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Surface Chemical Methods of Displacing Water and/or Oils and Salvaging Flooded Equipment

Part 4 - Aggressive Cleaner Formulations for Use on Corroded Equipment

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Washington, D.C.

PREVIOUS REPORTS IN THIS SERIES

"Part 1 - Practical Applications," H.R. Baker, P.B. Leach, C.R. Singleterry, and W.A. Zisman, NRL Report 5606, Feb. 23, 1961

"Part 2 - Field Experience in Recovering Equipment Damaged by Fire Aboard USS CONSTELLATION and Equipment Subjected to Salt-Spray Acceptance Test," H.R. Baker, P.B. Leach, and C.R. Singleterry, NRL Report 5680, Sept. 19, 1961

"Part 3 - Field Experience in Recovering Equipment and Fuselage of HH 52A Helicopter After Submersion at Sea," H.R. Baker and P.B. Leach, NRL Report 6158, Oct. 19, 1964

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ABSTRACT

The surface chemical techniques previously reported from this Laboratory for the removal of oily contamination, sea water, and fresh water from electronic and electrical equipment after flooding are not designed to remove the corrosion products which often form on some parts of equipment after salt water exposure. Thickened "paint-on" spot-cleaning compositions have been developed for the removal of such corrosion from aluminum, copper, brass, steel, cadmium plate, and zinc plate. The formulations employ solid chemicals to the maximum extent possible, the solids being combined with water or commercially available mineral acids just before use. The use of such aggressive cleaners may advantageously precede the surface chemical treatment described previously.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C02-15
BuShips Problem SR 007-08-04, Task 0617

Manuscript submitted April 15, 1965.

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SURFACE CHEMICAL METHODS OF DISPLACING WATER AND/OR OILS AND SALVAGING FLOODED EQUIPMENT

PART 4 - AGGRESSIVE CLEANER FORMULATIONS FOR USE ON CORRODED EQUIPMENT

INTRODUCTION

The procedure developed by this Laboratory for removing oily residues and/or sea water contamination from surfaces (1-10) uses an emulsion cleaner which can actively displace even Navy Special fuel from solid surfaces and at the same time dissolve salt deposits. The action of the cleaner is assisted by ultrasonic agitation whenever possible. After being cleaned, the equipment is ultrasonically rinsed in a tank of fresh water, the water is displaced by treatment with the NRL water-displacing fluid and preservative, and finally the equipment is oven dried at a modest temperature. After an electrical check for proper operation and replacement of defective components, the equipment is ready for service.

This salvage system (10) was used on a large scale to recondition electrical and electronic assemblies damaged by smoke, soot, sea water, and corrosive vapors during the fire on the aircraft carrier USS CONSTELLATION in December 1960. Since then the recovery system has been used extensively in governmental agencies for salvage of contaminated equipment and for routine cleaning of electronic equipment, teletypewriters, missile components, etc. The details of this method are outlined in the Appendix to this report.

If the salvage procedure is used on equipment damaged by flood or fire soon after the exposure, corrosion on the equipment is held to a minimum and removal of the products is routine. However, days or weeks often elapse after the equipment is damaged before salvage treatment can be started. During this interim, components may have corroded extensively; often it becomes necessary to introduce another step in the salvage process in order to satisfactorily renovate the equipment. The mild cleaners used in the removal of oily contaminants and sea water from sensitive electronic gear will not remove many of the corrosion products encountered; more active chemical cleaners are required. Because certain parts of electronic or electrical equipment will not tolerate aggressive cleaning agents, complete assemblies containing these components cannot be treated with such solutions. Some method for localized corrosion removal is called for; thickened "paint-on" cleaners which will not spread from the point of application offer a solution to the problem. Thickened paint removers have been commercially available for many years (11-13), but paint-removing chemicals are ineffective against corrosion products, and the thickeners usually employed in such compositions are not compatible with the chemicals required for rapid corrosion removal. The present work was undertaken to develop thickened corrosion removers for spot application to equipment as a preliminary step to the use of the integrated salvage procedure developed previously.

