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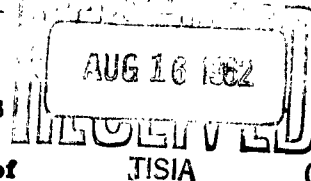
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Lab. Project 5319-42
Progress Report 3

26 JUL 1962

From: Commander, New York Naval Shipyard
To: Chief, Bureau of Ships (335) (3)

Subj: Hydraulic Fluids, Fire resistant synthetic phosphate ester;
Rust Inhibition of; Radioisotope Tracer Study of:
SR 001-03-01 Task 0606

- Ref: (a) BUSHIPS ltr R001-02-01 Ser 634A-254 of 10 Jul 1961
(b) Visit of MATLAB personnel (Codes 970, 975) to BUSHIPS
(Code 634A) of 18 May 1962
(c) NAVSHIPYDNYK Lab. Project 5319-42 Progress Report 2 of
7 Feb 1962
(d) MIL-P-16232B Phosphate Coatings, Heavy, Manganese or Zinc Base
(For Ferrous Metals) dated 9 Jul 1958



- Encl: (1) Effect of Temperature on Adsorption of Cellulube to Steel
Surfaces (23°, 70°, 130°C)
(2) Solvent Desorption of Cellulube from Steel Surfaces
(23°, 70°, 130°C)
(3) Rust Protection in Cellulube/Sea Water System by Cellulube
Containing Borate Ester, Plexol and Sulfonate (15 day Exposure)
Photo L-19259-1 (No pretreatment)
(4) Rust Protection in Cellulube/Sea Water System by Cellulube
Containing Borate Ester, Plexol and Sulfonate - 11 Day Exposure,
2 hr. pretreatment of Steel - Photo L-19259-2
(5) Effect of Plexol 305 on Demulsification of Cellulube/Sea Water;
0.5 and 24 hr. Settling Periods - Photo L-19259-3

1. The Material Laboratory is continuing its investigation of the mechanism of corrosion inhibition of the subject hydraulic fluids and the development of specific chemical compounds to impart improved rust inhibition and hydrolytic stability characteristics, as authorized by reference (a). Preliminary information regarding progress and scope of the investigation was discussed on the occasion of reference (b).

2. As indicated in reference (c), the Laboratory experiments involve the following phases:

- a. Surface chemical study of adsorption of the Cellulube 220 alkyl-aryl phosphate ester on steel surfaces using radioactively labeled (P-32) fluid. Information desired includes the nature, extent and orientation of the adsorbed film under various conditions.
- b. Synthesis of chemicals and/or formulations containing special functional groups for single and double phase (fluid/sea water) rust inhibition.

3. To broaden the utility of the Laboratory's results in this work, the investigation is aimed at providing materials and information which may also be effective in new formulations of fire resistant hydraulic fluids to be made available to the Bureau by various contractors. Since catastrophic effects are encountered under shipboard operations where the fluids are grossly contaminated (flooded) by sea water, the Laboratory is also under consideration compounds capable of emulsifying the sea water to remove the contamination from the hydraulic system, but which would at the same time permit rapid demulsification when the fluid is discharged into the storage tanks.

4. For evaluating the effectiveness of the synthesized formulations, two rust tests were used. One is the 48 hour conventional ASTM D-665 which is dynamic in nature. A modified static test which would reflect more severe conditions encountered in shipboard operations consists of the following sequential steps: soaking a polished steel rod in the fluid for two hours; removal of the rod; addition of sea water (2% by volume); emulsifying the sea water/ester mixture; and reinserting the steel rod without further mixing. In various periods of time, the phases separate and the upper portion of the steel rod is exposed to the sea water phase - the most aggravated or severe condition encountered.

RESULTS

5. Adsorption Studies - The results of the chemical adsorption of the radioactive Cellulube on steel surfaces at 130°C are graphically illustrated in enclosure (1). Chemisorption data at 23°C and 70°C previously reported in reference (c), are included for comparison purposes. These results indicate a rapid irreversible reaction of the Cellulube with the steel surface, with a strong temperature effect. The extent of phosphating by Cellulube, however, is less than 10% of that obtained by the inorganic salt sealing, acid phosphate treatment of reference (d). Chemical identification tests of the adsorbed film indicate essentially inorganic phosphate and absence of phosphide. The tenacity of the adsorbed film, essentially inorganic in nature, is indicated by the solvent extraction data of the chemisorbed film graphically illustrated in enclosure (2).

6. Rust Inhibitors - As outlined in reference (b), borate ester compounds are being investigated as double phase (sea water/hydraulic fluid) inhibitors. The additive should be capable of being leached out of the fluid when the latter is contaminated by water. The leached and/or hydrolyzed product should provide rust protection in the aqueous phase.

In order to simultaneously improve the solubility of the additive in the fluid, and the demulsification properties of the fluid/water mixture, the non-ionic surfactant-synergist Plexol-305 (Rohm and Haas) was utilized. The sodium salt of the hexylene glycol monoborate ester (U.S. Borax Co.) was dissolved in Plexol 305, and Cellulube 220 added to provide 1% borate ester with 2 and 10% Plexol 305. Formulations containing this mixture provided highly improved rust protection compared to the approved sulfonate

formulation regardless of whether the steel rod was or was not pretreated with the fluid prior to sea water exposure. Enclosure (3) shows the favorable action of the borate ester/Plexol-305 formulation after 15 days of contact with fluid/sea water without pretreatment of steel rods. Formulation B containing borate, plexol and sulfonate appears most effective. Enclosure (4) shows the effect on pretreated rods after 11 days of exposure to the fluid/sea water mixture. The rust inhibition of the borate ester is probably due to the leaching of the additive by the aqueous phase followed by controlled rate hydrolysis to produce the mildly alkaline sodium menoberate (pH 7.4).

