SUMMARY FOR FOAMING STUDIES DONE ON VARIOUS AFFF PRODUCTS

TEST SUBSTANCE

Identity: Mixtures containing perfluorooctanesulfonate, which may also be referred to as PFOS or FC-95 or as a component of AFFF products. (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt, CAS # 2795-39-3)

Remarks field: The test samples are AFFF products of various compositions.

STUDIES

The attached testing is a compilation of studies done to characterize the capacity of 3M's AFFF product line to create foam in various situations, and, in some cases, the effectiveness of various anti-foaming agents. This includes the effects of foaming on wastewater treatment processes.

DATA QUALITY

Reliability: No ranking of this data has been done. These studies are atypical, have no agency-approved procedure, and were designed to provide general guidance to customers and wastewater treatment operators who must address the issue of treating foam after using AFFF in a fire event.

OTHER

Submitter: 3M Company, Environmental Laboratory, P.O. Box 33331, St. Paul, Minnesota, 55133

Last changed: 6/28/00

Internal Correspondence

File: TDB FC-780 /ea

cc: D. R. Ricker - 53-4
C. S. Chow - 21-2W (58)

To: R. R. BURFORD - COMMERCIAL CHEMICALS DIVISION - 236-1

From: E. A. REINER - ENVIRONMENTAL LABORATORY (EE & PC) - 21-2W (58)

Subject: FC-780 FOAMING IN ACTIVATED SLUDGE

Date: AUGUST 15, 1979

3M

We conducted two sets of tests in the Environmental Laboratory to determine the FC-780 concentration that would cause foaming in activated sludge waste treatment systems.

The first set of tests involved shaking 10 and 100 mg/l of FC-780 in 100 ml of activated sludge. Return sludge was resuspended to 3000 mg/l in primary treatment* effluent from the St. Paul Metro Waste Treatment Plant (see Photos 1-5). After 30 seconds of vigorous shaking, less than one-half inch of foam formed at 100 mg/l (Photo 1). The jars containing the 10 mg/l FC-780 solution and the control both had slight foam that only covered the edges of the sludge surface.

Though little or no foam was formed at an FC-780 concentration of 10 mg/l, the sludges containing this concentration and 100 mg/l of FC-780 did not settle well after shaking (see Photo 5). Shaking in the presence of 10 mg/l of FC-780 entrained air bubbles in the sludge.

A second set of tests was then run in which aeration with an air sparger at 500 ml/min. replaced shaking (see Photos 7-10). No foam formed even at 100 mg/l, and no settling problems developed. These same samples, when shaken, behaved as in the first set of tests (see Photo 11).

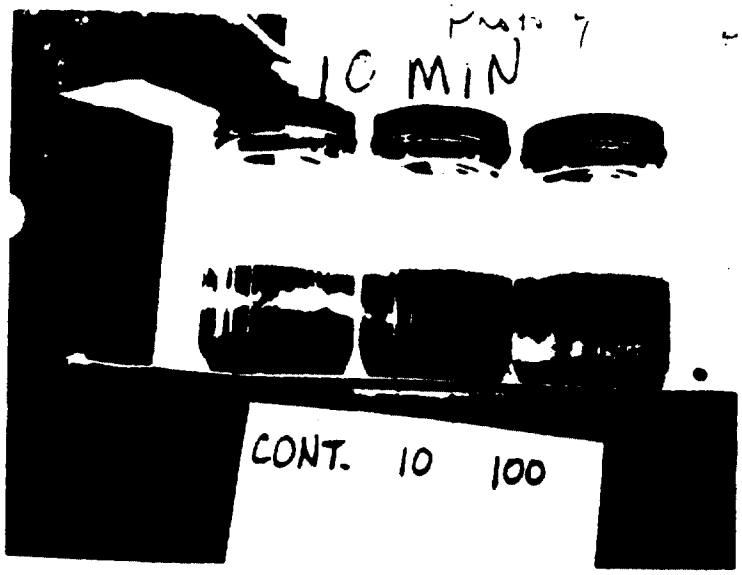
*Primary treatment is the first major step in wastewater treatment in which settleable solids are removed.

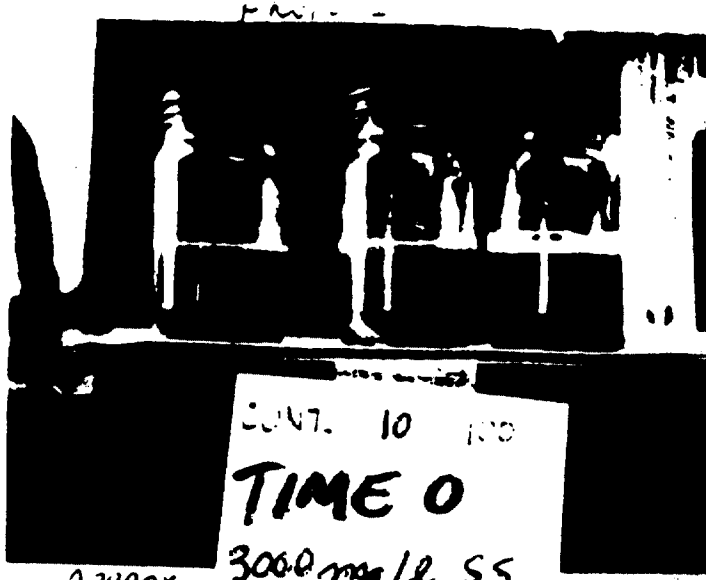
We feel the aeration test more closely simulates the conditions of a waste treatment system than the shaking test. Therefore, we don't anticipate serious foaming or settling problems below 100 mg/l.