Thickened aggressive cleaners should as far as possible meet the following requirements:

1. When applied to a vertical surface, the composition should be retained in a stable layer about 1/8 in. thick, without slipping or excessive bleeding (syneresis) of the liquid phase.

2. The liquids should react with the corrosion product at normal temperatures and modify it so that the resultant material can be flushed from the equipment with unheated water.
3. All traces of the cleaner should be easily removed by flushing with unheated water.
4. The thickened cleaner composition should be stable for short storage periods.

The work reported here was concerned with corrosion on aluminum, copper, brass, steel, magnesium, silver, cadmium plating, and zinc galvanizing coatings. Each requires a distinct formulation for optimum cleaning action. In order to simplify stocking these cleaners an attempt was made to use solid reagents wherever possible in the formulations and to keep the number of liquid acids required for the formulations to a minimum. A single thickener was sought which could be used in all formulations. Also, the number of surfactants and inhibitors was kept as low as possible.

DEVELOPMENT OF THICKENED AGGRESSIVE CLEANERS

The laboratory study showed that the essential components of thickened corrosion removal agents include: (a) acidic compounds that will react with the corrosion on the metal surface, (b) an inert thickener, (c) a surfactant (wetting agent) to enable quick and complete wetting of the corroded area, (d) an inhibitor to curtail reaction when the corrosion product is destroyed and clean metal is exposed, and (e) a diluent (such as water) to adjust the cleaner to the optimum strength and render it compatible with flushing water.

Acids such as sulfamic, citric, glycolic, oxalic, hydrochloric, phosphoric, sulfuric, and nitric were found to react usefully with corrosion products of the metals studied, the specific choice depending upon the metal to be cleaned. (Many alkaline cleaning combinations were studied, but none of them reacted rapidly enough to be useful for this type of application.) A variety of chemical combinations were studied in order to develop suitable formulas for removing corrosion from the metals most often utilized in the construction of naval equipment. Individual components and their combinations were evaluated on corroded metal specimens, until a formulation was found that would remove heavy corrosion in less than 5 minutes at room temperature. The metals were corroded by exposing them to sea water spray at room temperature until a heavy coating of corrosion product was obtained.

The thickener-to-liquid ratio in a suitable paint-on type aggressive cleaner should be the lowest that will permit the composition to meet the requirements listed above. Thickeners were first studied to determine their effectiveness in thickening water, an alkaline solution, and an acid solution. The relative effectiveness of each potential thickener was evaluated by determining the quantity of fluid thickened by 1.0 g of thickener to the consistency of a thick paint (Table 1). (The consistency implied by the term "thick paint" here corresponds to an apparent viscosity between 4500 and 12,500 cp at 12 rpm and between 3800 and 5000 cp at 60 rpm in the Brookfield viscometer. The system is non-Newtonian.)

The best thickener found for acidic solutions was of the fumed silica type represented in Tables 1 and 2 by Cab-O-Sil M-5. This was found to be a satisfactory thickener for all of the cleaner formulations developed. The thickening effect of Cab-O-Sil M-5 in acid solutions is given in Table 2. Weaker acid solutions did not change the thickening characteristics of the thickener to any great extent.