7. Demulsification - The addition of Plexol 305 at a conc. of 10% to the compounded Cellulube greatly accelerates the rate of separation of the fluid/sea water emulsion. On the other hand, 2% Plexol retards the demulsification rate. These facts are more clearly demonstrated in the photos of enclosure (5) showing the effects of the additives after 1/2 hour and 24 hours of standing.

8. Syntheses of New Additives - Syntheses of silicone monocarboxylic acid compounds which should possess water repellancy and metal chemisorptive properties have been initiated. A viscous, semi-solid product is formed from cold water hydrolysis of beta cyanoethylmethyl dichlorosilane. Although soluble with difficulty in phosphate ester, the compound imparts good rust protection in tap water with only limited benefit in sea water.

9. CONCLUSIONS

Chemisorption - Cellulube fluid forms on steel surfaces a strongly adsorbed phosphate film which is insufficient for rust protection by itself.

Rust Inhibitors

- a. Borate esters provide improved rust protection to steel surfaces in both single and double phase immersions containing sea water. Addition of synergist improves the solubility of the borate ester and accelerates the separation of the fluid/water emulsion. The effect of the slightly alkaline medium on hydrolytic stability must be studied prior to recommendation of such inhibitor formulations.
- b. In spite of their acidic nature (pH5), silicone carboxylic acid compounds possess rust inhibitive properties. Further chemical modification of the compound, such as phosphorylation of the silicon, is indicated to improve its solubility to attain improved sea water protective capabilities.

10. FUTURE WORK

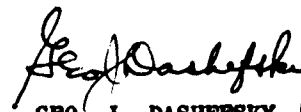
- a. Adsorption - Electron microscopy studies have been started to provide information on the phosphate chemisorbed compound using

electron diffraction techniques. Near infrared spectroscopic techniques have been developed to determine the amount of cresols formed by chemical reaction with steel and hydrolysis of the phosphate ester.

b. Rust Inhibitors

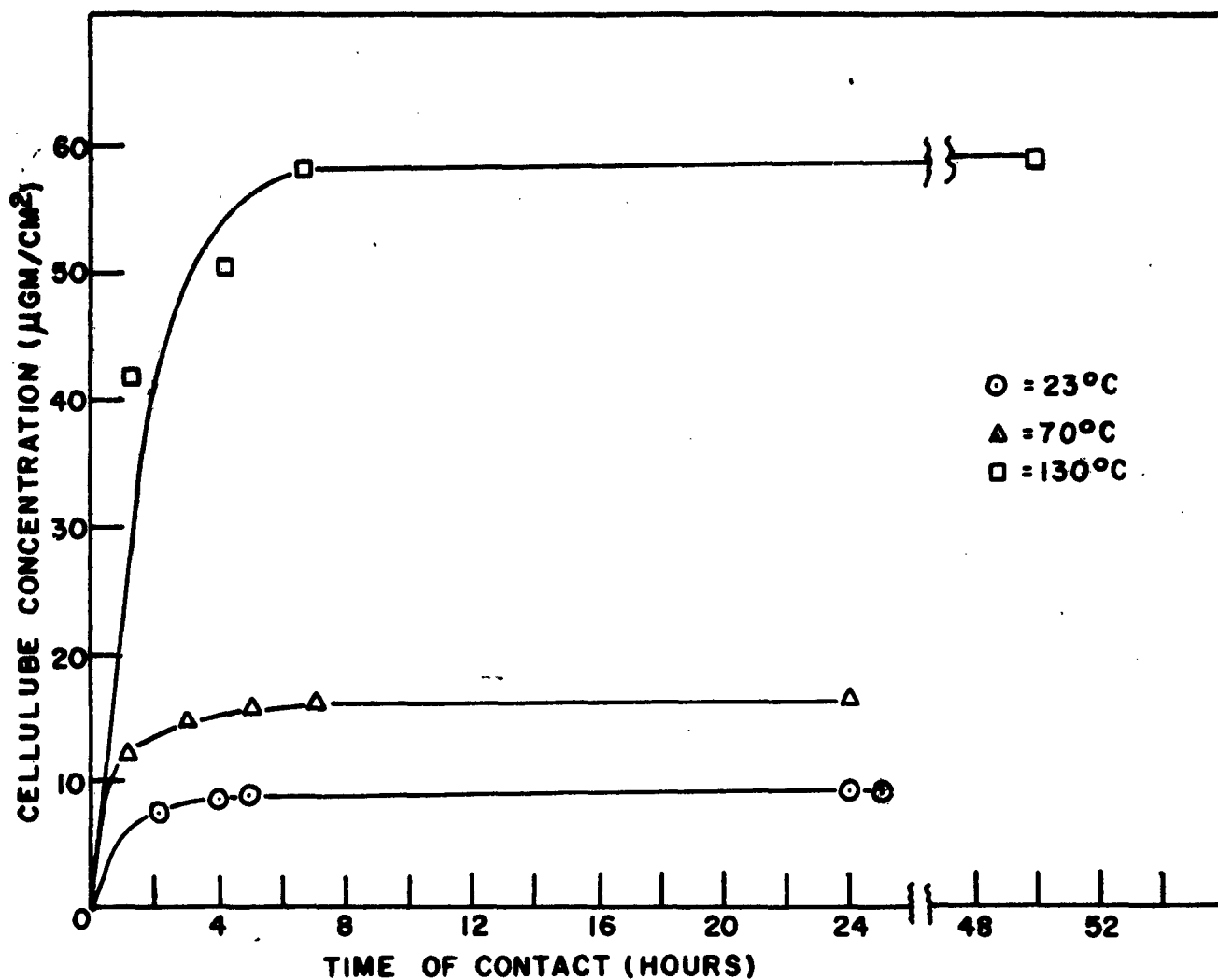
- (1) Longer chain glycol borate esters are being synthesized to improve the solubility of this class of additives. In this respect, the U. S. Borax Company is cooperating by supplying experimental compounds.
- (2) Phosphate esterification of the silicon carboxylic acid is being conducted with a view to improving solubility and sea water rust inhibitive properties.
- (3) A Fluorodicarboxylic acid has been synthesized at the Laboratory. Purification of the compound is presently being performed to be followed by evaluation of its rust protective properties.