Eric A Pearson

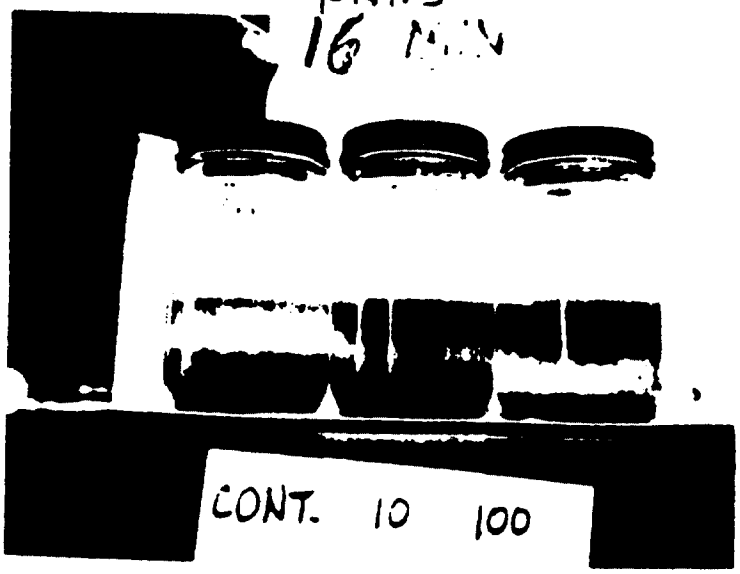
EAR/cen

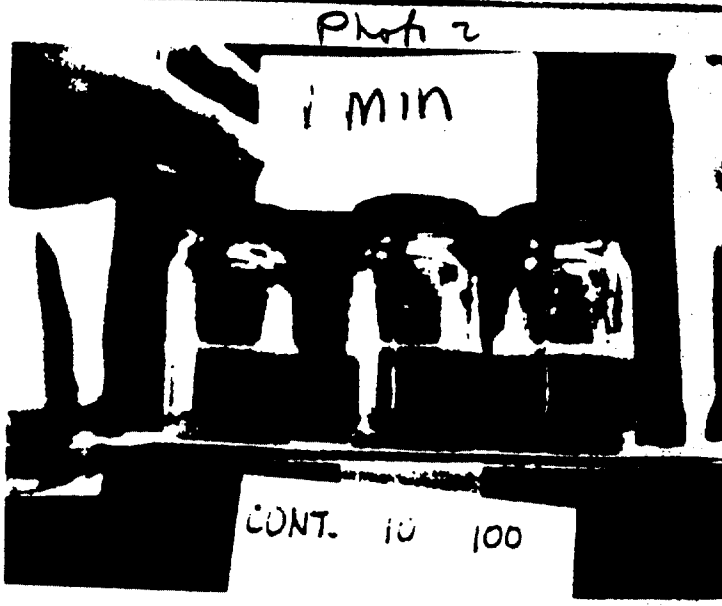
Attachments

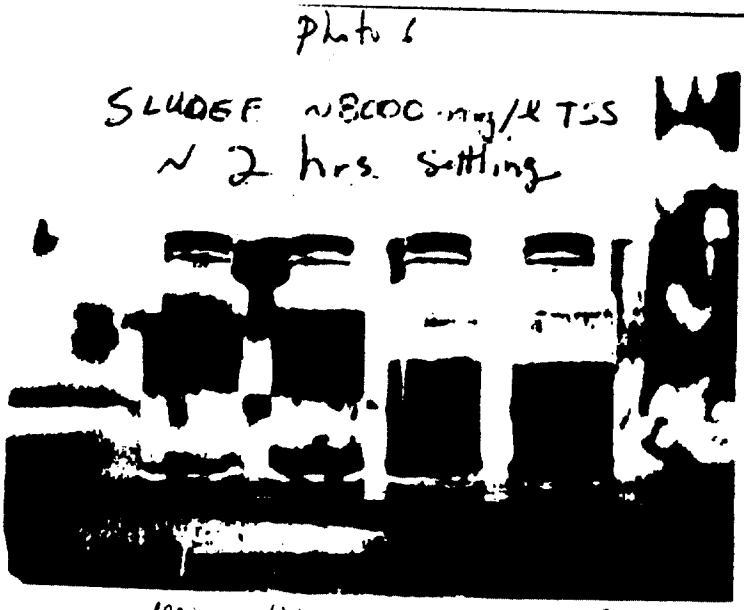




APPROX. 3000 mg/l SS







100 10 CONTROL

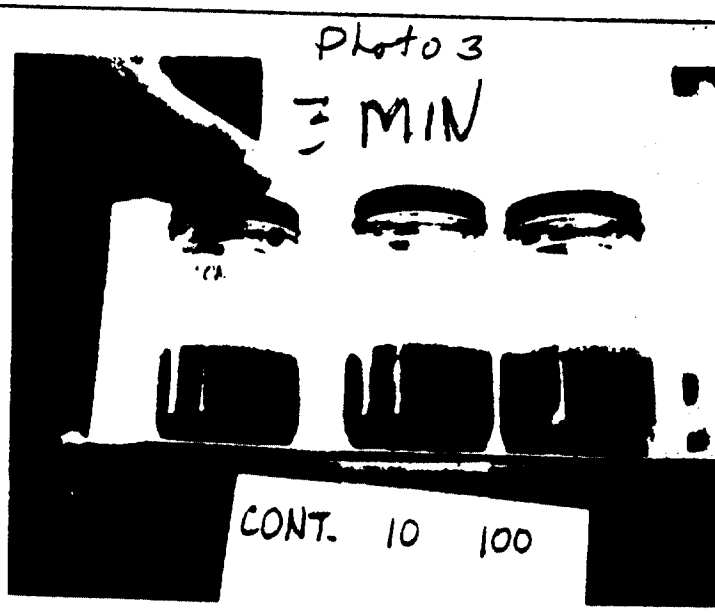


Photo 7

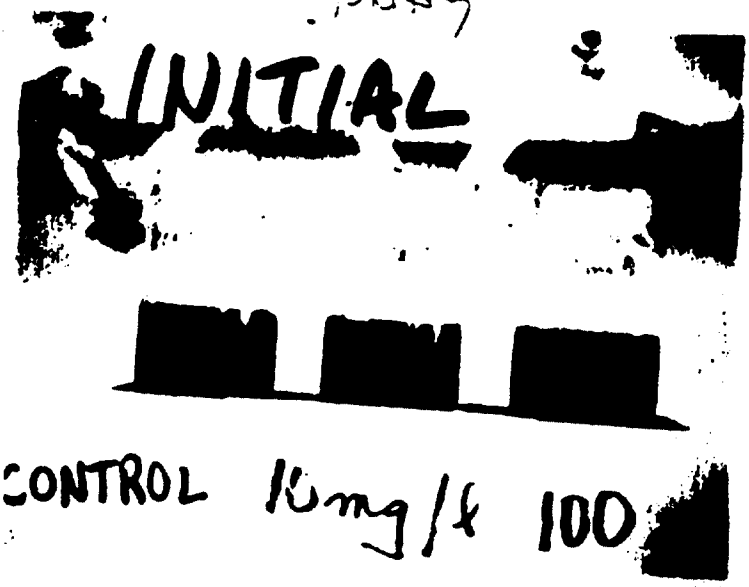


Photo 10

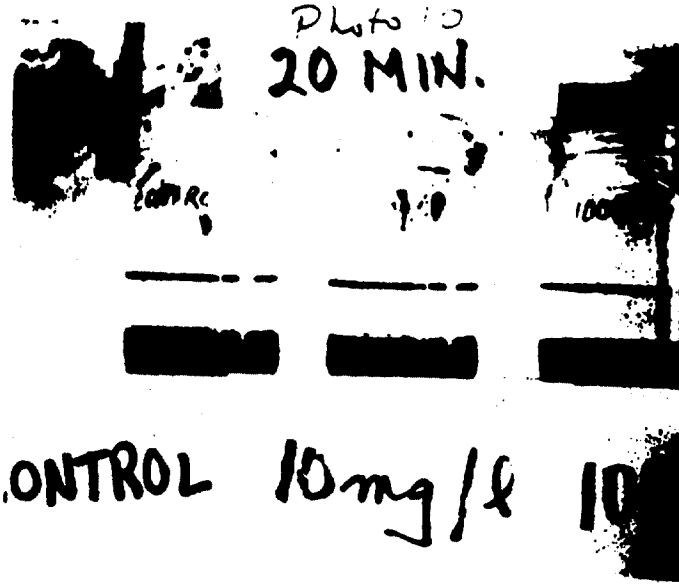
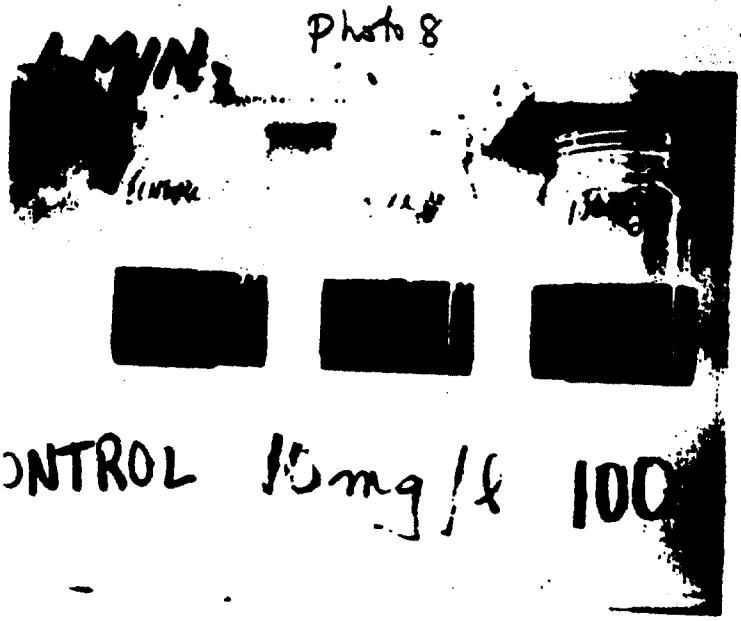


Photo 8



5 min aeration @ 500 ml/m

Photo 9

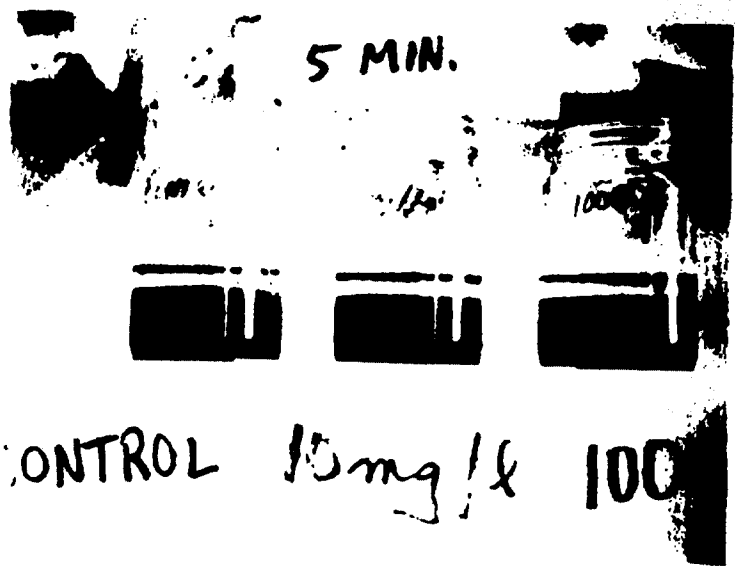
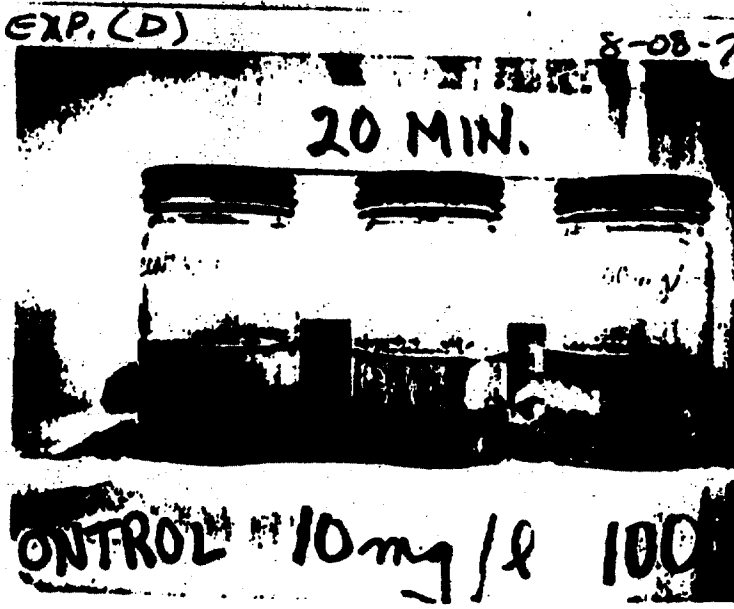


Photo 11



Form 10620-5-PWO
cc: LAB REQUEST BOOK – 42-5W

Please give to WAS

FC-780

3M "Action" 200 Pa

PRODUCT ECOLOGICAL ASSESSMENT
REQUEST FOR LABORATORY WORK

Ref: ENVIR. ASSESS. INQ. # _____
~~Commercial Cleaners~~ DIVISION
PRODUCT: FC-780 ~~FC-780B~~

LAB REQUEST NO. 5038

5/13/71

REQUESTER	LABORATORY
Name: Eric Reiner Phone No. 5079	Date Received Sample: 8-6-79
Request Date: ~~August 2 1979~~ 1979	Analyst: WAS
Project No.: 9970012700 Prob. No.	Date Completed: 8-13-79
Code No.:	Hours Spent: 5
Sample Date: Date Needed:	Y B P
Description: Foaming of FC 780 or ~~FC 780B~~	Please Call Requester If Delays Are Encountered.
Purpose of Tests: To see level that can be treated without foaming	

PHYSICAL & CHEMICAL PROPERTIES
- Heat of Combustion Cal/G (BTU/Lb.)
- Density
- Ash
- Other

WATER POLLUTION
- pH
- COD
- BOD_5
- BOD, Ultimate
- TOC
- GC
- Oxygen Uptake
- Dehydrogenase Activity (TTC)
- Other

SOME ADDITIONS WERE MADE SEE ATTACHED PROCEDURES

BIOASSAY
- Specify Organism and Method:

LEACHATE FROM LEACHING TEST
- pH
- COD
- BOD_5
- BOD, Ultimate
- TOC
- GC
- Bioassay
- Other

Foam Height. –

OTHER
- Bioaccumulation
- Persistence
- Degradation Products

Foam lasted (Time). –

Comments: –

Make a dilution series of ~~FC 780~~ FC 780 or ~~FC 780B~~ in DI water. (1) Add 10 ml of a 100 ppm ~~FC~~ Solution to 90 ml ~~Metro~~ of Metro Sludge (2) also add 10 ml of 1000 ppm FC780 (or B) Solution To 90 ml of Sludge and (3) add 10 ml of DI Water to 9ml of Sludge.

Place each Sludge mixture in a jar. Shake each jar ~~30 seconds~~ vigorously for 30 Sec.

describe the foam height and the length of time that it lasts in each jar.

~~Methanol~~

(1) 10ppm-780 (2) 100ppm 780 (3) Control

FOR RESULTS AND ACTUAL PROCEDURES FOLLOWED, SEE 3M TECHNICAL NOTEBOOK NO. 50278, pages 9-11.

(COPIES ATTACHED)

003047

White - Return to Requester Canary - Environmental Engrg. Office File Pink - Environmental Engrg. Lab Goldenrod - Return to Requester

PROJECT NO. 9970012700 (WAE) 9970012700

3M TECHNICAL NOTEBOOK NO. 50278 PAGE 7

Subject: FOAMING OF FC780, LOT 501 WHEN MIXED WITH MUNICIPAL WASTEWATER ACTIVATED SLUDGE. Date: 8-07-79

Object: TO SEE LEVEL OF FC 780, LOT 501 THAT CAN BE TREATED WITHOUT FOAMING.

Reference: ENVIRONMENTAL LAB REQUEST NO. 5038

SCOPE: Various concentrations of FC 780, LOT 501 were mixed with municipal wastewater treatment plant activated sludge from the Pigs Eye plant in St. Paul. The foaming characteristics were then observed.

The following experiments were performed. Throughout all of the experiments, the sludge was kept aerated until use.

Experiment # 1 (WAE) (A)

1. A dilution series of FC 780, LOT 501 in D.I. water of 10,000 - 1,000 - 100 mg/l was prepared.
2. 10 ml of each dilution of FC780, LOT 501 was added to 90 ml of the activated sludge.
   Note: The suspended solids concentration of the sludge was ≅ 8,000 mg/l according to Jim Wyzgowski from Pigs Eye.
3. 10 ml of D.I. water was added to 90 ml of sludge for use as a control.
4. Each mixture was placed in a jar and shaken vigorously for 30 sec.

OBSERVATIONS

Final concentration of FC 780 in mixture	FOAM HEIGHT AT TIME (CM) ZERO	1 MIN.	5 MIN.	20 MIN.
CONTROL	.2 cm	.1 cm	.1	NO FOAM
10 mg/l	.2 cm	.1 cm	.1	NO FOAM
100 mg/l	.5 cm	.3 cm	.2	.1 cm
1,000 mg/l	*	*	*	*

* foam filled the entire headspace of the (WAE) bottle.