The surfactant to be used in each formulation was chosen by trial to give quick wetting and penetration of the corrosion products for which the formulation was designed. It was

Table 1
Thickening Effect of Gelling Agents

Trade Name	Manufacturer	Solution*		
		Water (g)	Sulfuric Acid (95%) (g)	Alkali (50%) (g)
Napon	National Starch and Chem. Corp.	2	2	14
Col Flo 67	National Starch and Chem. Corp.	2	2	15
Kelcoloid HV	Kelco Company	40	2	11
Kelco Gel HV	Kelco Company	24	2	11
Napol B	A.E. Stanley Mfg. Co.	5	2	13
Napol L	A.E. Stanley Mfg. Co.	5	2	11
Cellulose Gum 7H	Hercules Powder Co.	48	2	22
Cellulose Gum 12MP	Hercules Powder Co.	20	2	30
Natrosol	Hercules Powder Co.	50	2	7
Bentone H-34	National Lead Co.	5	2	3
Ben-A-Gel E.W.	National Lead Co.	20	4	4
Cellosize (HEC)	Union Carbide Chem. Corp.	42	2	13
Cyanamer P-250	American Cyanamid Co.	24	8	5
Casein	Eastman Organic Chemicals	4	2	3
Gelatin	Eastman Organic Chemicals	15	2	2
Pectin	Eastman Organic Chemicals	12	2	4
Zein	Eastman Organic Chemicals	3	2	2
Jaguar 508	Stein, Hall and Co., Inc.	46	2	9
Cab-O-Sil M-5	Cabot Corp.	6	18	2
Carbopol 934	B.F. Goodrich Chem. Co.	30	8	52

*Grams of liquid thickened to ca. 8000 cp at 12 rpm in Brookfield viscometer by 1 g of thickener.

Table 2
Thickening Effect of Cab-O-Sil M-5 in Various Acids

Acid	Grams of Acid Thickened by 1.0 g Thickener
Sulfuric (95%)	18
Hydrochloric (37%)	15
Acetic (99.7%)	25
Phosphoric (85%)	12
Nitric (70%)	20

also selected for its ability to maintain its activity for several days in the presence of the acids employed. No attempt was made to evaluate all of the surfactants (wetting agents) available for study. From the readily available products surfactants were selected which would be stable in specific metal-cleaning formulations. Those finally chosen are given in Table 3.

Table 3
Surfactants (Wetting Agents) Used in the Paint-On
Type Corrosion-Cleaner Formulations

Trade Name	Chemical Type	Manufacturer	Form at 25° C
Igepal CO-880	Polyoxyethylated nonylphenol	Antara Chemicals Inc.	Wax
Benax 2Al	Sodium dodecyl diphenyl oxide disulfonate	Dow Chemical Co.	Powder
Renex 698	Polyoxyethylene alkyl aryl ether	Atlas Powder Co.	Liquid

Inhibitors of acid attack on clean metal are widely used in metal cleaning and boiler-scale removal. Those examined for use in thickened cleaners had been found effective in general metal-cleaning practice (14-18). The inhibitors chosen are commercially available chemical compounds rather than proprietary products of unknown or uncertain composition. The names of the inhibitors chosen appear in the formulations listed in Table 4.

Acid-inhibitor effectiveness was determined by observing the reduction the inhibitor produced in the rate of attack of the cleaner on bare metal surfaces. The inhibitor had to permit the destruction of the corrosion coating on the metal specimen but inhibit attack on the underlying metal. (The removal of the corrosion on cadmium plate and zinc plate usually resulted in the partial destruction of the plate, requiring surface repairs which will be discussed later in this report.)

Thickened cleaners were formulated from the ingredients discussed above, and the effectiveness of each formulation was evaluated by preparing corroded panels of the metals under study and then painting small ribbons of the thickened cleaner on the corroded panel. After waiting a maximum of 5 minutes, the panel was flushed with unheated tap water. The effectiveness in removing the corrosion products was observed by comparing the condition of the cleaned area with that of the area untouched by the thickened cleaner.

Of the many chemical formulations studied, those listed in Table 4 showed enough promise to justify study under field conditions. Such a study was difficult, however, because present Navy practice with electronic or electrical equipment which has corroded sufficiently in service exposures to provide a severe test of the aggressive cleaners described here would be to discard the material as worthless and not return it to a maintenance depot for reconditioning. In consequence, it has been difficult to arrange for significant field testing of the methods and materials developed in the laboratory. To bridge this gap, simulated field tests were devised.