11. In order to maintain the scope of the investigation in consonance with reduced Bureau funding for fiscal year 1963, it will be necessary to bring the phases of electron microscopy and additive syntheses to an appropriate stage of completion during the first quarter of FY 1963. The remaining effort will be directed solely to the surface chemistry and syntheses of one or two compounds (of 10b. above) which have demonstrated greatest potential as effective rust inhibitors.

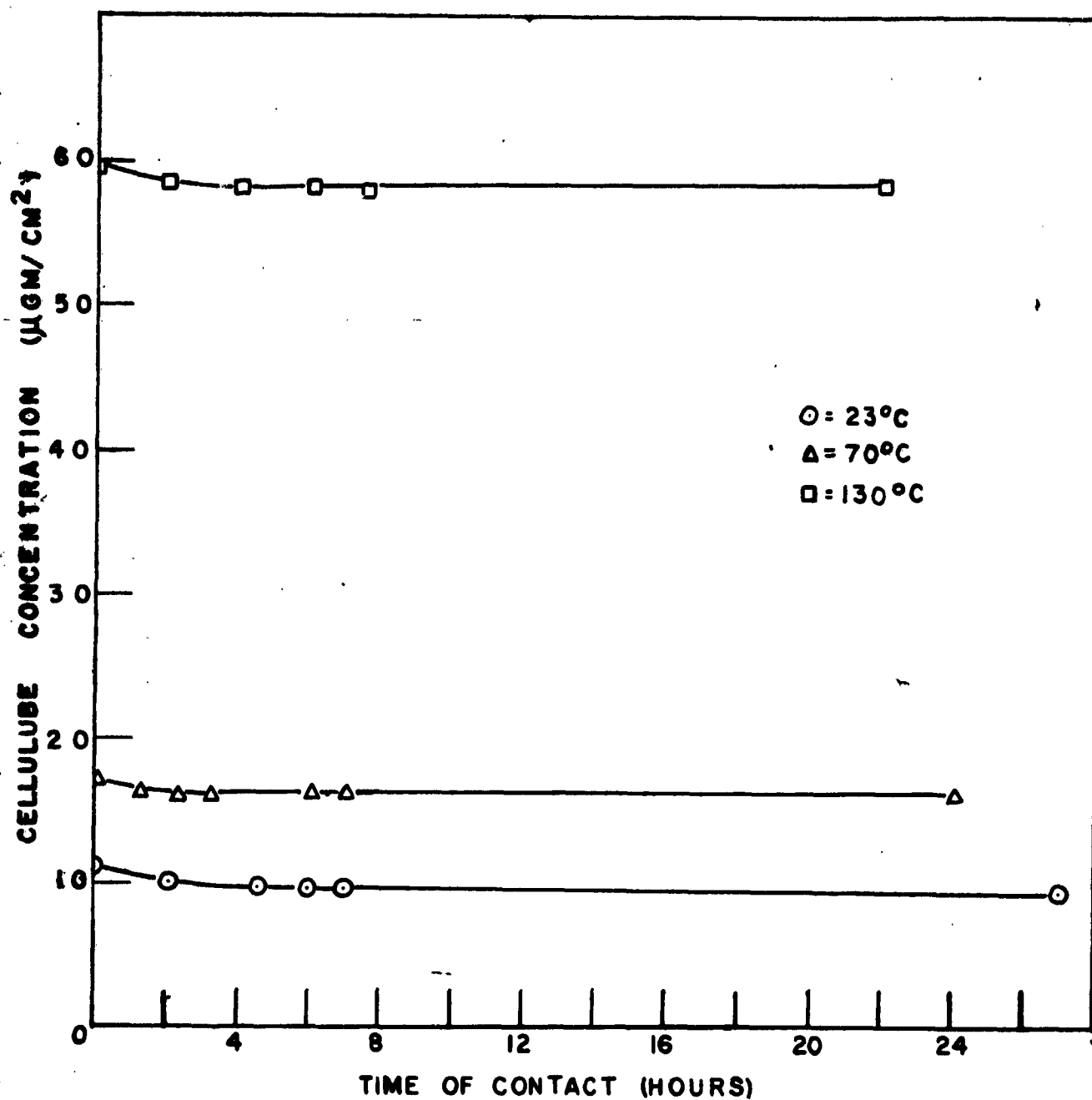

GEO. J. DASHEFSKY
By direction

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BUSHIPS (634A) (4)
(342B)
(320)