— cont. on page 8 —

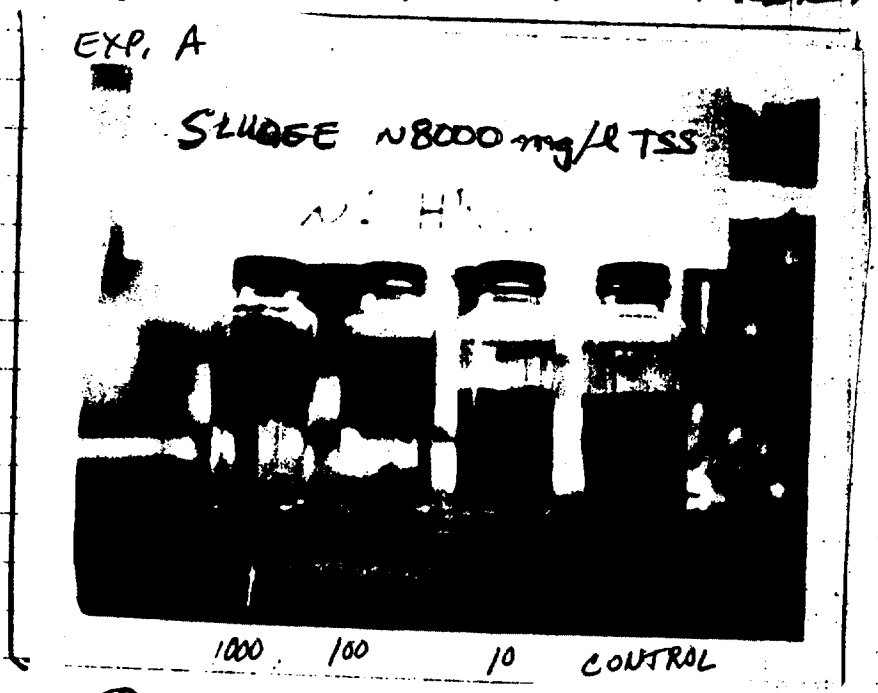
Signature Wade A. Sokil

Date: 8-07-79

ject:

Reference: cont. from page 7

Note: It was observed that the mixtures containing ~~F~~ 100 mg/l and 1,000 mg/l FC-780 did not settle very well. The photo below was taken ~2 hrs. after the mixtures were shaken.



EXPERIMENT #2 (B)

1. The activated sludge was diluted with primary influent from Pigs Eye to yield a final suspended solids concentration of ~3800 mg/l.
2. 10 ml ~~each~~ (WAS) of the 1,000 mg/l and 10 ml of the 100 mg/l FC-780, LOT 501 dilutions were added to 90 ml of sludge. (See No 1. of Exp (A) above.)
3. 10 ml of D.I. water was added to 90 ml of sludge for use as a control.
4. Each mixture was placed in jars and shaken vigorously for 30 sec.

— cont. on page 9 —

Signature Wade A. Schiel

Date: 8-07-79

ject:

Reference: cont. from page 8.

OBSERVATIONS

final FC-780 concentration		FOAM HEIGHT AT TIME ZERO	1 MIN.	3 MIN.	10 MIN.	16 MIN.
	CONTROL -	.2(cm)	.2 cm	.1 cm	.0	.0
	10 mg/l -	.3 cm	.2 cm	.1 cm	.0	0
	100 mg/l -	.8 cm	.7 cm	.4 cm	.3 cm	.3 cm

NOTE: It was observed that the settling of the sludge in the mixtures containing FC-780, LOT 501 was not as good as in the control.

See photos below and on back of this page.

carbon paper in upside down — copy did not go through.

W.A. Schiel
8-07-79

OBSERVATIONS

final FC-780 concentration		FOAM HEIGHT AT TIM ZERO	1 MIN.	3 MIN.	10 MIN.	16 MIN
	CONTROL -	.2 cm	2cm	.1 cm	0cm	0 cm
	10 mg/l -	.3 cm	2cm	.1 cm	0cm	0cm
	100 mg/l -	.8 cm	7cm	.4 cm	.3 cm	.3 cm

NOTE: It was observed that the settling of the sludge in the mixtures containing FC-780, LOT 501 was not as good as in the control.

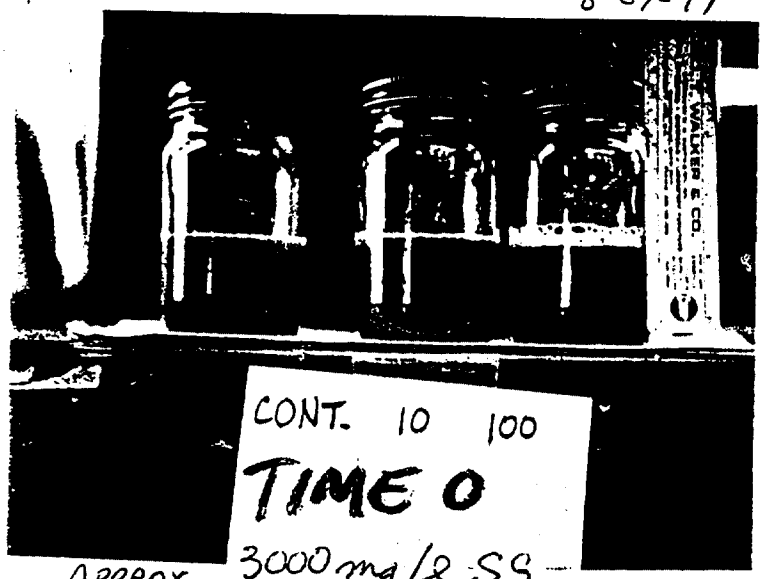
See photos on back of this page.

— cont. on page 10 —

Signature Wade A. Schiel Date: 8-07-79

Read and Understood Date:

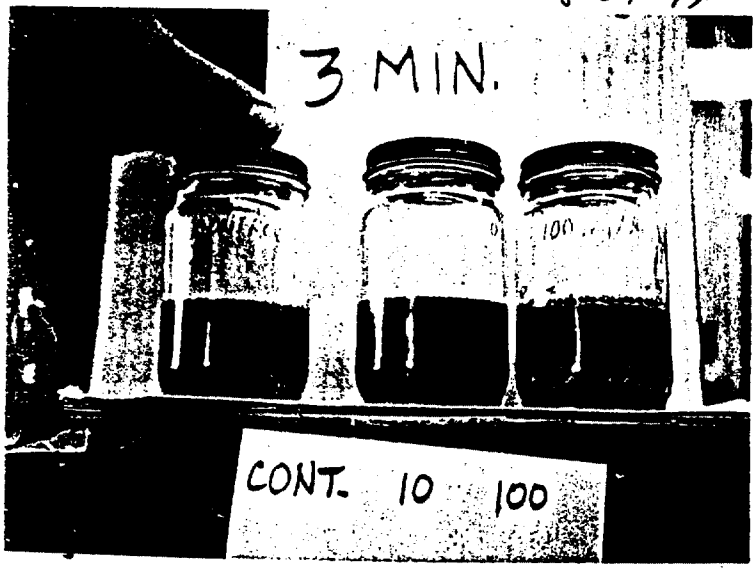
P. B 8-07-79



APPROX. 3000 mg/ℓ SS

EXP. B 8-07-7

P. B 8-07-79



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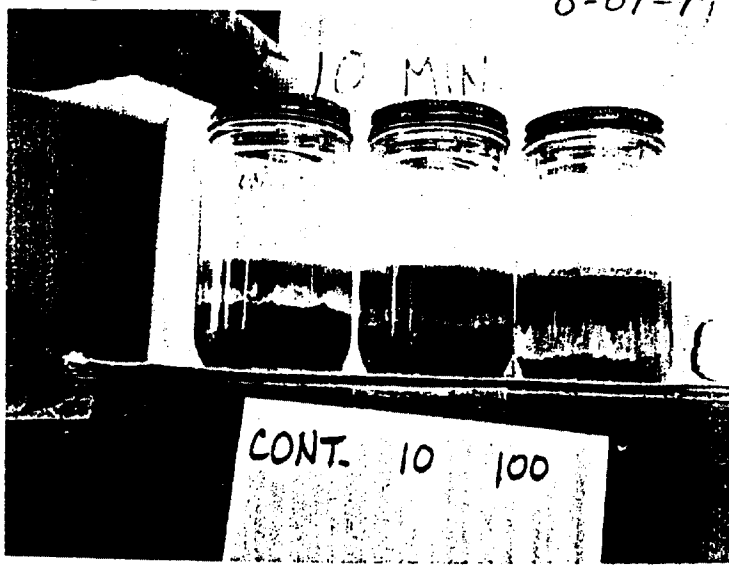

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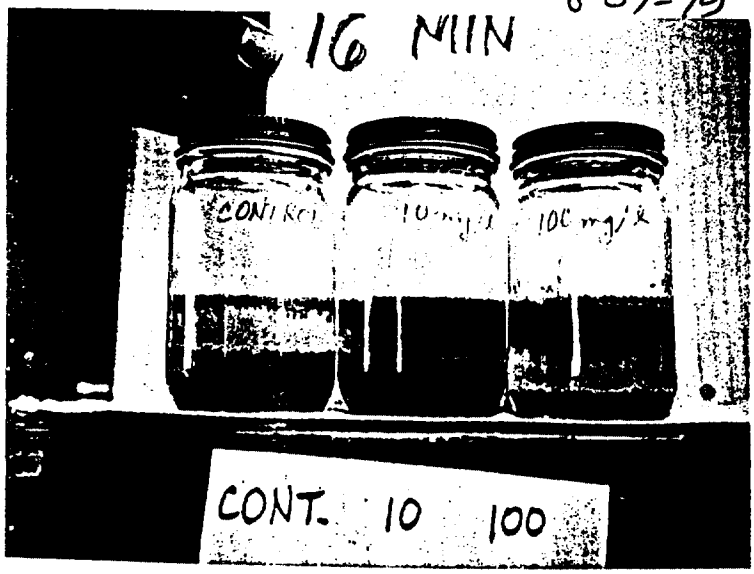


PROJECT NO. 9970012700 ~~9990012700~~ (WAS)

Subject:

3M TECHNICAL NOTEBOOK NO. 50278 10

Date: 8-07-79

bject:

Reference: cont. from page 9.

EXPERIMENT (C)

1. } Prepared ~~this~~ (WAS) the
2. } same as in Experiment (B) above.
3.
4. Each mixture was placed in a jar and aerated for 5 min. @ 500 ml/min., using gas dispersion tubes having fritted glass ends. (See photo on back of this page.)

OBSERVATIONS

~~At the end of the 5 min~~ (WAS)

1. no foaming during the aeration period.
2. after the ~~5~~ (WAS) aeration period, there was not any foam on the surface of the mixtures.
3. The settling of the sludge in the mixtures appeared to be uniform

See photos on back of this page.

W.A. Schiel
8-07-79

Rictus Septic
780 B Product
Toxicity Screen
Slent
1-10-83

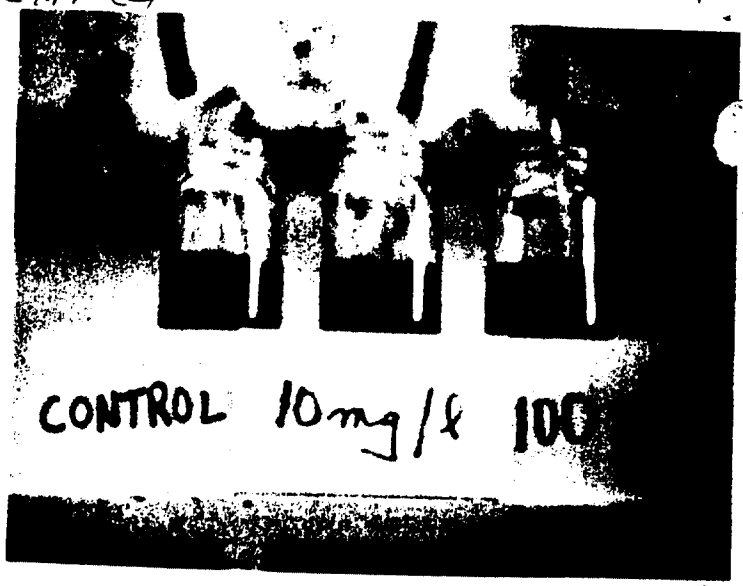
— cont. on page 11 —

Signature Wade A. Schiel

Date: 8-07-79

This photo was taken during the 5 min. aeration period.