A number of representative items of surplus equipment were exposed to weather and to sea water spray to corrode the different metals to a state in which the use of the

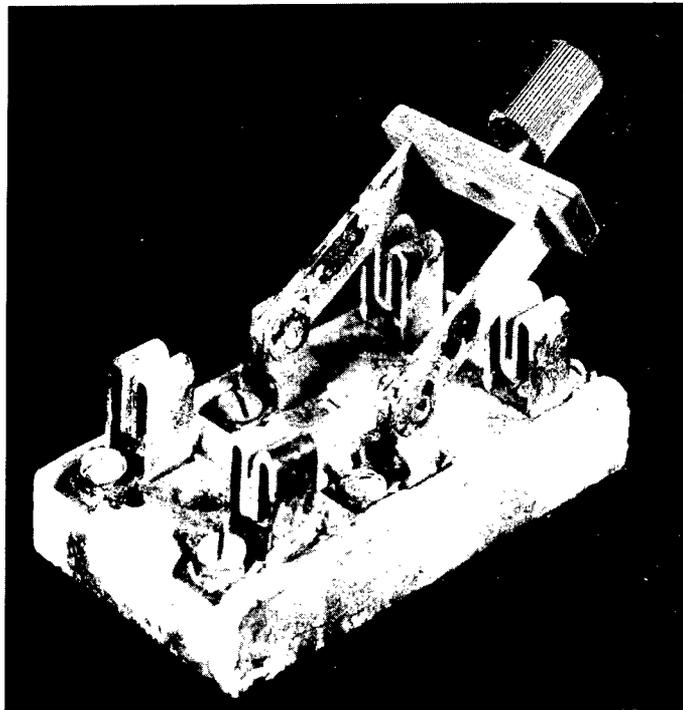
equipment would be considered impossible. These components were then spot cleaned with the appropriate paint-on type cleaning formulation (Table 4). This treatment was then followed by the routine salvage cleaning and drying procedures (10) summarized in the Appendix. See Figs. 1, 2, and 3 for before and after comparisons.

It is concluded from these studies that heavily corroded electrical equipment, bar switches, relays, mounting racks, etc., and mechanical equipment, tools, etc., constructed mainly of brass, copper, and steel can readily be cleaned and returned to useful service. Delicate electrical, mechanical, and electronic equipment having mainly magnesium and aluminum structural elements deteriorates rapidly when exposed to sea water and the weather. This damage is sometimes so extensive that recovery of the equipment is inadvisable except in an extreme emergency. On the other hand, if corrosion of the aluminum and magnesium parts has not weakened the gear structurally, it may be cleaned with the aggressive paint-on type cleaners and then carried through the usual salvage treatment (10) described in the Appendix.

MIXING AND USE OF THICKENED CLEANER FORMULATIONS

Mixing

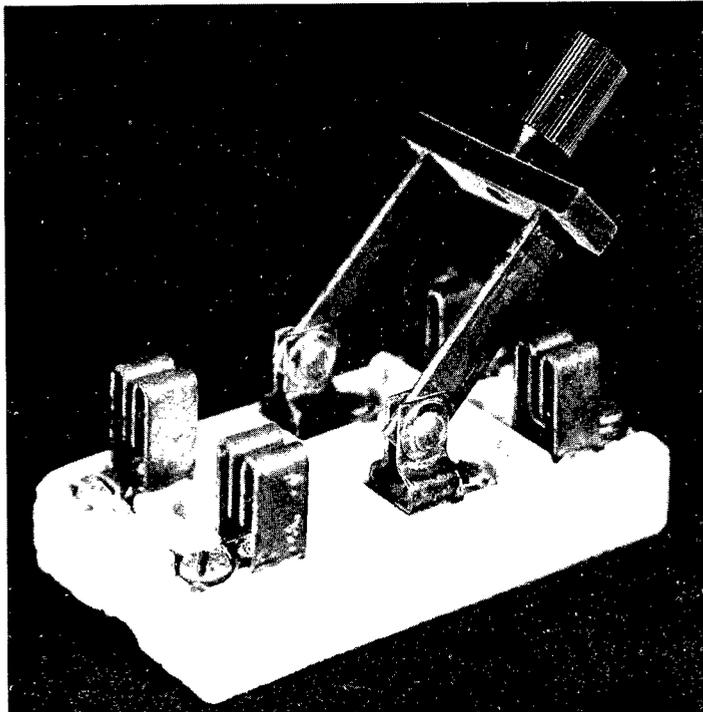
The formulations consist of two parts: (a) a number of dry solids which can be mixed and stored in compact form until the time of use, and (b) one or more of four common mineral acids which are to be diluted in water and used to dissolve or disperse the solids. (The zinc cleaner is an exception and must be made up completely at the time of use.)