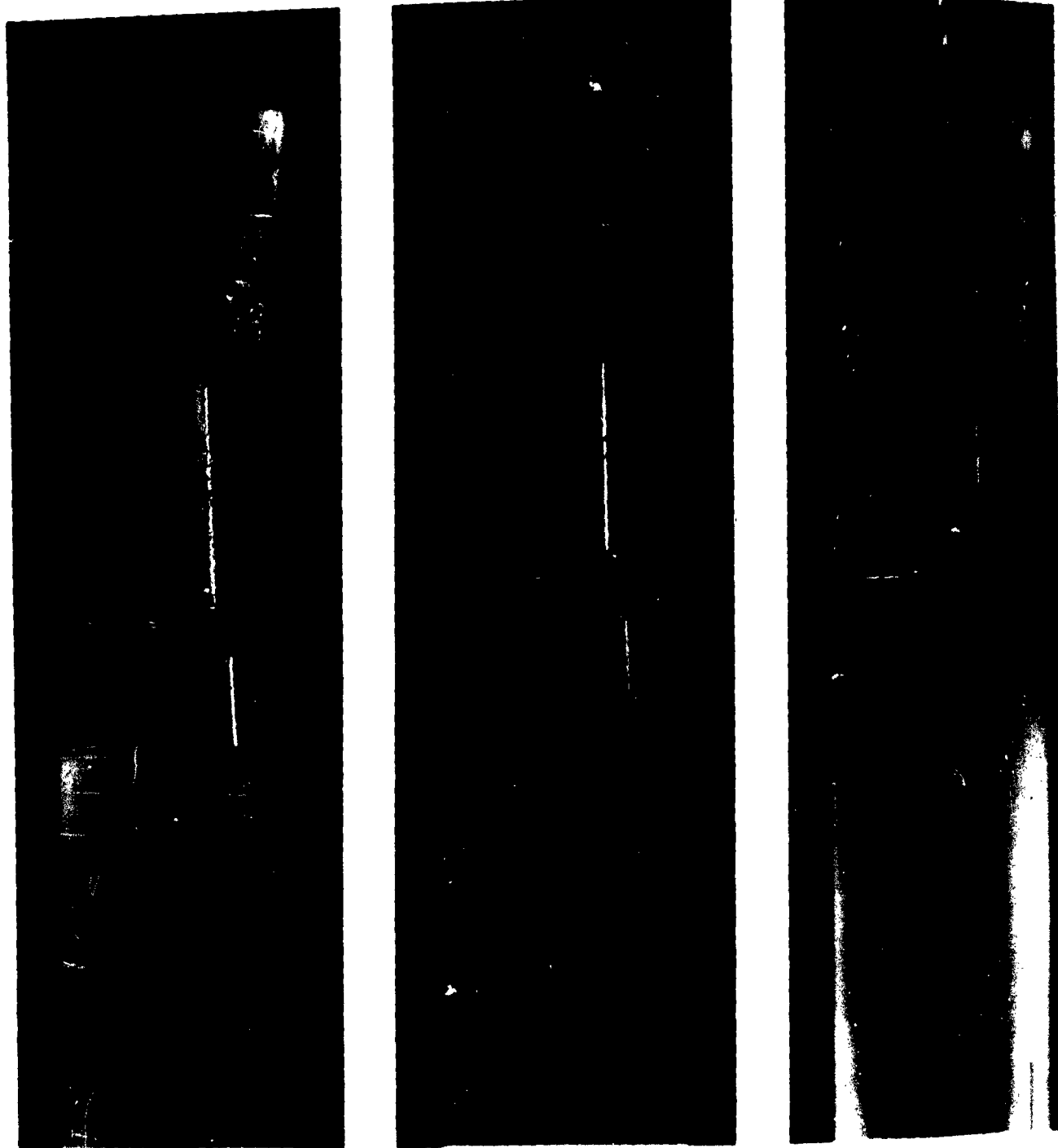
EES
British Defence Staffs (Navy Staff) (3)
(Formerly BJSM)
Main Navy Building
Washington 25, D. C.