EXP. (C)



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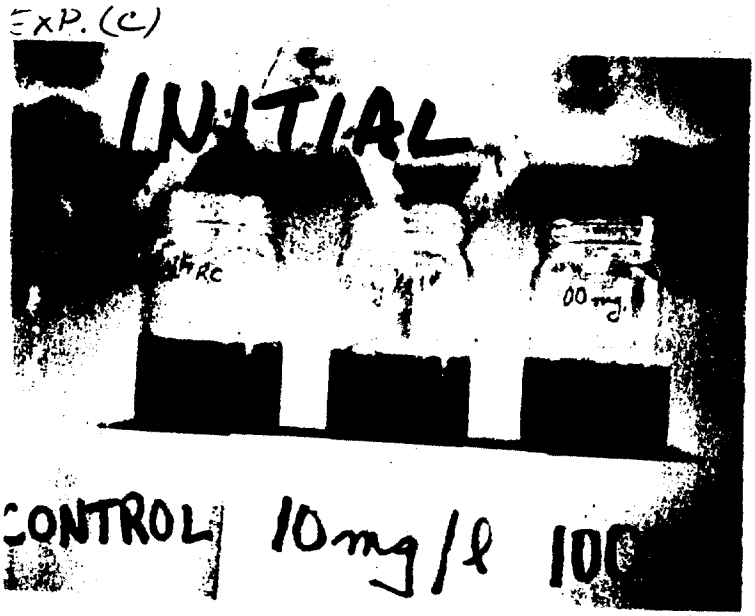

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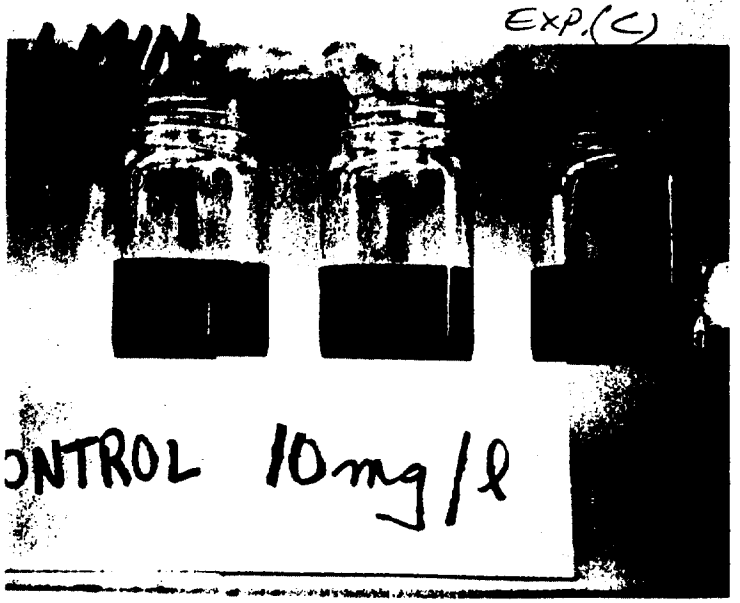
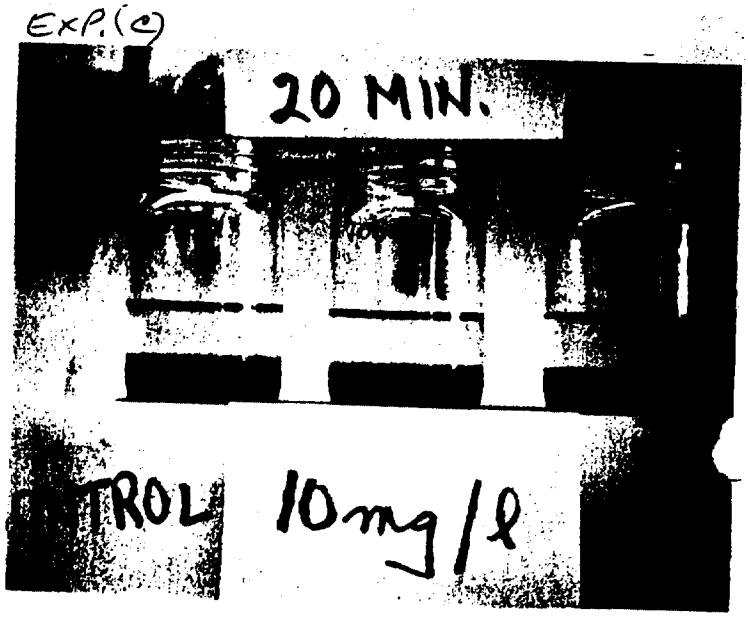


EXP.(C)

EXP.(C)



PROJECT NO. 9970012700 ~~9990012700~~ (WAS)

Subject:

3M TECHNICAL NOTEBOOK NO. 50278 11

Date: 8-08-79

Object:

Reference: cont. from page 10.

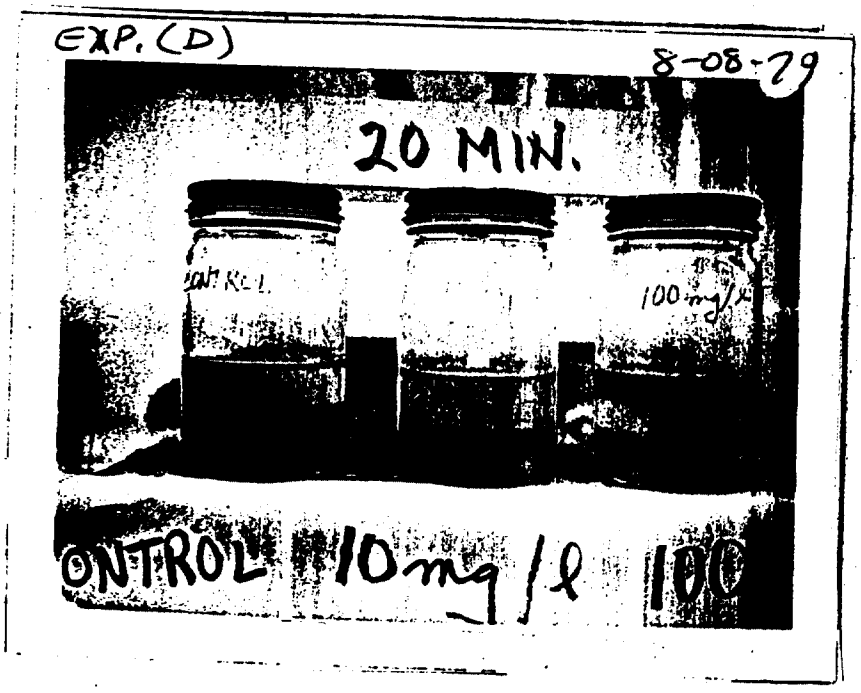
EXPERIMENT (D)

After the mixtures in Experiment (C) had sat uncovered at room temp. (~75°F) for ~17 hrs., they were capped and shaken vigorously for 30 sec. as in Experiments A & B.

Very little foam formed in any of the mixtures.

The settling in the mixtures containing FC-780, LOT 501 was not as good as the control, and resembled the settling in Experiments A and B.

The photo below was taken 20 min. after the mixtures were shaken.



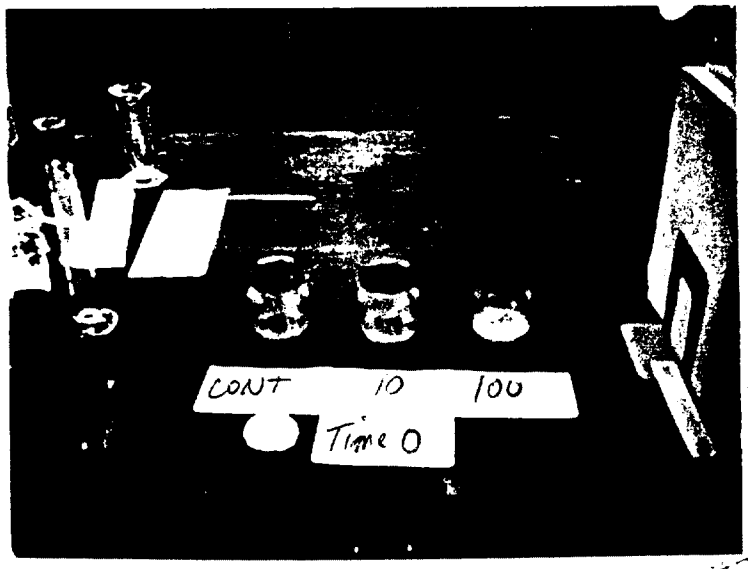
Signature Wade A. Schild

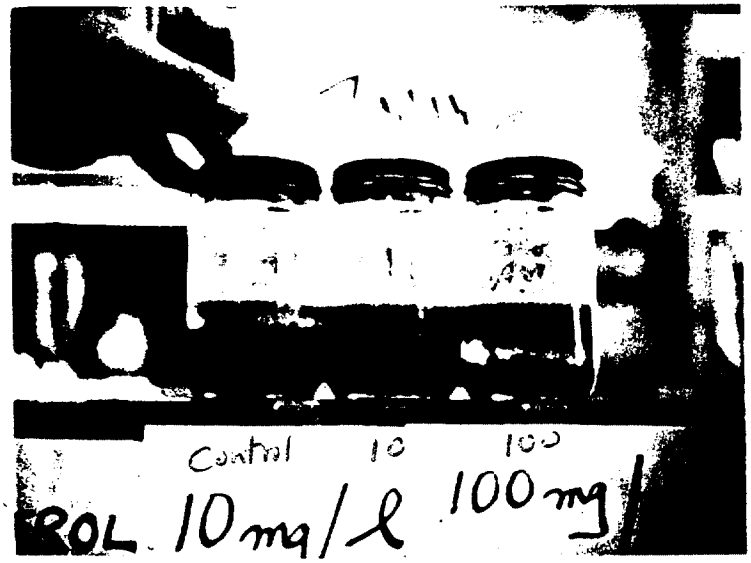
Date: 8-08-79

Read and Understood

Date:

8-7-75





LRN: 6812S

FOAMING STUDY RESULTS

LRN: 6912S

3M ENVIRONMENTAL LABORATORY
(AFFF Foaming Study)
Protocol Reference: EAR 6/13/81

Sample Description:
L-5439, cc814-28, F-6661, Lot 501

Date: 6/18/81
Analyst: W.A. Scheil

The activated sludge mixed liquor was obtained from the Metro Treatment Plant (Pig's Eye) on 6/18/81. The estimated MLSS concentration using the Spec. 20 technique was 2,100 mg/l. The concentration was not adjusted prior to running the foaming study.

The MLSS of the mixed liquor was analyzed using the standard protocol for TS and found to be 2,100 mg/l and 1,900 mg/l (duplicate analyses). TS Protocol Reference: Standard Methods, 14th Ed., pp. 89-98.

A stock solution of 1.0 g AFFF/100 ml was prepared by dilution with deionized water.

Five 250-ml graduated cylinders were filled to the 200-ml mark with the fresh mixed liquor. When the solids had settled far enough, aliquots of clear supernate were drawn off as follows: Cylinder #1 - 0 ml; Cylinder #2 - 0.30 ml; Cylinder #3 - 1.0 ml; Cylinder #4 - 3.0 ml; Cylinder #5 - 10 ml. Then the same volume of AFFF stock solution was added to the cylinders as the volumes of clear supernate drawn off. The cylinders were then covered with Parafilm® and mixed by inverting. This prepared a dilution series of 0, 15, 50, 150, and 500 mg/l of AFFF in mixed liquor.

The solutions were divided into two 100 ml aliquots. 100 ml was poured into 500-ml graduated cylinders and the other 100 ml was left in the 250-ml cylinders.