(a) Before cleaning

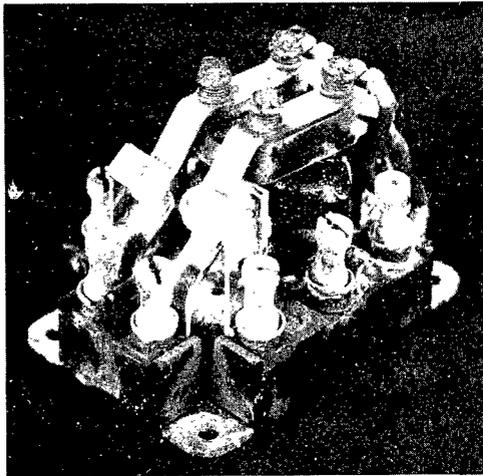
Fig. 1 - Corroded knife switch

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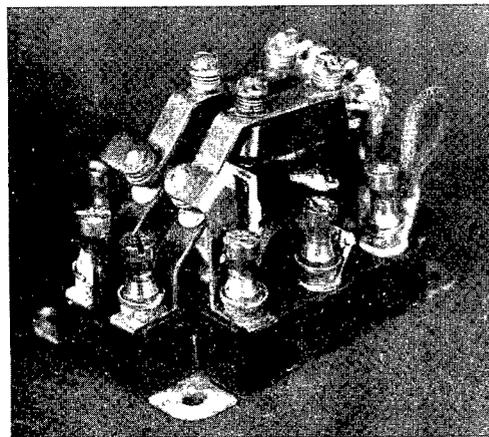


