water shows relatively minor differences in coatings 1, 4, and 5. A similar comparison of the solids formed with fuel C alone with the amount formed with fuel C plus sea water reveals a definite increase in solids formation when sea water is present. Further, sea water alone in contact with coated panels 4 and 5 results in the formation of more solids than any of the other four cases.

TABLE 5
SOLIDS FORMED AFTER 4 WEEKS OF CONTACT

	Total Weight of Solids, mg Coating Number			
	1	4	5	Average
Fuel A alone[1]	5	4	7	5
Fuel A + sea water[2]	6	4	5	5
Fuel C alone[1]	4	2	2	3
Fuel C + sea water[2]	5	7	18	10
Sea water alone[1]	8	38	55	34

[1] 400 ml of liquid.
[2] 200 ml fuel/200 ml sea water.

In some instances the solids were analyzed by atomic absorption to determine their contents of zinc, iron, and silicon. These instances all represented 24-week contact times and involved fuels A, B, C, and F in contact with coatings 1, 4, and 5. In every case zinc contents were two to nine times greater than either the silicon or the iron. In fact, zinc contents averaged from 17% of the solids in the case of the three panels in contact with fuel F to 28% in the experiments with fuel C. With all fuels, silicon ranked second in magnitude to zinc and averaged from 3% with fuel B to 9% with fuel A. When silicon contents were averaged by coating, coating 1 with an average of 15% silicon in the solids yielded the highest silicon contents, because coatings 4 and 5 yielded only 4% and 3% silicon, respectively. Coating 1 is known to use an ethyl silicate vehicle, so the high silicon levels are consistent with known facts. However, coating 4 is also known to use a silicate vehicle, so the nature of the vehicle alone is insufficient to explain the differences. In all instances, iron contents in the solids were of lowest magnitude and averaged less than 1%. In summary, the solids were found to contain an average of 24% zinc, 7% silicon, and less than 1% iron. The balance of the weight of solids is probably represented by organic matter (from coating binder flakes and from insoluble soaps) and by oxides or other inorganic compositions of the metals.

Modified static experiments, in which the area of coating in contact with a given volume of fuel was varied, yielded the concentrations of zinc in the fuel shown in table 6. Fuel A was used in all these experiments. Figure 6 shows that, at the lower values of the area/volume ratio (the square feet of coating surface in contact with a gallon of fuel), the amount of zinc in the fuel after a given period of time is a linear function of the area/volume ratio; i.e., the more area in contact with the fuel, the faster the zinc content increases in the fuel portion. At the higher values of the area/volume ratio, there is a deviation from the linear, such that the zinc concentration in the fuel is found to be less than would be anticipated from an extrapolation of the linear relationship. This implies that, at the higher area/volume ratios, the area is no longer the controlling factor in the rate reaction. The controlling factor is the residual acidity of the fuel.

TABLE 6 - RESULTS OF STATIC EXPERIMENTS AT SEVERAL AREA/VOLUME RATIOS (Fuel A/Coating 1 Used in all Experiments)

Volume of Fuel ml	No. of Panels	Fuel Contact Area ft^2	Area/Volume Ratio ft^2/gal	Zinc in Fuel[1] after		
				1 Day	1 Week	4 Weeks
2,000	1	0.065	0.124	1	3	-
800	1	0.065	0.308	3	15	28
500	1	0.065	0.495	12	18	42
200	1	0.065	1.236	15	55	99
200	2	0.131	2.472	20	58	94

[1] In mg/100 ml fuel.

In these experiments it was noted that the area of red rust on a panel surface increased with an increase in the volume of sea water in contact with that surface. At the lowest area/volume ratio (0.124 ft^2/gal), the entire area was found to be coated with rust. These observations indicate that the inorganic zinc coating used provided inadequate protection of the underlying steel panel.

