Lit Report file a

NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6180-148:HBP:cak

13 Mar 1979

From: Commanding Officer, Naval Research Laboratory
To: Commander, Tyndall Air Force Base (Det. 1 Civil & Environmental Engineering Development Office)
Tyndall AFB, Florida 32403

Subj: Draft copy of final report on the project "Improved Environmental Properties for AFFF," forwarding of

Encl: (1) Copy of subject report.

1. A draft of the final report on the subject project is forwarded herewith as enclosure (1) for your comments. After receipt of your comments, a copy suitable for photographic duplication will be prepared for return to you for issuance as a joint report.

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Improved Environmental Properties for AFFF		5. TYPE OF REPORT & PERIOD COVERED 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR*(s)* Henry B. Peterson		8. CONTRACT OR GRANT NUMBER*(s)*
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, D. C. 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE February 1979 13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* • 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A study of the environmental properties based on Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and fish toxicity was made on three of the chief components of AFFF materials: fluorocarbon and hydrocarbon surfactants and solvents. Based on these findings an AFFF formulation was devised to minimize the environmental impact of the material. The new material was successful in reducing the BOD & COD but at some

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

sacrifice in toxicity and fire performance when compared to other new products which became available.

In other studies related to the disposal of AFFF waste, alum in the Dissolved Air Floatation process was found useful as a pretreatment procedure in lessening the load on a municipal treatment plant.

A dye in AFFF concentrate made it possible to use a color comparator or spectrometer for determining the concentration of AFFF solutions in the field, as an alternative method to the hand refractometer.

TABLE OF CONTENTS

PREFACE

This report was prepared by the Fire Suppression Section of the Combustion & Fuels Branch, Chemistry Division, Naval Research Laboratory, under AFCEC project for Detachment 1 (CEEDO) ADTC, Tyndall AFB, Florida.

This report summarizes work done between September 75 and February 79. CAPT Lawrence W. Redman was the Project Officer.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public including foreign nations.

This technical report has been reviewed and is approved for publication.

IMPROVED ENVIRONMENTAL PROPERTIES FOR AFFF

I - INTRODUCTION

BACKGROUND

The introduction of Aqueous Film Forming Foam (AFFF) as a material for the suppression of ground fires involving aircraft fuels in 1964 seems to have coincided roughly with increasing concern over the environment. For this reason questions arose over the environmental aspects of AFFF which had never been asked of its predecessor, protein-type foam.

Early on the concern was primarily with safety to personnel working with AFFF and those who might be subjected to contact with it through its application. At this time the word of its sole manufacturer, 3M, was relied on by virtue of the long-time experience in manufacturing fluoro-chemicals. Later concerns were expressed over testing shipboard systems at sea and in port, and then the run-off from fire schools into open natural drainage ways and finally the run-off into sanitary sewers.

These concerns resulted in the start of detailed toxicity studies on marine life and also on the biological and chemical oxygen demands, BOD & COD, of which this project was one.

PROJECT HISTORY

This project to improve the environmental properties of AFFF originally initiated with the Tri-Service Aircraft Ground Fire Suppression & Reserve System (AGFSRS). Authorization was given NRL by MIPR7615-76-05064 in June 75 and funding followed later that year.

In accordance with the original plan two manufacturers who had produced products qualified to meet MIL-F-243905 and a third manufacturer who had submitted a product were solicited for interest in undertaking a cooperative program. Only The Ansul Company expressed interest and they were awarded a contract in June 1976. A plan to study the environmental characteristics of individual components of the concentrate to replace the worst offenders with less detrimental materials was agreed on. The final objective was to deliver 100 gallon of concentrate demonstrating the improved properties. The material was received in May 1977 and a report describing the steps leading to it was received in January 1978.

Additional funds were made available for continuation of the work by the Air Force Civil Engineering Center in October 1976 by MIPR FY8452-76-65015. By this time the emphasis had shifted from trying to modify the concentrate to finding how to handle it as a waste material. A proposal on this aspect was received from the 3M Co.; however, one judged to be superior was received from the Navy's Civil Engineering Laboratory and funds were transferred to them in August 1977. Their investigation was to cover possible pretreatment of AFFF run-off from training grounds prior to entry into municipal waste treatment plants. The final report is yet to be received.

AFFF CONCENTRATE DEVELOPMENT

A complicating factor in the study and evalution of the environmental aspects of AFFF has been the rapidity with which new foumulations have been developed and introduced. Evaluation of one material would hardly be complete when a new product would make the previous work obsolete. (Since the first AFFF specification in 1965, two basic specifications, three revisions, and eight amendments have been issued.) The 3M products used by the military have been: FC-183, FC-194, FC-195, FC-196, FC-199, FC-200, FC-206, and FC-780. Currently FC-780B is undergoing qualification testing.