(b) After salvage

Fig. 1 (cont'd.) - Corroded knife switch

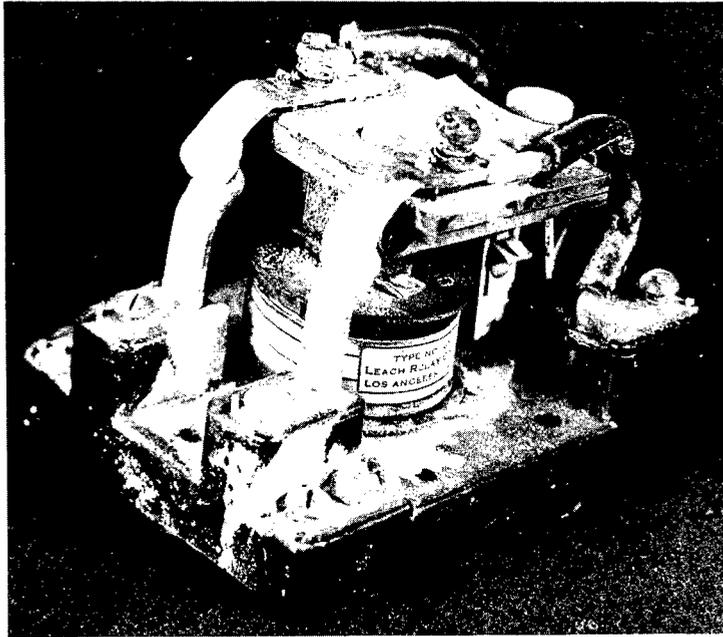


(a) Before cleaning

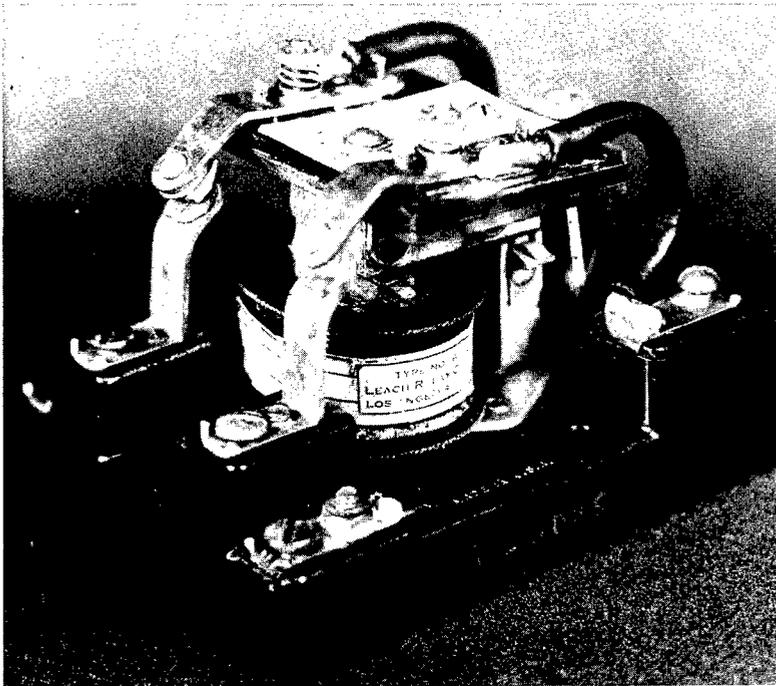


(b) After salvage

Fig. 2 - Corroded relay



(a) Before cleaning



(b) After salvage

Fig. 3 - Corroded relay

Certain safety precautions must be observed in the mixing and use of these cleaners. The liquid ingredients are listed in Table 4 in the order in which they should be added to the vessel containing the solid ingredients. The liquids must be added in this sequence to prevent possible spattering of strong acid during mixing. Always pour acid in small installments into the total amount of water called for.

The aggressive cleaners attack skin or clothing as well as the corrosion products on metallic surfaces. The vapors given off by some of these cleaners when they are applied to corroded surfaces are toxic. For these reasons, such cleaners should be used only in regular maintenance depots or where safety facilities exist. Personnel should wear safety goggles and protective clothing such as rubber aprons and gloves. All work of mixing formulations, applying thickened cleaner to corroded surfaces, as well as the flushing of cleaner and corrosion from equipment, should be carried out in a well-ventilated area where fumes will be drawn away from the worker. Once these formulations have been mixed, they should not be closed in unvented containers. Freshly mixed formulations are more reactive than the same preparations after they have stood in equilibrium with air for several weeks, so only the quantity needed for a week's work should be mixed at one time. The vented containers should be stored in a mechanically ventilated area. Glass or polyethylene containers are suitable for short-term storage of the formulations described.

Use

The aggressive thickened paint-on type cleaners are used as follows:

1. Identify the corroded metal and select the appropriate cleaner.
2. Carefully apply the thickened cleaner to the corroded metal surface with a brush.*
3. Within a few minutes (not over 5) flush the thickened cleaner and corrosion residue from the surface with fresh water. If all the corrosion has not been removed, the cleaning process should be repeated on resistant areas. (Once the thickened cleaner has been flushed from the equipment, the latter can be safely handled while subjecting it to the recovery process.)
4. Clean the entire equipment by the method developed by this Laboratory for recovering flooded equipment. This method is fully described in references 4, 5, and 10, and it is summarized in the appendix to the present report.