Enclosure I. EFFECT OF TEMPERATURE ON
ADSORPTION OF CELLULOSE
TO STEEL SURFACES



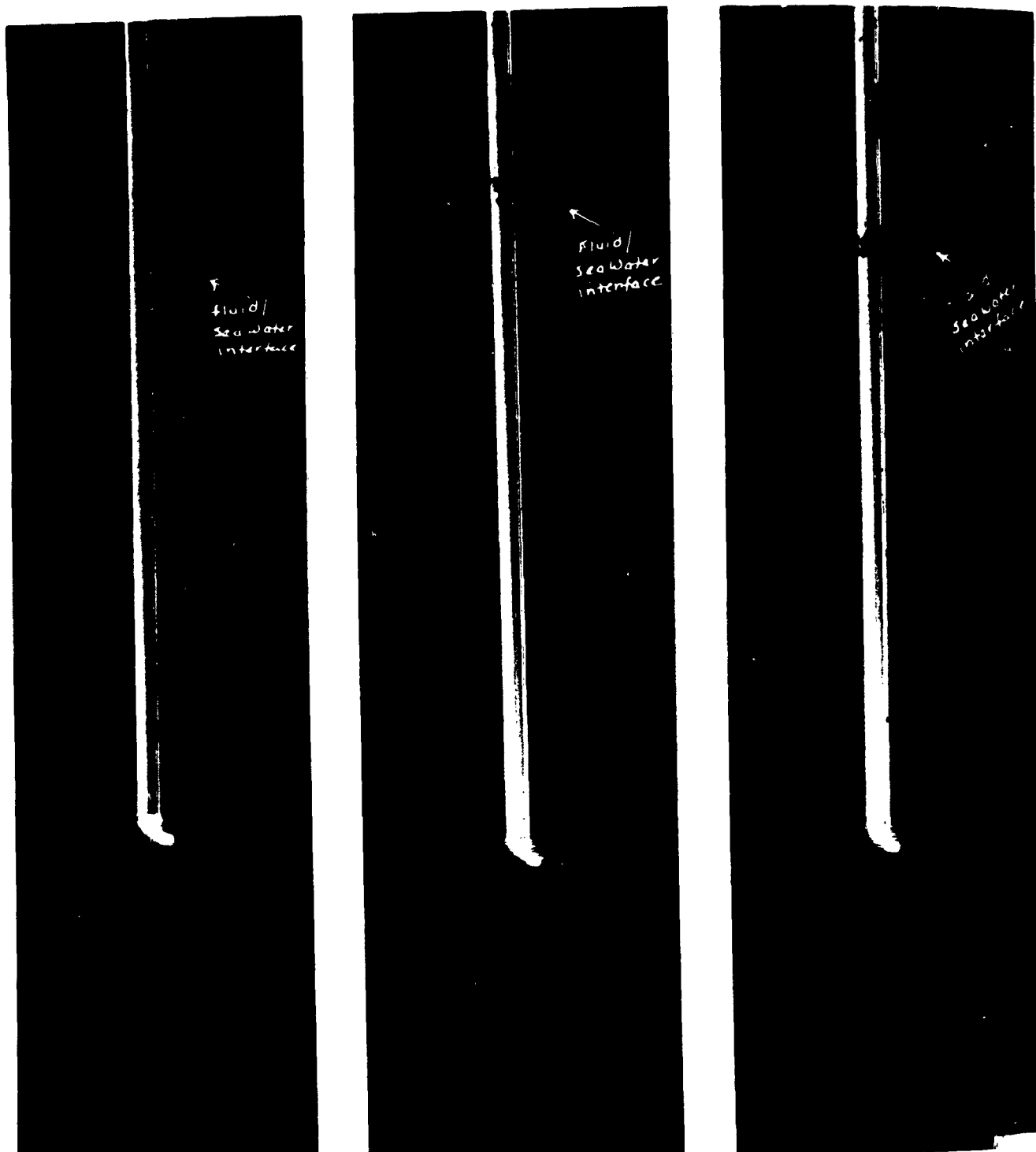
Enclosure 2. SOLVENT DESORPTION OF CELLULOSE
FROM STEEL SURFACES



MATERIAL LABORATORY

LAB. PROJECT 5319-42

Rust Protection in Cellulube/Sea Water System
A - Borate Ester and Flexol 305
B - Borate Ester, Flexol 305 and Sulfonate
C - Sulfonate
15 Day Exposure No pretreatment Enclosure (3)
PHOTO L-19259-1