AFFF CONCENTRATION ANALYSIS

Although seemingly unrelated to the environmental improvement of AFFF, some of the effort in the project has been devoted to methods for determining the concentration of AFFF solutions. This function is important for checking checking the proper operation of the proportioning device in a foam system. The Navy has had recurring proportioning problems aboard ships and such a function is vital. The Navy's aircraft rescue and fire vehicles use fixed-orifice proportioning and are not subject to variation; however, many other vehicles use variable proportioners. In the past, concentrations have been measured in the field with a low-cost hand refractometer which determines the refractive index of the AFFF solution supplied to the nozzle. The accuracty of the device is dependent on the refractive index of the concentration. If it is too close to that of water, the difference between 5 and 6% solutions, for example, are too subtle to pick up. The refractive index of the concentrate in turn is related to the solvents used in their preparation. The solvents are generally environmentally undesirable and the manufactures have been reducing

the concentrate refractive index. This creates a field problem in concentration analysis. Hence, the search for alternative analysis techniques.

SECTION II - NEW CONCENTRATE

EXISTING CONCENTRATE PROPERTIES

The criteria for evaluating the environmental properties have been limited to BOD, COD and fish toxicity. Biodegradability is measured by the BOD/COD ratio; when the BOD value equals the COD value, the material is considered completely biodegradable.

The known environmental properties of the concentrates which had been qualified prior to awarding the developmental contract to the Ansul Co. are summarized in Table 1 together with data on a concentrate which had been submitted by Ansul.

Table 1 - Environmental Data

Concentrate	Date Qual.	COD mg/l	BOD mg/l	BOD/ COD	Fish Tox. TC_{50} ppm
3M FC 199	Apr. 71	550,000	18,000	0.03	398
FC 200	Feb. 72	730,000	450,000	0.61	97
(1)		690,000	590,000	0.86	76
FC 206	May 74	500,000	411,000	0.82	1080
(1)	-	430,000	480,000	>1	2674
(2)		420,000	420,000	1.0	1820
Nat'l Aer-o-water 6	Oct 73	350,000	300,000	0.86	225
(1)		385,000	450,000	>1.	-
Ansul K74-100	-	210,000	159,000	0.76	1100

(1) Data obtained by Naval Ship Research & Development Center, Annapolis Laboratory; Memo of 1 October 74, File: 2853-509.

(2) 3M Co. data by ltr of 18 Jan 77 to NRL.

All other data from USAF Environmental Health Laboratory, Kelly AFB, TX; Biodegradability and Toxicity of Ansul K74-100 Aqueous Filming Forming Foam;Rpt. EHL(k) 75-3 of Jan. 75.

The afore cited data provide a basis for evaluating the advancement made by the Ansul contract. It is to be noted that considerable progress had already been made in reducing the toxicity and raising the biodegradability of the product.

Regulatory agencies usually accept any substance which has a LC_{50} value greater than 1000 ppm to be non-toxic and non-hazardous. By this definition the 3M concentrate being procured, FC-206, was already in the "safe" range.

COMPONENT STUDY

In performing the contract work Ansul studied nine (9) AFFF components including fluorocarbon and hydrocarbon surfactants and solvents. Certain preferred combinations were then tested for foaming and fire performance. They concluded that the toxicity was related to the surfactants rather than the solvent.

Their detailed final report is attached to this report as Appendix A.

FINAL FORMULATION

One hundred gallons of a final formulation, designated 1-6-054, were delivered to NRL in May 1977 for additional testing.

Table 2 compares the properties of the new material with the FC-206 being procured at that time and the Ansul product then on the Qualified Product List (QPL).

Table 2 - Product Comparison

Property	Ansul 1-6-054	Ansul QPL	FC-206
BOD, ppm	234,000	267,000	487,000
COD, ppm	238,100	430,000	428,000
BOD/COD	0.98	0.62	1.14
Fish Toxicity LC_{50}, ppm	1474	4787	2500
$28ft^2$ fire ext. sec.	41	28	30
burnback, sec.	316	430	594
Foam expansion	4.1	8.7	10.0
drainage time, min.	3.0	3.6	4.2

It may be noted that there was a considerable reduction in the COD level of the newly developed concentrate and this was a desirable achievement; however, the toxicity was greater and the performance lower. It was concluded that the product represented an overall advancement in the specific direction desired. The Ansul report was forwarded to the other manufacturers for guidance in their future work in this area.