If zinc or cadmium plate is corroded extensively, the aggressive cleaner frequently removes most of the plating, thus leaving the steel area unprotected against further corrosion. The appearance of the zinc- or cadmium-plated steel can be improved and the steel can be protected against further rusting by treating it with a wash primer (19), then applying two coats of the corrosion-inhibiting primer (20) and two coats of the lacquer (21). The surface renovation process should be performed only after the entire equipment has been subjected to the recovery process through the drying cycle (step 4 of the Appendix).

Aluminum and magnesium alloy components are often badly scarred by corrosion. The physical appearance of this salvaged equipment can be improved by treating the

* Acid swabbing brush, Federal Stock Catalog, FSC Group 9, Class 7920, Section 79-2010, Federal Spec. H-B-643, Type II, hog bristle rifflings, or stiff horsetail hair (Stock No. 7920-514-2417).

aluminum with alcoholic phosphoric acid, drying, and then painting immediately with a zinc chromate primer such as that supplied under specification Mil-P-8585A (20). Two coats of primer should be used, the second after the first is thoroughly dry. These should be followed by two coats of lacquer such as that supplied under specification Mil-L-8641A (21). The clean magnesium (if it was not too badly deteriorated before salvage) should be treated with an aqueous solution of nitric acid and sodium dichromate, rinsed with water, dried, and immediately treated with a wash primer such as that supplied under specification Mil-P-15328B (19). This should be followed with two coats of the corrosion-inhibiting primer (20) and then two coats of the lacquer (21).

CONCLUSIONS AND RECOMMENDATIONS

1. Corroded equipment can often be salvaged by using the thickened paint-on type aggressive cleaners described here prior to application of the routine salvage system.
2. It is recommended that the information contained in this report be made available to maintenance depots throughout the Department of Defense for use in the recovery of corroded equipment.

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APPENDIX

OUTLINE OF PROCEDURE FOR RECOVERY OF EQUIPMENT AFTER REMOVAL OF CORROSION UTILIZING THE THICKENED PAINT-ON TYPE AGGRESSIVE CLEANERS

PROCEDURE

1. After the thickened aggressive cleaner and loosened corrosion products have been flushed from the equipment, the latter should be freed of sea water, salts, and residual cleaner by exposure to the emulsion cleaning composition in an ultrasonic bath. Pressure spray application or immersion in an air-agitated tank may be substituted if circumstances require, but they are less efficient.
2. Flush equipment with fresh water spray or dip to remove emulsion cleaner, and rinse in ultrasonic bath of fresh water (if possible).
3. Blow rinse water off the equipment with clean compressed air and follow with spray of water-displacing composition (Spra-Dri Moisture Control for Electronics, Type II, or Spra-Dri Moisture and Rust Control, Type I, for electrical and mechanical equipment containing ferrous parts).
4. Dry equipment in an oven at 120° to 160°F (depending on the temperature tolerance of the equipment) for several hours or overnight. When an oven cannot be used, a portable hot air blower may be substituted, or the equipment may be allowed to dry at room temperature for a longer time.
5. Electrical or electronic equipment should be checked for proper operation, defective components replaced, and adjustments made before returning it to service.

CHEMICALS REQUIRED

1. Water-Displacing, Rust-Inhibiting Composition (Moisture and Rust Control, Type 1) - This composition is commercially available in pressurized aerosol cans or in drums from the Spra-Dri Company, Division of Perfecting Service Company, Charlotte 6, N.C., under the designation Spra-Dri Moisture and Rust Control, Type I. It is formulated as follows:

n-butyl alcohol (1-butanol)	93.75 wt-%
2,6-di-tertiary butyl,4-methylphenol*	0.25 wt-%
basic barium dinonylnaphthalene sulfonate (50% inhibitor concentrate in naphtha) †	6.00 wt-%
	<u>100.00 wt-%</u>

* This is an oxidation inhibitor supplied under the trade name "Parabar 441" and is available from Enjay Chemical Company, a division of Humble Oil and Refining Company, 15 West 51st Street, New York, N.Y.

