



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6180-525:HBP:pij

Prob. No. 61C05-19D

29 Oct 76

From: Commanding Officer, Naval Research Laboratory
Washington, D. C. 20375

To : Commander, Aeronautical Systems Division (ASD/AEG)
Wright Patterson Air Force Base, Ohio 45433

Subj: R&D Final Report on DOD-AGFSRS-76-10 (MIRP FY 7615-76-
05064) Improved Environmental Impact Properties for
AFFF Materials; forwarding of

Encl: (1) Two copies of subject report

1. Enclosure (1) is forwarded herewith for your information
and retention.

21 October 1976

Subj: R&D Final Report on DOD-AGFSRS-76-10 (MIPR FY 7615-76-05063)
Improved Environmental Impact Properties for AFFF Materials

Encl: (1) Work Statement from NRL Contract N00173-76-C-0295
(2) NSRDC/A ltr 2853:AMM 3160 dated 16 July 1976

1. A contract was signed, effective 29 June 1976, with the Ansul Co. to perform experimental work pertaining to the environmental characteristics of AFFF formulations and components thereof. A detailed statement covering the program is given in enclosure (1). A copy of Ansul's final report will be forwarded upon receipt at NRL. This is scheduled for December 1976.

2. Under separate contract with DTNSRDC/Annapolis, studies were completed on the recently qualified AFFF concentrate made by the Ansul Co. These results are given in enclosure (2).

3. This is a final report on the subject contract. The remaining work to be done at NRL after completion of the Ansul contract will be carried out under the sponsorship of the Air Force Civil Engineering Center.

H.B. Peterson (ED)

Henry B. Peterson
Head - Fire Suppression Section
Chemical Dynamics Branch
Code 6180 - Chemistry Division

Encl (1) to NRL ltr
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NRL Prob C05-19D

SECTION F - DESCRIPTION/SPECIFICATIONS

CONTRACTOR'S PROPOSAL

F-1. PROPOSAL OBJECTIVE

- a) The purpose of this work is to explore the development of experimental AFFF formulations that would exhibit reduced impact on the environment while retaining certain fire suppression characteristics. In particular it is proposed to examine the effect of the AFFF formulation components on the biological oxygen demand of the concentrate. In light of results previously obtained with available concentrates, fish toxicity is not considered to be a problem and therefore will not be investigated.
- b) It is furthermore proposed that the requirements of the MIL-F-24385 Amendment 8 and the proposed revision thereto will not apply to the present investigation. There will in all probability be a trade off between biological impact and physiochemical characteristics. Fire performance and corrosion characteristics are of primary importance whereas refractive index, pH, viscosity, foam expansion ratio, and surface interfacial tension are of lesser importance.
- c) The generally accepted method for determining proportioned or premixed solution composition is to measure the refractive index of the solution. In order to get acceptable accuracy and precision with field type refractometers, solvent levels of 15-20% are currently used in commercial products. It is assumed that these levels are deleterious from a biological aspect. Some effort will be expended in evaluating alternate analytical techniques for the measurement of AFFF solution concentration.

1.2 PROGRAM STEPS

a) Raw Material BOD₂₀

Twenty day BOD studies will be conducted on typical fluorocarbon surfactants, hydrocarbon surfactants and solvents. The purpose will be to determine the effect of chemical composition on BOD₂₀.

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SECTION F - (Cont'd)

b) BOD₂₀ Design Experiment

Investigate the effect of component concentration and type on BOD₂₀. Candidate formulations will be selected based on this investigation.

c) Formulation Design Experiment

Formulations will be selected based on the BOD₂₀ investigation and screened for fire performance and physiochemical properties. This will include corrosion characteristics, concentrate stability in addition to fire performance.

d) Analytical Methods Evaluation

An investigation of alternate analytical methods for determining solution concentration will be conducted to determine if a simple method for use in the field is feasible.

STATEMENT OF WORK (NRL's)

ENVIRONMENTALLY IMPROVED AQUEOUS FILM FORMING FOAM (AFFF)

F-2. INTRODUCTION

The present formulations with respect to fire suppression are highly effective. However, improvements are desired in the environmental area; i.e., development of compositions that have a reduced impact on the environment without loss of fire suppression effectiveness.

2.1 TECHNICAL TASKS

- a) The Contractor shall explore the development of experimental AFFF formulations that would exhibit a reduced impact on the environment while retaining fire effectiveness.
- b) The proposed study will examine the effect of AFFF formulation components on the biological oxygen demand (BOD), chemical oxygen demand (COD), biodegradability, toxicity toward sewage bacteria, fish toxicity, effect of component concentration on selected environmental/biological parameters, formulation design experiments, and analytical methods evaluation.

SECTION F - (Cont'd)

2.1.1 TASK I - Raw Material BOD₂₀ and COD

Twenty-day BOD studies shall be conducted on typical fluorocarbon surfactants, hydrocarbon surfactants and solvents. The purpose will be to determine the effect of chemical composition on BOD₂₀. Chemical oxygen demand (COD) measurements, toxicity toward sewage bacteria, and fish toxicity (kill fish) will also be made on the above materials.

2.1.2 TASK II - Biodegradability and BOD₂₀ Design Experiment

Investigate the effect of component concentration on biodegradability and BOD₂₀. Candidate formulations will be selected based on this investigation.