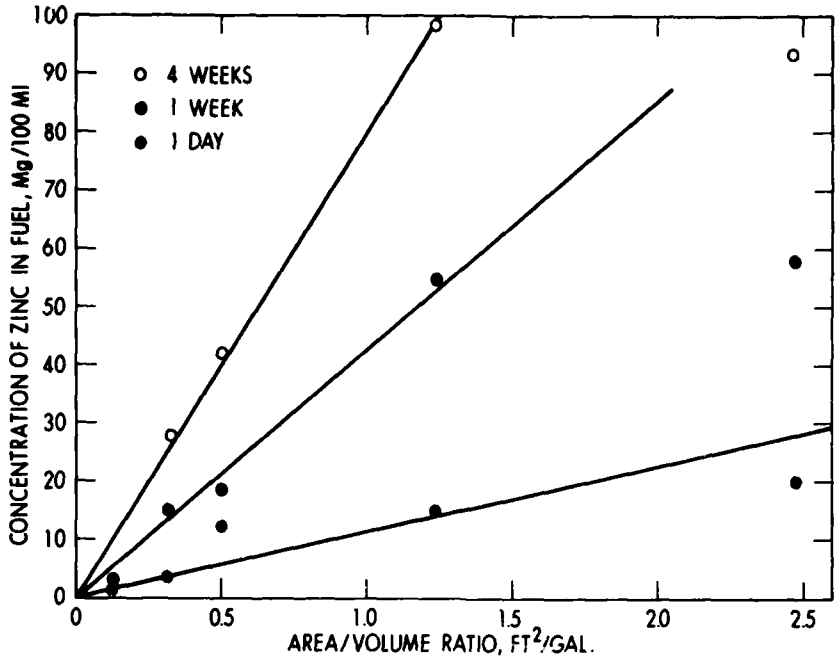


Figure 6 - Effect of the Area/Volume Ratio on the Amount of Zinc in Fuel A after Contact with an Inorganic Zinc Coating for 1 Day, 1 Week, and 4 Weeks

REPLENISHMENT EXPERIMENTS

A total of 188 replenishment experiments involving three fuels and five inorganic zinc coatings were made. In 93 of these experiments the fuel and sea water were replaced weekly without attempting to remove any reaction products from the coated panel. In the other 95 experiments the panels were scrubbed gently with a soft rubber device. These are referred to as the "no scrub" and "scrub" experiments, respectively. Tests of fuel A with all five coatings lasted from 14 to 30 weeks. Experiments with fuel B involved only coatings 2, 3, and 4 and lasted from 12 (with coatings 2 and 3) to 25 weeks (with coating 4). Experiments with fuel C involved only coating 4 and lasted for 25 weeks. Although the fuel and sea water were replaced weekly, the zinc content of the replaced fuel was not necessarily determined each week. For example, in the fuel A experiments with coating 5, zinc was determined in fuel removed after the experiment had lasted 1, 2, 3, 4, 8, 10, 12, 14, 16, 18, 21, 22, 25, 26, 28, and 30 weeks.

Table 7 presents typical zinc contents of fuel for both the scrub and the no-scrub experiments. A slight but statistically significant increase in the zinc content of the replaced fuel is evident when the coating has been scrubbed. This is consistent with the known fact that corrosion reactions are sometimes self-limiting as a result of the deposition of corrosion products on the reacting surface, a situation which limits the diffusion of the corrosive agent to the reactive surface. In such cases, the removal of the deposit, such as would be caused by scrubbing in these tests, results in an increased rate of attack. The scrubbing action of incoming fuel or ballast water may have a similar effect on a coating in a ship's fuel tank.

TABLE 7 - COMPARISON OF TYPICAL ZINC CONTENTS OF FUEL IN REPLENISHMENT SCRUB AND NO-SCRUB EXPERIMENTS

Total Elapsed Experiment Time Weeks	Zinc in Replaced Fuel, mg/100 ml			
	Fuel A/Coating 2		Fuel B/Coating 3	
	No-Scrub	Scrub	No-Scrub	Scrub
1	34	36	24	25
2	31	32	28	30
3	33	33	32	32
4	33	33	32	34
8	35	40	31	35
10	30	43	18	20
12	27	27	6	6
14	11	15	-	-
Total	234	259	171	182
Average	29	32	24	26

Figure 7 shows how the zinc content of replaced fuel (after a week in contact with a coating) varies with the total length of time the coating has been in contact with fuel. The curves are based on the averages of all scrub-type experiments in which a fuel was in contact with a coating. For fuel A this means that each point represents the average of five data points (five scrubbed coatings). For fuel B (three coatings) each point on the plot represents three data points, and for fuel C with a single coating each point represents one data point.