MATERIAL LABORATORY

LAB. PROJECT 5319-42

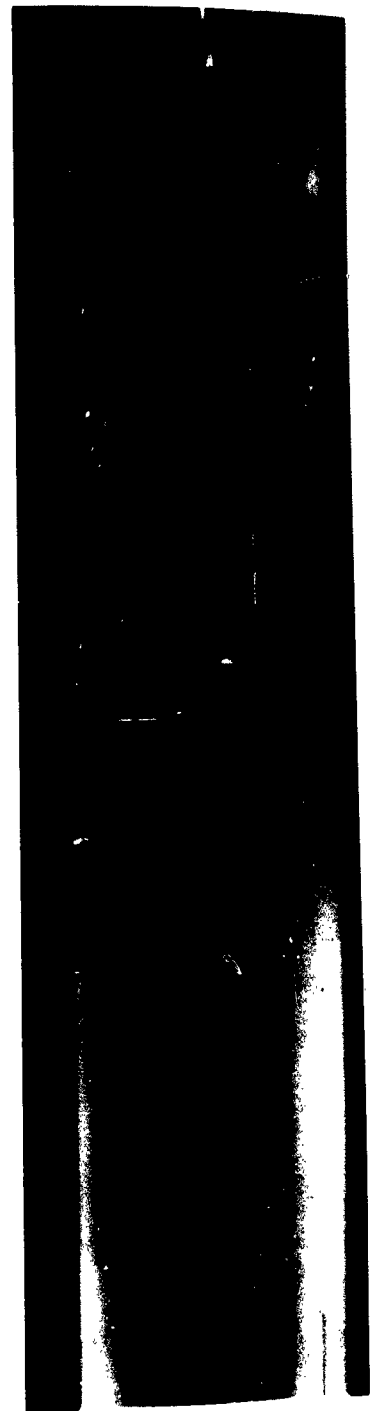
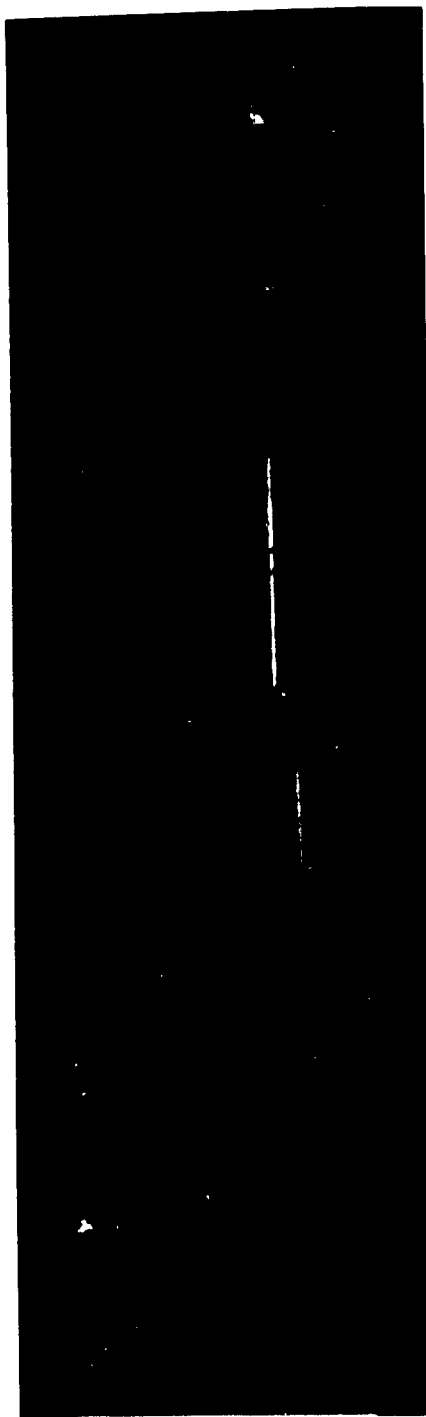
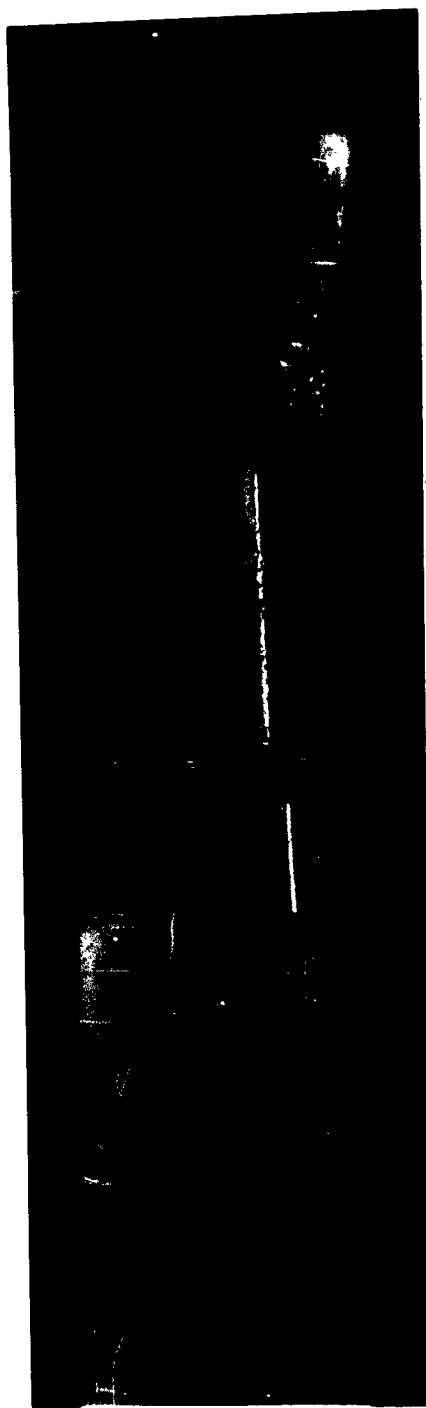
Rust Protection in Cellulose/Sea Water System