SHAKE TEST

The portions which were left in the 250-ml cyinders were covered with Parafilm® and vigorously shaken for 30 seconds and then allowed to stand.

Photographs were taken and the foam volumes were measured at the following intervals:

		Foam Volume(ml)			
AFFF Conc.	Time 0	1 Min.	5 Min.	20 Min.	1 Hour
0 mg/l	2	0	0	0	0
15 mg/l	2	0	0	0	0
50 mg/l	6	2	0	0	0
150 mg/l	16	8	4	2	0
500 mg/l	36	30	22	10*	10*

*The foam appeared less dense then previous observation.

LRN: 6912S

Date: 6/18/81
Analyst: W.A. Scheil

AFFF FOAMING STUDY - continued

The foam volume (ml) was measured in lieu of foam height by reading the graduates on the cylinders.

The settling of the solids was observed after 1 hour.

AFFF Concentration	Volume of Settled Solids	Volume of Floating Solids
0 mg/l	20 ml	10 ml
15 mg/l	16 ml	11 ml
50 mg/l	10 ml	12 ml
150 mg/l	9 ml	13 ml
500 mg/l	6 ml	12 ml

After 1 hour of settling, the cylinders were swirled and a photograph was taken after 1 minute of settling. See photo titled 'Swirled After 1 Hour Settling, T=1 Min.' The cylinders were then swirled a second time and a photograph was taken after 20 min. See photo titled 'Swirled a 2nd Time, T=20 Min.' At this point, the settling of the solids appeared uniform in all concentrations.

AERATION TEST

The 100-ml portions which were poured into the 500-ml cylinders were each aerated for 5 minutes at approx. 500 ml of air per minute using gas dispersion tubes with fritted glass ends.

Foam in the 500-mg/l solution had to be controlled from coming over the top of the cylinder by swirling the air supply tubing.

The foaming in the 150 and 500-mg/l solutions carried considerable amounts of the mixed liquor solids up the sides of the cylinder and in the body of the foam. Almost all of the solids in the 500-mg/l solution were removed from solution during the aeration period. See photos titled 'During Aeration' and 'After 5 Min. Aeration.'

At the end of the aeration period, the cylinders were covered with Parafilm® and inverted several times to wash the solids off the sides. After this, the foam volumes were measured at the following intervals:

LRN: 6912S

Date: 6/18/81
Analyst: W.A. Scheil

AFFF FOAMING STUDY - continued

AFFF Conc.	Foam Volume(ml) Time 0	1 Min.	5 Min.	20 Min.	1 Hour
0 mg/l	0	0	0	0	0
15 mg/l	0	0	0	0	0
50 mg/l	0	0	0	0	0
150 mg/l	5	0	0	0	0
500 mg/l	15	10*	10*	10*	5*

*The foam appeared less dense than the previous observation.

The settling of the solids appeared uniform in all concentrations.

EAR 5/13/81

PROTOCOL FOR AFFF FOAMING STUDIES

1. Obtain fresh activated sludge mixed liquor from Metro treatment plant.

2. Using the Spec 20 technique and the graph of adsorbance at 600 nm versus SS, adjust MLSS to 2000 mg/l by DI water addition or by centrifugation and discarding supernatant.

3. Make 500, 150, 50, 15, and 0 mg/l solutions of AFFF in 200 ml of this sludge.

4. Divide each solution into 2, 100 ml parts. Placing 1/2 in a jar with at least 200 ml of head space and the other half in 500 ml volumetric cylinders.

5. Cover and shake each jar vigorously for 30 seconds.

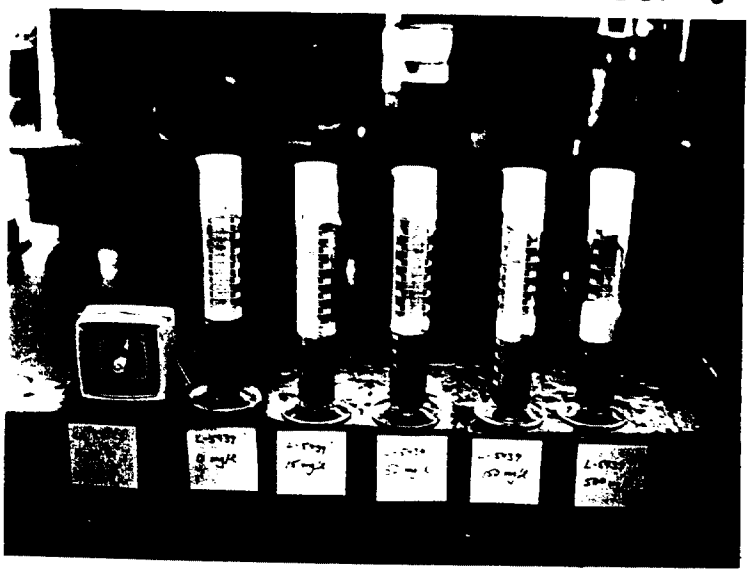
6. Take photographs and measure foam height immediately after shaking (time 0) and at 1 minute, 5 minute, 20 minute, and 1 hour. Also observe and photograph how well sludge settles.

7. Aerate the AFFF sludge mixtures in the volumetric cylinders for 5 minutes at 500 ml of air per minute using gas dispersion tubes with fritted glass ends.

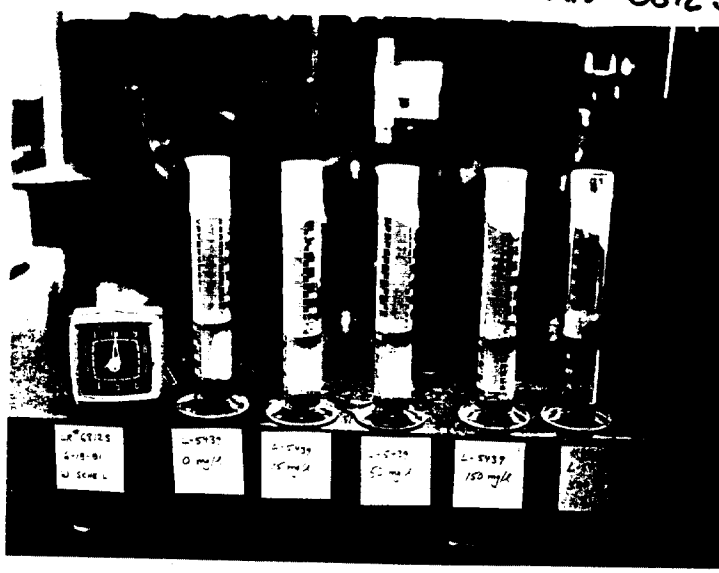
8. Again, observe foam height or volume and sludge settling, again make photographs.

AFFF FOAMING STUDY, LRN: 6812S

TIME = 0 LRN: 6812S



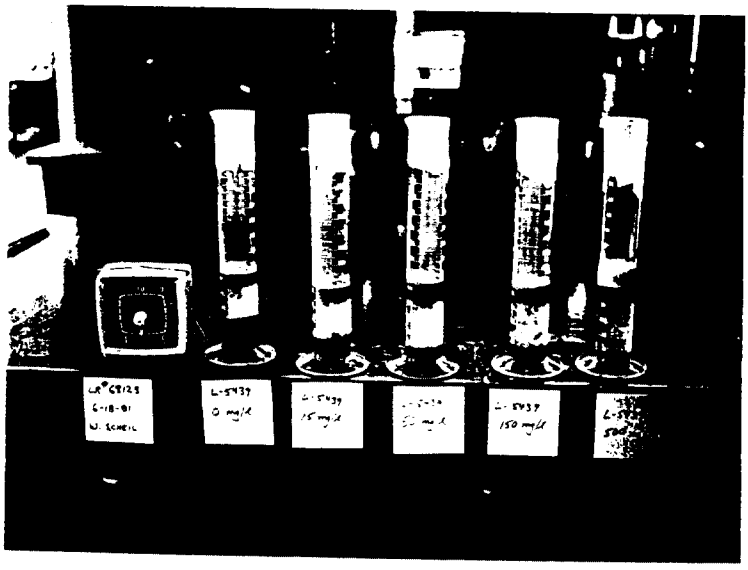
TIME = 20 MIN LRN: 6812S



TIME = 1 MIN.

TIME = 1 HOUR LRN: 6812S

TIME = 5MIN LRN: 6812S

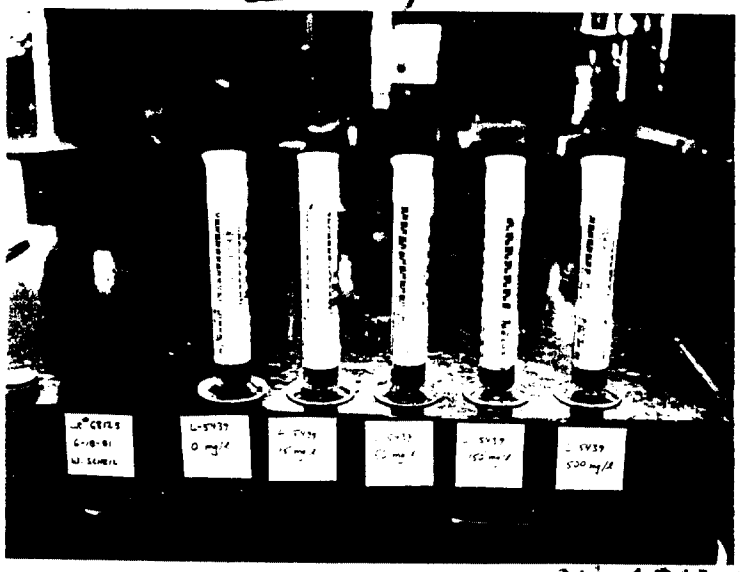


SHAKE TEST PHOTOS
AFFF FOAMING STUDY, LRN: 6812S

SWIRLED AFTER 1 HOUR SETTLING, T= 1 MIN.

LRN: 6812

SWIRLED A 2ND TIME, T= 20 MIN.



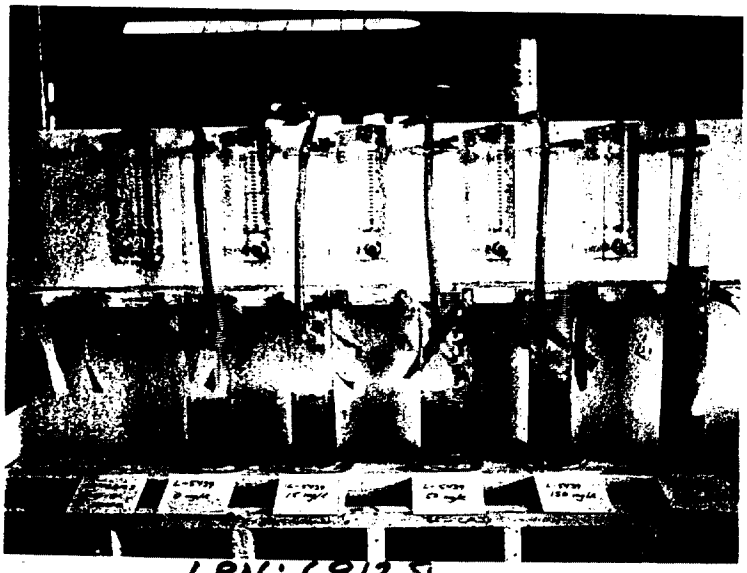
LRN: 6812

BEST COPY AVAILABLE

003062

AERATION TEST PHOTOS
AFFF FOAMING STUDY, LRN: 6812S

DURING AERATION - AFTER 30 SEC.