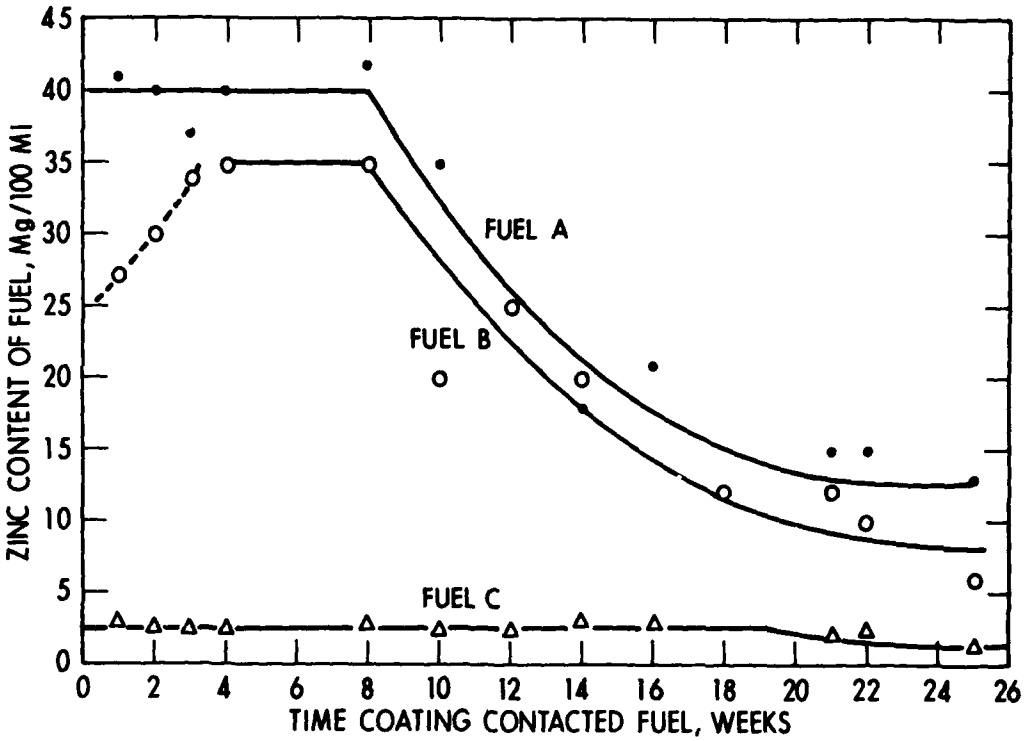


Figure 7 - Variation of the Zinc Content of Replaced Fuel (after a Week in Contact with a Coating) as a Function of the Total Number of Weeks the Inorganic Zinc Coating had Been in Contact with Fuel in the Replenishment Experiments

The shape of the curves in figure 7 leads to some interesting speculations. If the curves for fuel A is examined, it will be noted that the amount of zinc picked up by the fuel in a week of contact remains essentially constant at about 40 mg/100 ml for the first 8 weeks of the experiment and then decreases exponentially to reach an asymptotic value of about 12 or 13 mg/100 ml. Except for a period of 2 or 3 weeks during which an increasing level of zinc is obtained, fuel B is seen to follow a similar pattern with an asymptote of about 8 or 9 mg/100 ml being reached after 22 weeks. Fuel C may exhibit a much longer initial period of relatively constant zinc pickup (roughly 18 to 20 weeks as drawn), but the overall level of zinc is only about 2.5 mg/100 ml, so that the decrease after 21 weeks may represent merely a variation resulting from the general precision of measurements at this low level of zinc in the fuel. The

zinc in the fuel during the initial period is at the same level as that obtained in a 1-week static experiment. For fuel A the average of zinc levels for the five coatings after a 1-week static experiment is 44 mg/100 ml compared with the initial replenishment level of 40 mg/100 ml. For fuel B the comparable static/replenishment averages for coatings 2, 3, and 4 are each 29 mg/100 ml, and for fuel C the values are 2.5 and 4 mg/100 ml.