A - Borate Ester B - Borate Ester, Flexol 305 C - Sulfonate
and

Flexol 305 Sulfonate
11 Day Exposure 2 hr. pretreatment

PHOTO

Enclosure (4)
L-19259-2



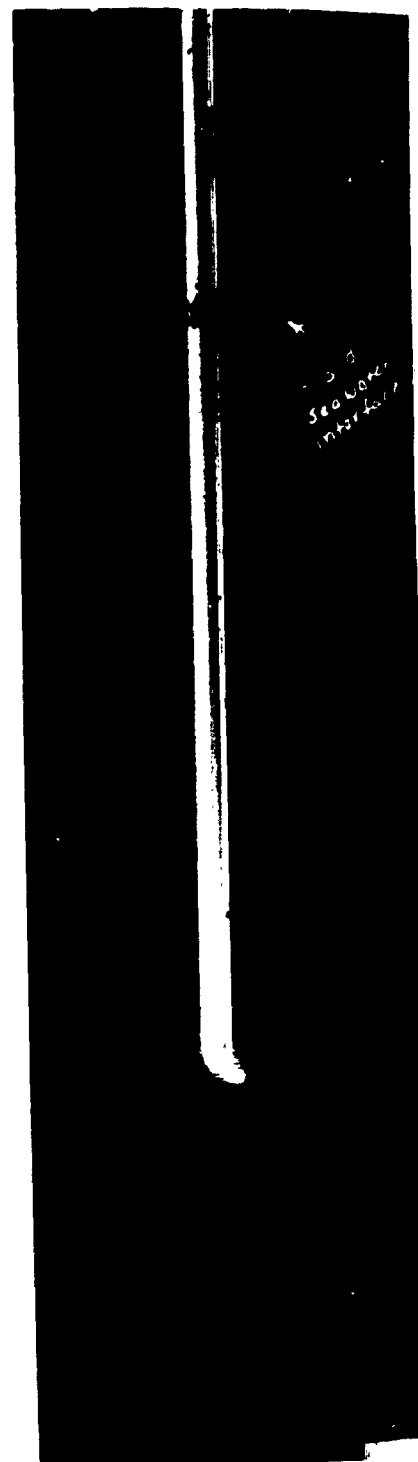
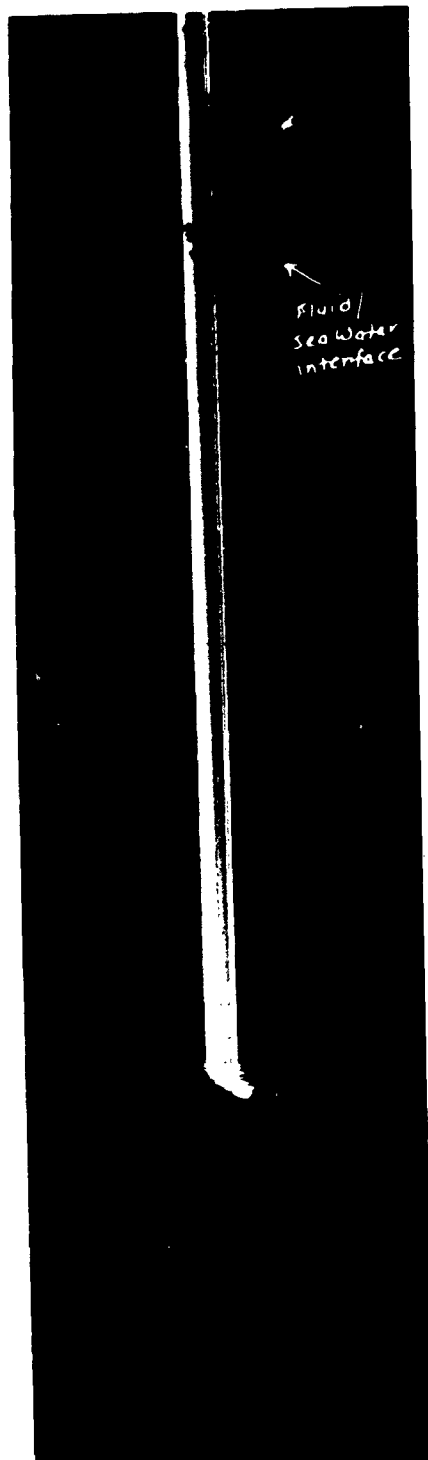
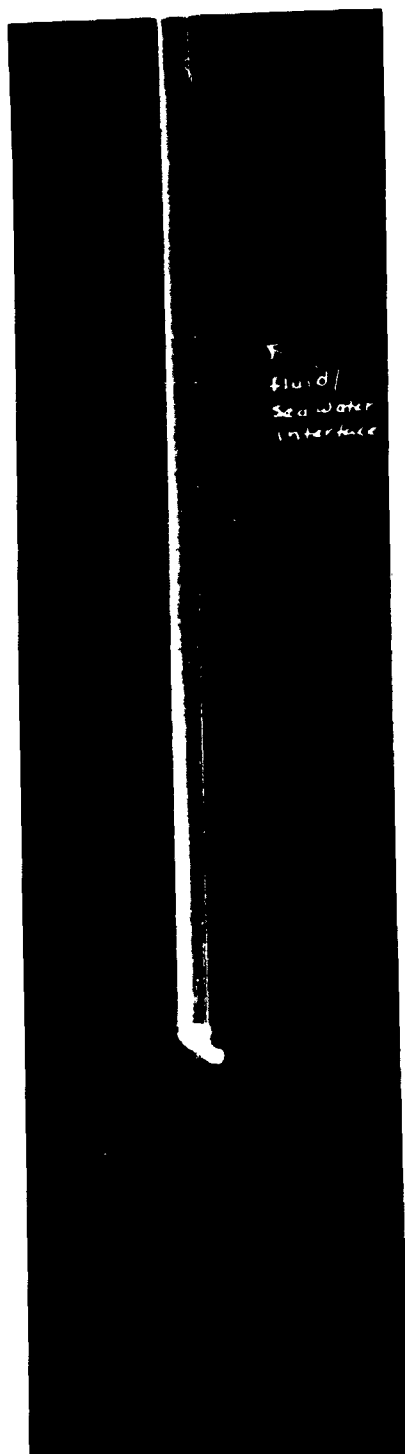
MATERIAL LABORATORY