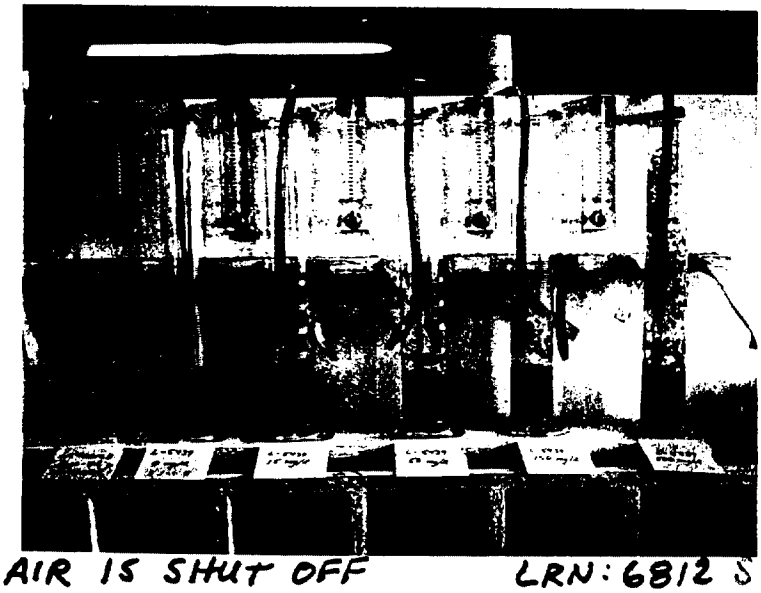


LRN: 6812S

DURING AERATION - AFTER 1 MIN.

LRN: 6812S

AFTER 5 MIN. AERATION



AIR IS SHUT OFF LRN: 6812S

AERATION TEST PHOTOS
AFFF FOAMING STUDY, LRN: 6812S

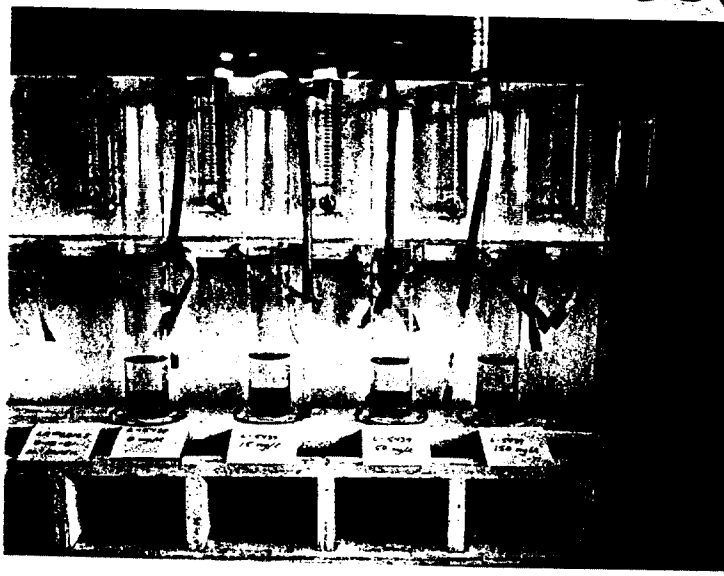
TIME = 0 LRN: 6812S

(AFTER INVERTING)

TIME = 20 MIN. LRN: 6812

TIME = 1 MIN LRN: 6812S

TIME = 1 HOUR LRN: 6812



TIME = 5 MIN LRN: 6812S

3M ENVIRONMENTAL LABORATORY

CRN 1625
FILE
SEE W.A. Schaal
DATE 3-15-82 SHEET NO.

FOAMING STUDY — SHAKE TEST

ANALYSIS FORM 1038A

PROTOCOL REFERENCE
EAR 5/13/81

		FOAM HEIGHT – ml				VOLUME OF SETTLED SOLIDS @ 60 MIN (ml)	
		TIME 0	1 MIN.	5 MIN.	20 MIN.	60 MIN.	
		A	B	C	D	E	F	G	H	J	K	L	M	N	O	P	R
1	FC-203C, LOT-501																
2																	
3	0 ~~0~~ mg/l	0	–	0	0	0		15									
4	10 ~~10~~ "	2	–	0	0	0		15									
5	50 ~~50~~ "	10	–	0	0	0		~~13~~									
6	150 ~~150~~ "	15	–	3	TRACE	TRACE		15									
7	500 ~~500~~ "	30	–	25*	23*	18*		14									
8	WAS 5/21/82																
9		* THE FOAM WAS LESS DENSE THAN IT WAS AT PREVIOUS READING															
10																	
11																	
12																	
13	FC-206C, LOT-502																
14																	
15	0 ~~0~~ mg/l	0	–	0	0	0		15									
16	10 ~~10~~ "	0	–	0	0	0		15									
17	50 ~~50~~ "	8	–	0	0	0		15									
18	150 ~~150~~ "	20	–	TRACE	0	0		18									
19	500 ~~500~~ "	40	–	14	8	5		16									
20	WAS 5/21/82																
21																	
22																	
23																	
24																	
25	NOTE: THE ONE MINUTE OBSERVATIONS WERE NOT MADE.																
26																	
27	Protocol Reference: EAR 5/13/81 Protocol for AFFF FOAMING STUDIES																
28																	
29																	
30																	

Settling appeared uniform. The cylinders were hand swirled during the settling period after the (5 min) and (20 min) readings to help facilitate settling of floating solids. The solids appeared to be floated because of entrapped air bubbles from the vigorous shaking steps.

Settling appeared uniform. The cylinders were inverted after the (20 min) reading to facilitate settling of floating solids - See note below

0030

3M ENVIRONMENTAL LABORATORY

FILE LR# 7625

FOAMING STUDY — AERATION TEST

SEE W. A. SCHEIL

ANALYSIS FORM 1038A

DATE 3-15-82 SHEET NO.

PROTOCOL REFERENCE
EAR 5/13/81

		FOAM HEIGHT - ml				VOLUME OF SETTLED SOLIDS @ 60 MIN (ml)	
		TIME 0	1 MIN.	5 MIN.	20 MIN.	60 MIN.	
FC-203C, LOT-501							
0 ~~0~~ mg/l		0	—	0	0	0	15
10 ~~10~~ "		0	—	0	0	0	15
50 ~~50~~ "		10	—	0	0	0	15
100 ~~100~~ "		25	—	5	TRACE	0	13
500 ~~500~~ "		100	—	85*	80*	70*	11**
WAS 5/21/82							
FC-206C, LOT-502							
0 ~~0~~ mg/l		0	—	0	0	0	15
10 ~~10~~ "		0	—	0	0	0	15
50 ~~50~~ "		TRACE	—	0	0	0	15
100 ~~100~~ "		10	—	TRACE	0	0	15
500 ~~500~~ "		110	—	55*	50*	15*	12
WAS 5/21/82							

Settling appeared uniform.

Settling appeared uniform.
Some solids were lost from the highest concentration during aeration.

* foam less dense than it was at previous reading
** some of the solids were lost during aeration steps

NOTE: THE ONE MINUTE OBSERVATIONS WERE NOT MADE.

PROTOCOL REFERENCE: EAR 5/13/81 Protocol for AFFF Foaming Studies

003066

FORM 10620 8-PWO

File: Page No.

ENVIRONMENTAL ENGR. LAB – WORK SHEET

SAMPLE DESCRIPTION

LRN# 7625

Date: 3-12-82

Analyst: W. A. Schmidt

Hrs.:

FOAMING Study – NOTES

Mixed liquor activated sludge –

collected from Pigs Eye Metro Wastewater Plant on 3/12/82

TSS by Spectro method – 2,700 mg/l

Adjusted to ~2000 mg/l by adding 875 ml Deionized H_2O to 2500 ml of sludge.

The mixed liquor was then refrigerated until use on 3/15/82.

Test date: 3/15/82. Protocol Reference: EAR 5/13/81 (See Env. Lab Reg. # 6912 S)

The analyzed MLSS (TSS) of the adjusted mixed liquor was determined to be 2100 mg/l using the Env. Lab standard protocol for TSS.

W. A. Schmidt
3-17-82

Reviewed by:

EAH 5/13/81

PROTOCOL FOR AFFF FOAMING STUDIES

Obtain fresh activated sludge mixed liquor from Metro treatment plant.

Using the Spec 20 technique and the graph of adsorbance at 600 nm versus SS, adjust MLSS to 2000 mg/l by DI water addition or by centrifugation and discarding supernatant.

Make 500, 150, 50, 15, and 0 mg/l solutions of AFFF in 200 ml of this sludge.

Divide each solution into 2, 100 ml parts. Placing 1/2 in a jar with at least 200 ml of head space and the other half in 500 ml volumetric cylinders.

Cover and shake each jar vigorously for 30 seconds.

Take photographs and measure foam height immediately after shaking (time 0) and at 1 minute, 5 minute, 20 minute, and 1 hour. Also observe and photograph how well sludge settles.

Aerate the AFFF sludge mixtures in the volumetric cylinders for 5 minutes at 500 ml of air per minute using gas dispersion tubes with fritted glass ends.

Again, observe foam height or volume and sludge settling, again make photographs.

CR # 7625

Conc

0
10
50
100
500

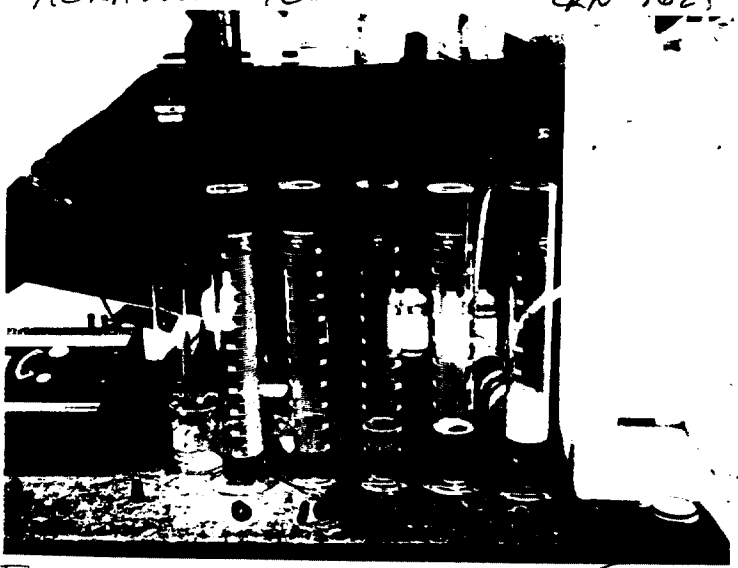
LRN 7625

FC-203C DURING AERATION

AERATION TEST

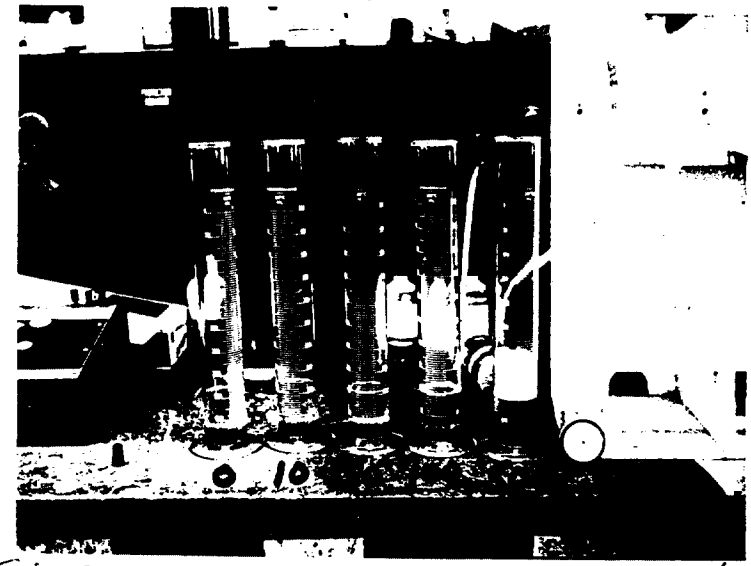
FC-203C 1 MIN

AERATION TEST LRN 7625



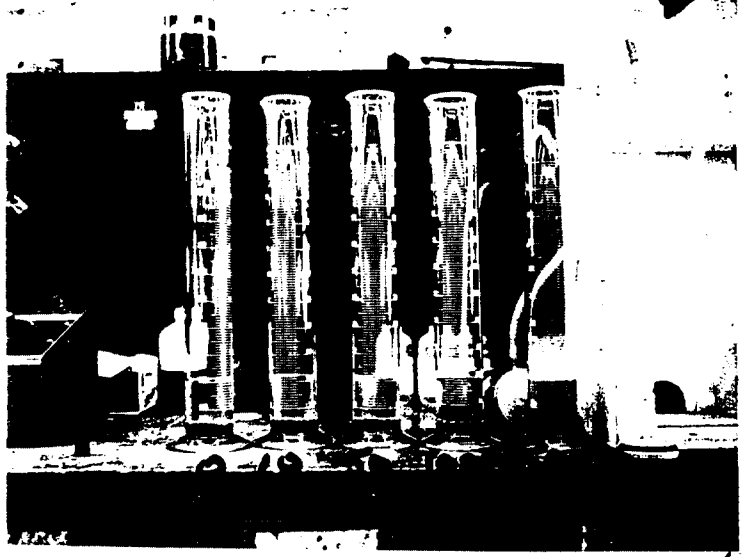
FC-203C 5 MIN.