The decreasing levels of zinc in fuels A and B after about 8 weeks in the system indicate that some factor other than the fuel/coating combination is becoming dominant. Several hypotheses attempting to explain this phenomenon have been proposed, but no attempt has been made to determine the exact mechanism. According to one hypothesis, the zinc particles act as sacrificial anodes which are gradually depleted so that the area of zinc available for attack decreases and/or the reaction surface of the zinc recedes into a pit, resulting in a longer diffusion path for the active corrosive agents to travel before reaching the zinc. Either would result in a slower reaction, so that less zinc would get into the fuel. According to another hypothesis, insoluble zinc compounds deposit on the active zinc sites and inhibit reaction. According to a third hypothesis, the coating gradually flakes off the panel, leaving a lesser surface of zinc to react with the fuel since the flakes drop through the fuel into the water, hence to the bottom of the container, where the zinc is no longer available for reaction with the fuel. Regardless of the exact mechanism, the experiment indicates a decrease in zinc pickup by the fuel after a period of time.

DYNAMIC EXPERIMENTS

If diffusion of reactive materials to the zinc surface is the rate-controlling process, then motion of the fuel past the surface of the coating should increase the rate of reaction by reducing the thickness of the boundary layer of fuel. The dynamic experiment is designed to investigate this hypothesis by providing motion past the panel surface in a manner simulating the back-and-forth motion of fuel in a ship's tank. Table 8 shows that the zinc dissolved by fuel A does indeed increase (double from 15 to 31 mg/100 ml) under dynamic conditions during a 1-day experiment. There appears to be a slight increase under dynamic conditions (from 50 to 56 mg/100 ml) during an experiment lasting a week, but this increase is

not statistically significant. On the other hand, the quantity of solids produced under dynamic conditions does not increase significantly whether the experiment lasts 1 day or 1 week (2 versus 2 and 4 versus 2 mg/100 ml, respectively).

TABLE 8 - COMPARISON OF RESULTS[1] FROM DYNAMIC AND STATIC EXPERIMENTS (Fuel A Used in all Experiments)

Coating	Experiment Duration	Dynamic Conditions		Static Conditions	
		Zinc in Fuel	Solids	Zinc in Fuel	Solids
1	1 day	34	3	15	2
	1 week	56	4	55	2
4	1 day	38	2	11	2
	1 week	58	3	42	2
5	1 day	21	2	19	2
	1 week	54	4	53	2
Average	1 day	31	2	15	2
	1 week	56	4	50	2

[1] All values expressed as mg/100 ml fuel.

GENERAL

A rough estimate of the amount of zinc that might be found in fuel from various shipboard fuel tanks, if the tanks were coated with an inorganic zinc coating, can be obtained from the data already presented. For example, the fuel oil service tank on a certain destroyer has an area/volume ratio of about 0.1 ft^2/gal and holds enough fuel to last for about 4 hours at full power or about 28 hours at average cruising conditions. The relatively short time that a fuel remains in this tank and the low area/volume ratio indicate that the amount of zinc that enters the fuel will be dependent upon the area and the time of contact, since there would be insufficient time for concentration factors to vary appreciably. If the fuel in the tank has the same high neutralization number (1.38 mg KOH/g) as the 28.9° API gravity fuel A used in the laboratory studies, figure 6 can be used to estimate the zinc in the fuel at the end of a day. The resulting value of 1 mg/100 ml can then be

adjusted to the 4- and 28-hour periods. This procedure gives values of about 2 and 13 ppm, respectively, after converting from mg/100 ml values (1 mg/100 ml = approximately 11 ppm). Obviously, if fuel sat in the tank while the ship was tied up at the dock for an extended period, higher zinc levels would be reached, as indicated below.