LAB. PROJECT 5319-42

Rust Protection in Cellulube/Sea Water System
A - Borate Ester and Flexol 305
15 Day Exposure

B - Borate Ester, Flexol 305 and Sulfonate
No pretreatment Enclosure (3)
PHOTO L-19259-1

C - Sulfonate



MATERIAL LABORATORY

LAB. PROJECT 5319-42

Rust Protection in Cellulube/Sea Water System

**A - Borate Ester
and**

**B - Borate Ester, Flexol 305
and**

C - Sulfonate

Flexol 305

Sulfonate

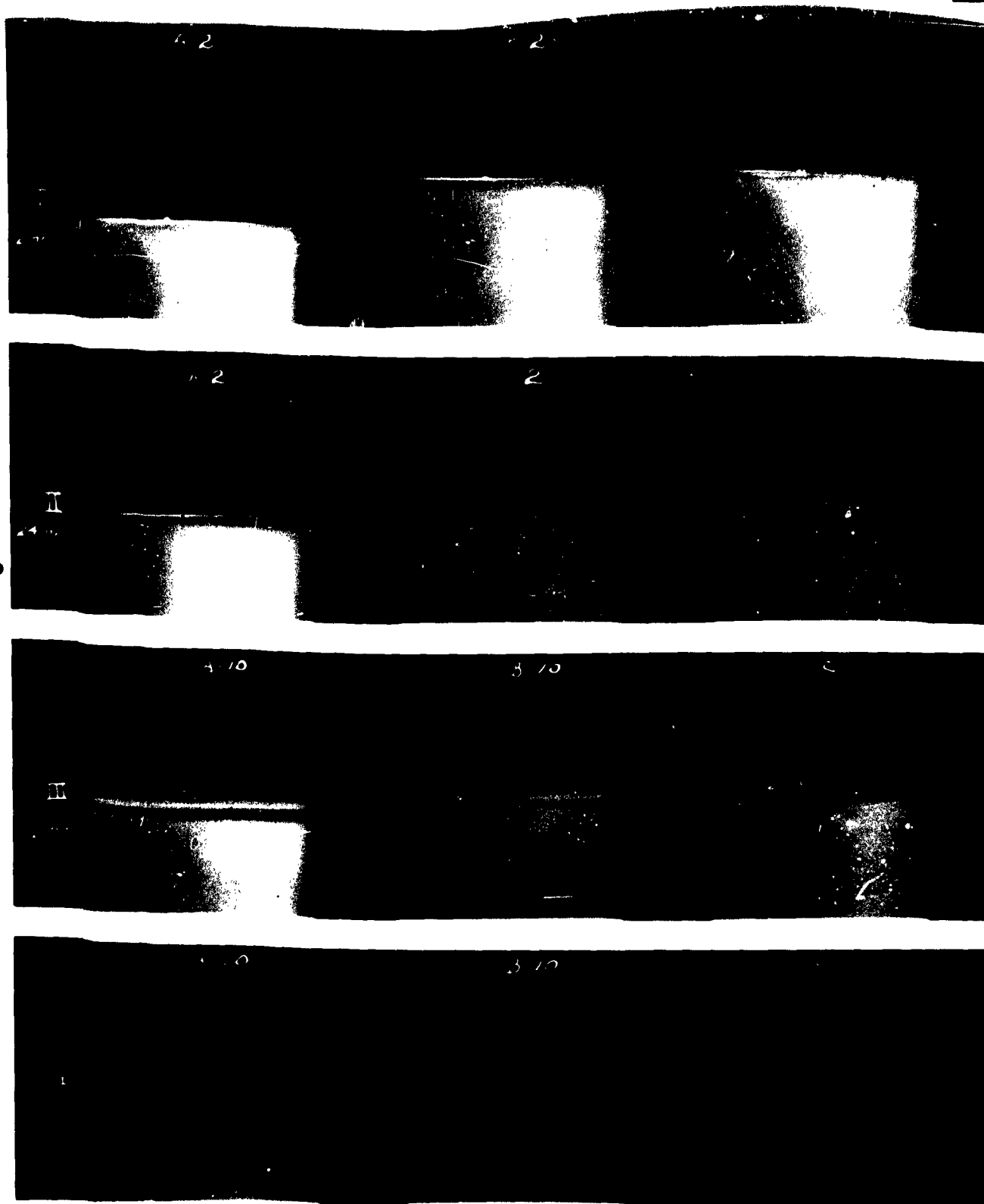
11 Day Exposure

2 hr. pretreatment

Enclosure (4)

PHOTO

L-19259-2



MATERIAL LABORATORY

LAB. PROJECT 5319-42

Effect of Plexol-305 on Demulsification of Cellulube/Sea Water

**A-2 - B.E., 2% Plexol B-2 - B.E., 2% Plexol C - Sulfonate
and Sulfonate**

**A-10 - B.E., 10% Plexol B-10 - B.E., 10% Plexol
and Sulfonate**

Enclosure (5)

I, III - 0.5 hr. Settling

II, IV - 24 hr. Settling

PHOTO L-19259-3