Aeration Test



FC-203C 20 MIN

Aeration Test LRN 7625



FC-203C 60 MIN

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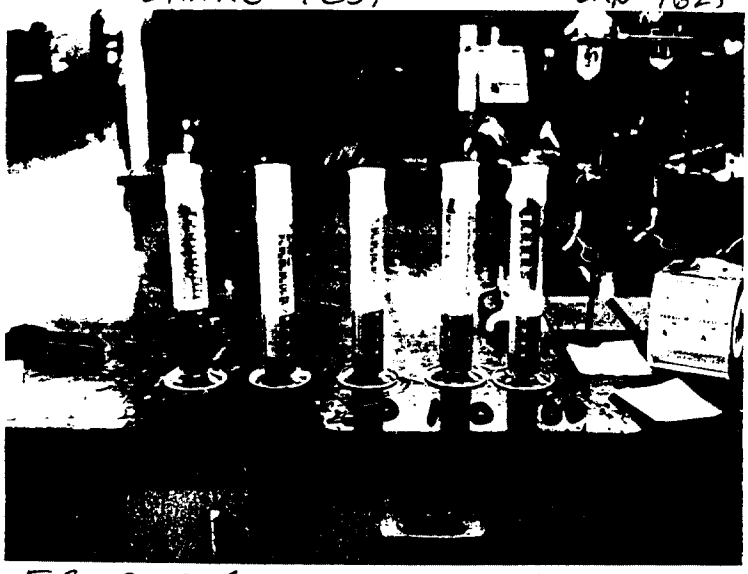
SHAKE TEST LRN 7625



FC-203C T= 0 MIN.

BEST COPY AVAILABLE

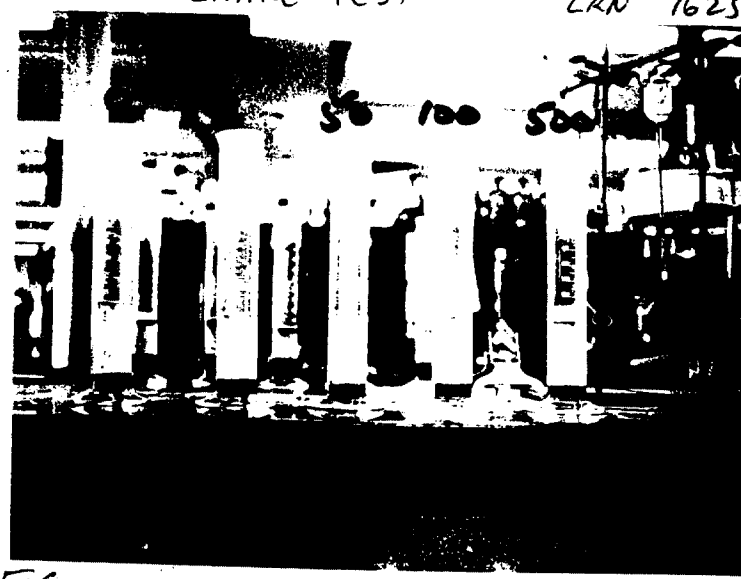
Photo @ 5 MIN.
was not taken.

W.O. Schuh
3-17-82

SHAKE TEST LRN 7625

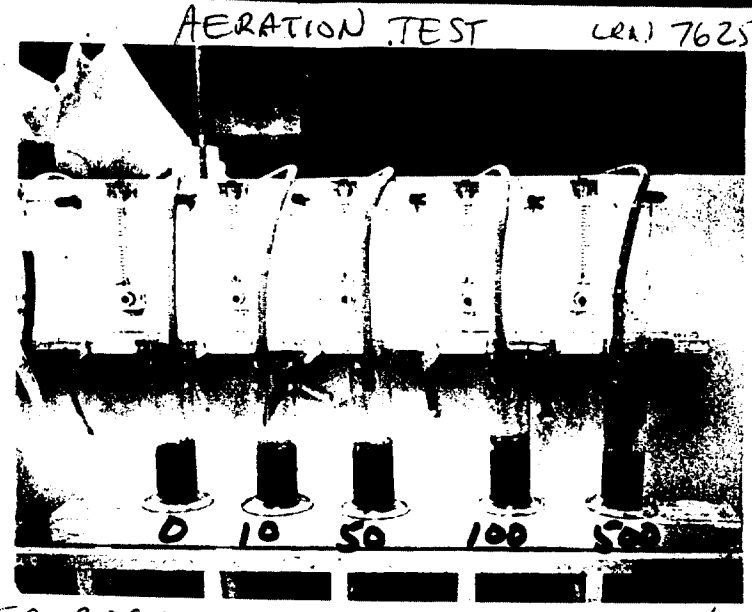
-203C 20 MIN

SHAKE TEST LRN 7625

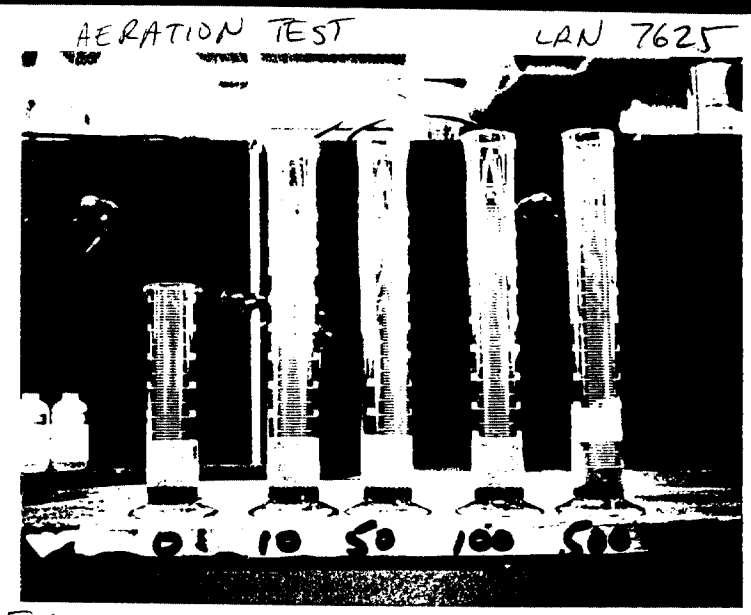


FC-203C 60 MIN

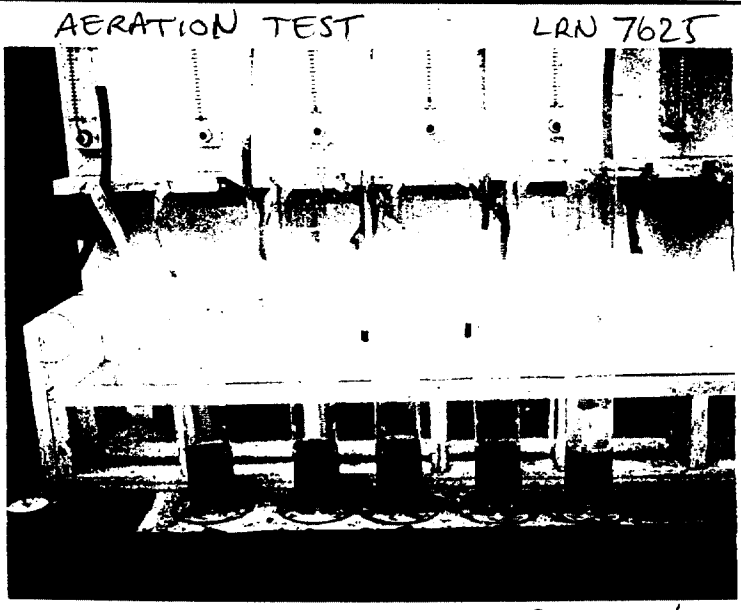
003070



FC-206C DURING AERATION



FC-206C 20 MIN



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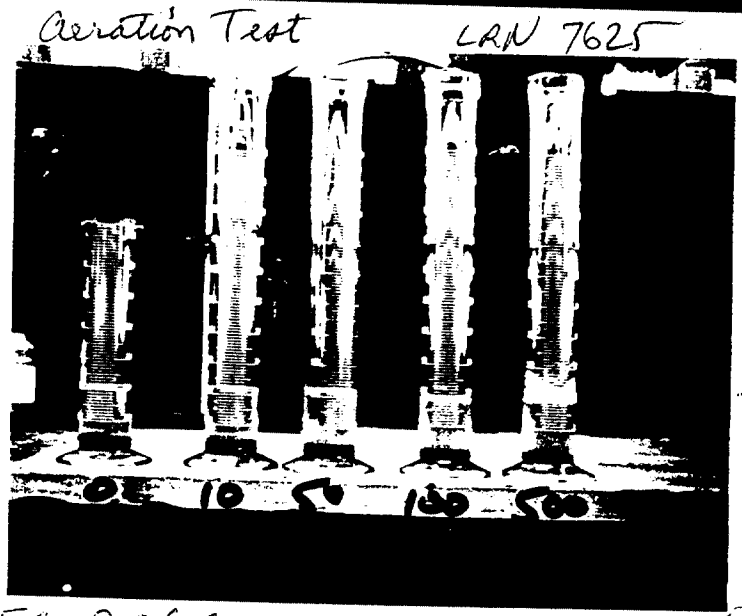
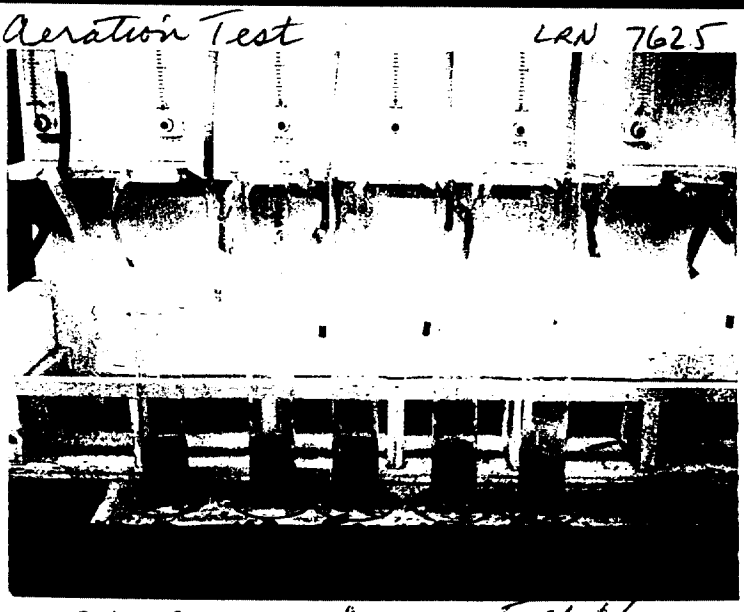