2.1.3 TASK III - Formulation Design Experiment

Formulations shall be selected based on the BOD₂₀ biodegradability investigation and screened for fire performance and physiochemical properties. This will include corrosion characteristics, concentrate stability in addition to fire performance.

In the event that a more highly concentrated material (to be used in less than a 6% solution) is desired, all environmental properties shall be adjusted to a 6% datum base.

2.1.4 TASK IV - Analytical Methods Evaluation

An investigation of alternate analytical methods for determining solution concentration shall be conducted to determine if a simple method for use in the field is feasible.

3. PERFORMANCE FIRE MEASUREMENTS

3.1 Compare fire performance of the new formulation with that of formulation currently manufactured and employed in the field - by the same test methods. Fire performance test procedures shall conform to Paragraph 4.7, Mil-F-24385 (NAVY) Amendment 8, as applicable.

SECTION F - (Cont'd)

4. RECORDS

- 4.1 Processing, formulations, method of preparation, aging, stabilization, and other pertinent parameters shall be maintained so that your process and materials can be later accurately duplicated, so that future programs may be coordinated or compared to the results and conclusions of your current study. These records shall be available for perusal by NRL Scientific Officer for a period of 1 year following completion of the work.

5. DELIVERABLES

- 5.1 1. The contractor shall provide NRL a final summary report on all tasks and sub-tasks of this study. It shall consist of summaries of all studies and experiments along with theoretical or experimental based conclusions or recommendations.
2. 100 gallons of experimental concentrate of the final selected formulation.

SECTION G - PRESERVATION/PACKAGING AND PACKING

- 1 Material shall be crated in accordance with best domestic commercial practices to assure safe delivery to the Naval Research Laboratory.
- 2 Marking: Receiving Officer, Naval Research Laboratory, Washington, D. C., 20375, Contract Number NOO173-76-C-0295.
- 3 The Contractor shall mark all shipments under this contract in accordance with the edition of MIL-STD-129 "Marking for Shipments and Storage", in effect on the date of the contract.
- 4 The Contractor shall comply with FED STD 313 (Symbols for Packages and Containers for Hazardous Industrial Chemical and Materials) to the extent applicable.



DEPARTMENT OF THE NAVY
NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER
HEADQUARTERS
BETHESDA, MARYLAND 20834

ANNAPOLIS LABORATORY
ANNAPOLIS, MD 21402
CARDEROCK LABORATORY
BETHESDA, MD 20034

IN REPLY REFER TO:
2853:AMM
3160

16 JUL 1976

From: Commander, David W. Taylor Naval Ship R&D Center
To: Director, Naval Research Laboratory, Code 6180
Subj: Ansul, AFFF, Ansul Co., Marinette, Wisconsin 54143, 6% concentrate,
DOT Formulation No. A-71108, Bioassay of
Ref: (a) Work Request No. N00173-76-WR-60166
Encl: (1) Report TM-28-76-29, "DTNSRDC Standard Static Marine Bioassay
Procedure for Shipboard Chemicals"

1. In compliance with reference (a), listed below are the results of the
bioassay tests of Ansul:

- | | |
|------------------------------------|--|
| A. <u>Fundulus sp.</u> | LC ₅₀ = 4,287 ppm in 96 hrs |
| Killifish | |
| B. <u>Artemia salina</u> | LC ₅₀ = 3,937 ppm in 72 hrs |
| Brine Shrimp | |
| C. <u>Pseudomonas nigrifaciens</u> | Bactericidal = 50,000 ppm in 96 hrs |
| Bacterial Species | Bacteriostatic = 40,000 ppm in 96 hrs |
| D. <u>Thalassiorira pseudonana</u> | LC = <4000 ppm in 96 hrs |

2. The results of the Biochemical Oxidation Demand (BOD) and the Chemical Oxidation Demand (COD) tests along with a comparison of the BOD test in saline and non-saline waters are listed on page 2. These tests were performed by Code 2860 according to the 13th Edition, 1971 of "Standard Methods for the Examination of Water and Waste-Water."

Encl (2) to NRL LTR RPT
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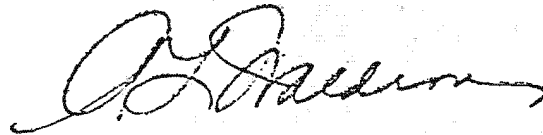
Subj: Ansul, AFFF, Ansul Co., Marinette, Wisconsin 54143, 6% concentrate,
DOT Formulation No. A-71108, Bioassay of

RESULTS OF BIOCHEMICAL OXYGEN DEMAND (BOD)
AND
CHEMICAL OXIDATION DEMAND (COD) STUDY OF ANSUL

TEST DURATION (DAYS)	DILUTION	BOD (mg./l.)	
		With NaCl	Without NaCl
5	1:30,000	1.8 5.4 X 10 ⁴	1.4 4.2 X 10 ⁴
	1:100,000	1.2 1.2 X 10 ⁵	0.9 0.9 X 10 ⁴
10	1:30,000	1.4 4.2 X 10 ⁴	oxygen depleted
	1:100,000	1.9 1.9 X 10 ⁵	4.3 4.3 X 10 ⁵

COD = 4.09 X 10⁵ mg./l.

3. The results of the "In Vivo" tests indicate that Ansul has a relatively low level of toxicity and the BOD and COD test results indicate a reasonably high level of biodegradability.



J. L. Williams
By Direction

Copy to:
NAVSEC (SEC 6101)