SECTION III - SPECIFICATION REVISION

As a result of the work and data generated under the stimulus provided by this Tri-Service/Air Force funded project, the MIL specification for AFFF (MIL-F-29385) was revised in 1977 to include environmental requirements. These requirements were for a maximum allowable COD of 500,000 ppm, a minimum BOD/COD ratio of 0.85, and a minimum TC_{50} for fish toxicity of 1500 ppm.

SECTION IV - MATERIAL DISPOSAL

WASTE TREATMENT STUDY

It has been mentioned earlier that when additional funding became available it appeared desirable to channel this money into studying the disposal of AFFF waste. Specificially, the Navy was encountering a problem with the run-off from the Fire Fighting School in Norfolk VA. The waste was not being accepted by the Hampton Roads Santitation District and methods for pretreatment were being sought. The Naval Civil Engineering Laboratory (NCEL) in Port Hueneme, CA was already involved in the problem and welcomed the additional financial support.

It is believed that the work done by NCEL has made a valuable contribution to bettering the methods for AFFF disposal. This knowledge applies not only to the Navy but to the Air Force which has similar fire training school installations and also has the problem of handling the run-off from hangar sprinkler systems. A draft of the NCEL report is attached as Appendix B.

SECTION V - METHODS FOR AFFF CONCENTRATION ANALYSIS

REFRACTIVE INDEX

In the early days of protein foam, NRL devised a method of determining the concentration of agent in foaming solutions using a refractometer to measure the index of refraction of the unknown solution. With the introduction of AFFF the same method was carried over. The differences in refractive index between water and AFFF concentrate were great enough to permit acceptable accuracy even when using low-cost, simple, instruments. Normally in the laboratory more sophisticated instruments were employed for greater accuracy.

As AFFF materials developed over the years, their refractive index became lower and lower and approached that of water. Accuracy of readings became less satisfactory. Also the need for taking readings became more widespread and the training level of operators dropped off. Manufacturers were less than enthusiastic about maintaining the level of refractive index, to say nothing of increasing it, and alternative methods were sought.

ALTERNATIVE METHODS

Again the manufacturers have not been helpful in preparing alternative procedures. One instrument looked at was the spectrometer but there are naturally occurring adsorption bands in the visible light wavelength range. Strong adsorption bands in the ultra-violet range make a MV device useful for laboratory work, but such instruments are expensive and not suitable for field use.

Addition of a dye might make it possible to use a spectrommeter or colorimeter operating in the visible range. The idea would be to add the dye to the concentrate at the time of manufacture. At the time of usage, a calibration curve would be prepared, as presently done with the refractometer, to eliminate any batch variations or stability problems. Readings could be taken with a commercially available device, such as the Bausch & Lomb Minispec with a meter readout, or a color comparator, such as used for swimming pool water tests.

In the work statement prepared for the Ansul contract, they were requested to look into the dye scheme. Their conclusion was that a dye could be used for this purpose and recommended Ciba-Geigy, Diphenyl Brilliant Blue FF Super 1. A detailed description of the work is included as a part of Appendix A.

Further testing at NRL showed that 300 mg/l of the dye in the concentrate made good workable solutions at the 6 percent level. The amount of dye was added to concentrates made by 3M, Ansul, and National and stored at 150°F for 10 days. No problems of compatibility were observed.

ADDITIONAL WORK

Additional work is necessary in both areas. In the case of the refractometer, statistical experiments are needed in order to verify the degree of accuracy with different types of refractometers in the hands of untrained personnel. Also needed is a determination of the concentrate's refractive index in order to achieve an acceptable degree of accuracy in the field.

A companion study on the use of the dye technique by untrained personnel is needed for a comparison with the refractometer. Other factors such as cost need investigation.

SECTION VI - CONCLUSIONS

Establishing some of the environmental characteristics of certain potential constituents of AFFF has served to guide the way to minimizing its impact on the surroundings. The specification covering the procurement of AFFF has been expanded to assure a limitation on toxicity and require a high level of degradability.

In the pretreatment of run-off waste from fire schools, alum in the dissolved air floating process was found helpful in making the waste acceptable to municipal treatment plants.

A technique of adding dye to AFFF concentrate was found to offer an alternative method to using the refractive index for determining the concentration of AFFF solutions in the field.

APPENDIX

Appendix A - Final Report; Environmentally Improved AFFF; N00173-76-C-0295; the Ansul Co., December 13, 1977.

Appendix B - Technical Memorandum 282TM, "Fire Fighting School Waste Treatment Study," Richard Samm and Paul Rinkowski, Civil Engineering Laboratory; August 1978.

LIST OF TABLES