† This is a rust-inhibitor concentrate containing 50% inhibitor in naphtha solution. It is supplied under the trade name NA-SUL BSB by the R.T. Vanderbilt Company, Inc., 230 Park Avenue, New York, N.Y.

2. Water-Displacing Composition, Type II - This composition differs from Type I, above, by containing less rust inhibitor. It is intended for final water displacement on cleaned electronic equipment. It is available in aerosol cans or in drums as Spra-Dri Moisture Control for Electronics, Type II, from the same source as Type I.

This material may also be formulated locally, if desired. It has the following composition:

n-butyl alcohol (1-butanol)	98.75 wt-%
2,6-di-tertiary butyl,4-methylphenol*	0.25 wt-%
basic barium dinonylnaphthalene sulfonate (50% inhibitor concentrate in naphtha) †	1.00 wt-%
	<u>100.00 wt-%</u>

The rust-inhibitor concentration in this composition is reduced to avoid difficulties with switch contacts. Type II should not be used when maximum rust inhibition is required. Either water-displacing formulation is prepared by dissolving first the oxidation inhibitor and then the rust-inhibitor concentrate in the butyl alcohol and mixing thoroughly.

3. Concentrate for Preparation of Emulsion Cleaner - This material has the composition given below:

Dry-cleaning solvent, Type II, Fed. Spec. P-S-661, Navy Stock No. W6850-285-8011 (55-gal drums), W6850-274-5421 (5-gal cans)	91 vol-%
Diesel fuel oil, Type I, Mil. Spec. Mil-F-16884, SHIPS, Navy Stock No. WF9140-255-7764 (5-gal cans)	8 vol-%
Surfactant, nonionic	<u>1 vol-%</u>
	100 vol-%

Polyethylene glycol 400 monooleate, S1006, a product of Glyco Products Company, Inc., Empire State Building, New York, N.Y., is the surfactant recommended. However, Detergent, General Purpose, Mil. Spec. Mil-D-16791C-AN1-Type II, Navy Stock No. 7930-531-9716 (5-gal cans), can be used if the surfactant suggested is not available.

The cleaner concentrate is prepared by dissolving the surfactant and the diesel fuel in the dry-cleaning solvent. Immediately prior to use, the concentrate is emulsified with water in proportions of from 15 to 50 vol-%, depending upon the degree of oily contamination to be removed.

* This is an oxidation inhibitor supplied under the trade name "Parabar 441" and is available from Enjay Chemical Company, a division of Humble Oil and Refining Company, 15 West 51st Street, New York, N.Y.

† This is a rust-inhibitor concentrate containing 50% inhibitor in naphtha solution. It is supplied under the trade name NA-SUL BSB by the R.T. Vanderbilt Company, Inc., 230 Park Avenue, New York, N.Y.

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d.		
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13. ABSTRACT The surface chemical techniques previously reported from this Laboratory for the removal of oily contamination, sea water, and fresh water from electronic and electrical equipment after flooding are not designed to remove the corrosion products which often form on some parts of equipment after salt water exposure. Thickened "paint-on" spot-cleaning compositions have been developed for the removal of such corrosion from aluminum, copper, brass, steel, cadmium plate, and zinc plate. The formulations employ solid chemicals to the maximum extent possible, the solids being combined with water or commercially available mineral acids just before use. The use of such aggressive cleaners may advantageously precede the surface chemical treatment described previously.		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Corrosion Aggressive cleaners Equipment salvaging Paint-on cleaners Thickener Surfactant Inhibitor						

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