As another example, the same destroyer has a stern tank for which the area/volume ratio is slightly above 0.2 ft^2/gal. Under cruising conditions, the fuel in this tank may not be required for 10 days or more. Interpolation between the 1- and the 4-week lines in figure 6 yields an estimated zinc content of 10 mg/100 ml (approximately 114 ppm) after 10 days of storage. However, if the ship makes a practice of bunkering before the need for fuel from this tank arises, then fuel may remain in the tank for extended periods of time. Given sufficient time, the zinc in the fuel may reach some equilibrium value where the rate at which zinc enters the fuel from the coating is the same as the rate at which zinc leaves the fuel by various means, such as by deposition of insoluble zinc compounds on the coating or by passing through any water layer to the bottom of the tank as insolubles. A plot of the data in figure 6 at the 0.2 ft^2/gal point provides an estimate of this equilibrium value as being about 20 mg/100 ml (roughly 230 ppm).

The estimates of the quantity of zinc in fuels from these two tanks are probably maximum values, because studies have revealed a lesser level of zinc entering fuel from coatings that have aged through replenishment of the fuel in contact with the coating and because the data were based on the fuel with the highest neutralization number of the fuels used in the research program. However, the values are realistic for the situation where a freshly coated tank is filled with a high neutralization number ND fuel. Moreover, these estimates are consistent with the concentrations of zinc reported by Garner and Evans,[4] if the effect of a higher neutralization number is taken into account.

If the fuel is left in the tank long enough to create a zinc level of 20 mg/100 ml in the fuel and if that fuel is then pumped to a furnace or engine through a filter, then the filter will have to be capable of handling any zinc compounds that might form in the fuel. If all the zinc is present as insoluble zinc compounds and if the fuel flow rate is 30 gpm,

then some 72 lb/day of zinc will be deposited on the filter as a compound weighing perhaps four or five times the zinc it contains, i.e., perhaps 330 lb/day. If the zinc compounds are soluble, they will pass with the fuel to the combustion area where the oxide or sulfate could form at a rate of 90 or 178 lb/day, respectively (over 600 and over 1200 lb/week, depending upon the compound formed). Some fraction of these quantities would deposit in engines or boilers, restricting passages, leading to hot spots or valve burning, and creating operating problems.

CONCLUSIONS

- Inorganic zinc coatings are not suitable for use in tanks intended for ND fuel service because zinc levels in the fuel can become appreciable.

- The amount of zinc in a fuel in contact with inorganic zinc coatings reaches a maximum in 2 to 4 weeks and thereafter declines slowly to about 80% of its maximum value after 20 weeks.

- The rate of zinc acquisition by a fuel in contact with inorganic zinc coatings:

  - Is increased in the presence of sea water.

  - Is increased by an increase in the acidity of the fuel.

  - Is increased by an increase in the area of the coating in contact with the fuel.

  - Is less when the fuel is in contact with an old coating that has been contacted with many batches of fuel than it is in contact with a freshly applied coating.

- Inorganic zinc coatings simultaneously in contact with both fuel and sea water tend to flake.

RECOMMENDATIONS

- Prohibit the use of inorganic zinc coatings in ND service on new construction to eliminate a source of zinc compound deposits in boilers and engines and thus reduce maintenance and repair costs.

- If ND fuels must be stored in existing shipboard tanks coated with inorganic zinc coatings, never allow the fuel to remain in the tank any longer than necessary.

- Keep the quantity of free sea water in contact with the fuel as small as possible with the available stripping system.

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13. ABSTRACT

The results of an investigation into the compatibility of the new Navy Distillate-type fuel with inorganic zinc fuel-tank coatings are reported. Interaction between Navy Distillate fuel and the representative coatings used in the investigation was indicated by visible change in the coatings and by increased levels of zinc in the fuels. The concentration of zinc in a fuel was found to depend upon the acidity of the fuel and upon the length of contact between fuel and coating. Coatings which had been contacted by many batches of fuel were found to release less zinc to a fuel than did newly applied coatings. On the basis of the data obtained in this investigation, the maximum concentration of zinc that might be found in a fuel stored for a long time in a typical tank protected with an inorganic zinc coating is in the order of magnitude of 20 milligrams per 100 milliliters (about 230 parts per million). It was concluded that the use of inorganic zinc coatings should be prohibited in Navy Distillate service.

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