FC-206C 60 MIN



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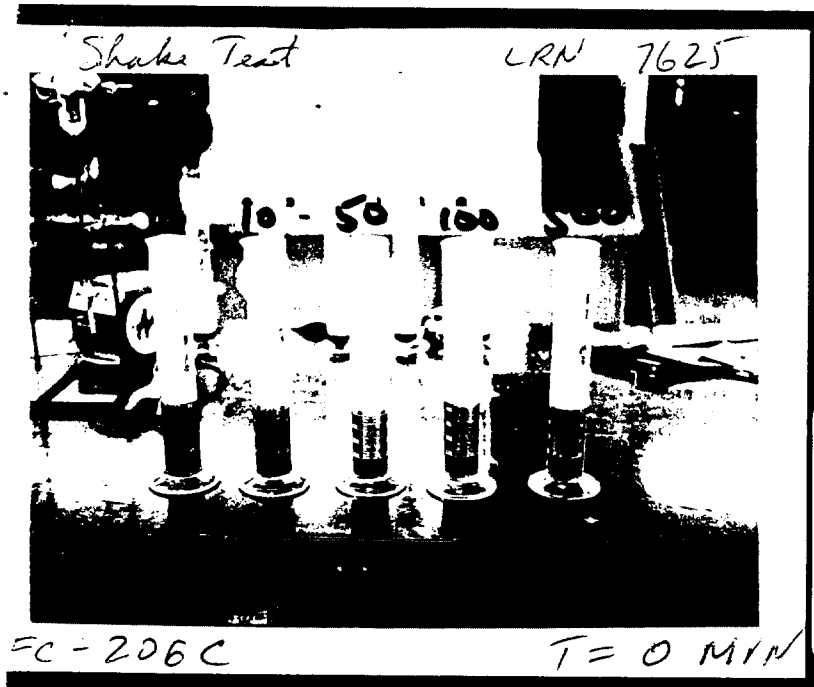
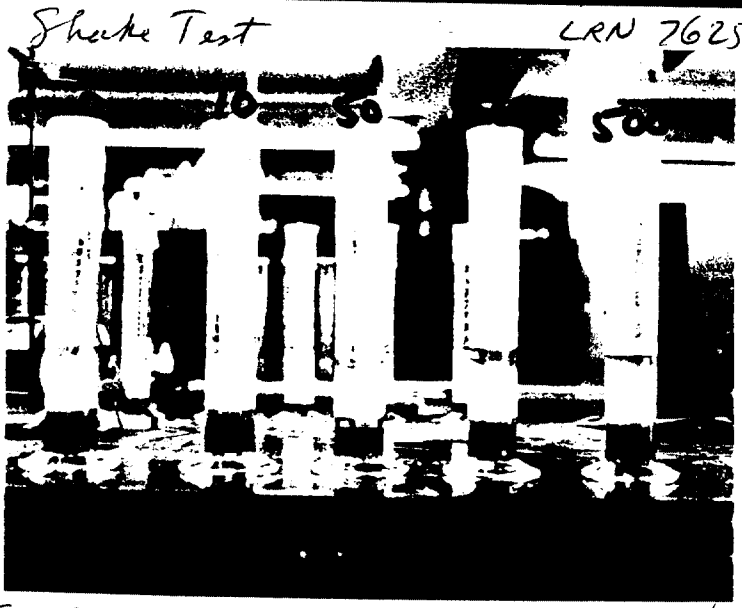
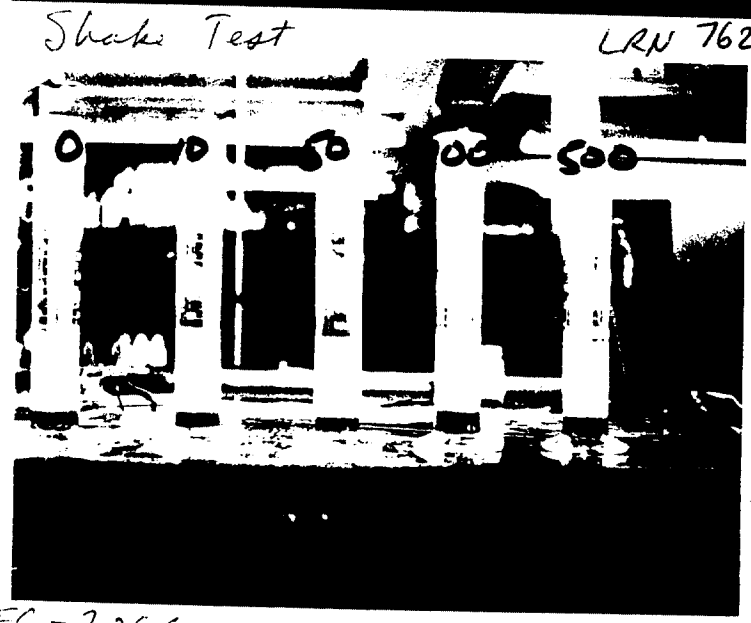


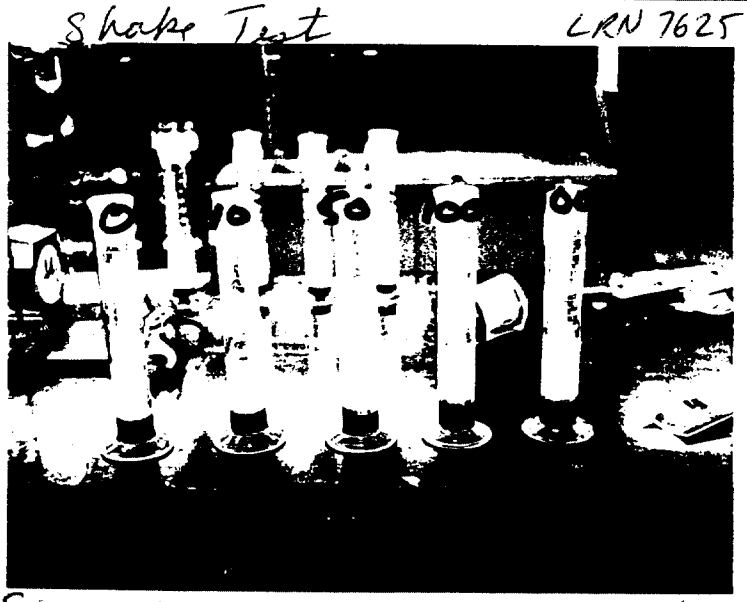
FC-206C T = 0 MIN



FC-206C 5 MIN



FC-206C 60 MIN



FC-206C 20 MIN.

Form 10620 - 8 - D - PWO

first stop
How much antifoamer

Environmental Lab — Work Sheet

Lab Request No. H1480

Page _____ of _____

Sample Description

Antifoamer

Date: 3/16/90

Analyst: SJ

SW5214 mg/L	FC203CE mg/L	Foam Produced *
10	1000	yes
18	1000	yes
32	1000	yes
56	1000	yes
100	1000	none to slight

Per EAR to SAB antifoamer usage dose 1:6

For sludge respiration test used 200 mg/L. (1:5)

* Solution contained SW5214 Antifoamer, FC203CE at 1000mg/L and Millipore Milli-Q® water only.

Technical Report Summary

Form 6747 - 11 - H

3M

To: Patent & Technical Communications Services — 201-2C-12

Report Summary must be typewritten. Guidelines are on reverse side. If report is printed on both sides of paper, send two copies to P & TCS.

Document Number:	Department Number: 0222	Project Number:	Report Number: (Place additional D.N.s in Abstract area)

To

M. T. Pike - 236-1B-33

Author(s)

T. J. Morgan, R. D. Howell

Division/Department

Environmental Engineering & Pollution Control

CC: 01 Loc: 089

Project Description

EPP Research and Development

Report Title

The Effectiveness of Selected Antifoam Agents in Suppressing Foam...

Date Typed: 8/19/92

Employee Number(s): RDH-295864

Organization Code: EE&PC

Period Covered

Keywords

Light Water Brand AFFF
Aqueous Film Forming Foam
Foam
Antifoam Agents
Defoaming Agents
Foam Supression
Waste Disposal
Wastewater Treatment

Project Objective & Report Abstract

3M recommends to customers that AFFF usage wastes be disposed of by diluting the waste and flushing it into a running sewer that flows to a wastewater treatment system. If the AFFF in the sewage is not sufficiently dilute, foaming may occur in the aeration basin of wastewater treatment systems. This may cause cleanup problems and reduced efficiency in the treatment works.

In this study, the effectiveness and relative cost of commercially available antifoam products were evaluated. The experimental work consisted of adding the antifoam and 3M AFFF products to an aerated solution of water or activated sludge mixed liquor. The effectiveness of the antifoams was determined by their ability to prevent foaming in the aerated solutions.

In the initial screening tests, the 31 antifoams supplied by nine manufacturers were evaluated for their ability to control foaming by a 500 mg/L solution of AFFF in a deionized water solution. Twelve antifoams passed this test. A second set of tests consisted of successively adding an AFFF solution to an aerated antifoam solution. Additions of the AFFF stock solution caused the concentration of AFFF to increase in the solution while the antifoam concentration decreased.

Nine antifoams were found to be effective in these experiments: GE Silicones Antifoam Emulsion AF-72, Antifoam Emulsion AF-93, and Antifoam Emulsion AF-9020; Henkel Defoamer WB-209 and Foammaster ™ DS; Union Carbide SAG 2001 Organosilicone Emulsion; Wacker Silicones Antifoam Agent SE-36, Antifoam Agent SWS-214, and Antifoam Emulsion SRE.

Of these, the most cost effective are Henkel WB-209, GE Silicones AF-9020, Henkel Foammaster ™ DS, and Wacker Silicones SRE.

Report Type

- ☒ R & D Research and Development
- ☐ PILot Plant
- ☐ MANufacturing
- ☐ Management SUMmary
- ☐ TRP Trip or Field Report
- ☐ FACtory Experiment
- ☐ ENGineering
- ☐ ROI Record of Invention
- ☐ TECh. Service
- ☐ GOVt. Project
- ☐ OTHER

Security

☒ Open Report and Summary ☐ Closed Report - Open Summary

3M Chemical Registry ☐ New Chemicals Reported — Use form 6092 to enter into Chemical Registry

Notebook Reference

For P & TCS Use Only ▶ Film Code | Number of Pages

Information Liaison Initials

P & TCS Editor Initials

003074

THE EFFECTIVENESS OF SELECTED ANTIFOAM AGENTS IN SUPPRESSING FOAM CAUSED BY LIGHT WATER BRAND AFFF SOLUTIONS

INTRODUCTION

Aqueous film forming foams (AFFF) are water based, surfactant containing products used primarily to control combustion hazards and extinguish fires involving hydrocarbon liquids. In their use, AFFF agents are diluted in water and sprayed through a foam forming nozzle so that the foam spreads over the hydrocarbon liquid. Application of AFFF prevents and extinguishes Class B fires by spreading a vapor-sealing film over the liquid fuel. This vapor seal inhibits reflash even when the foam blanket is ruptured and also enables the product to be used to prevent ignition of non-ignited spills. In addition, AFFF provides excellent penetrating and wetting qualities when used on Class A fires. After their use, waste AFFF solutions from actual or simulated fire fighting activities are partially biodegradable and have low toxicity to aquatic organisms including the microorganisms in wastewater treatment systems. Therefore, wastes from AFFF usage can be discharged at controlled rates into a wastewater treatment system for disposal.

A disposal problem inherent to improperly handled AFFF wastes is foaming in wastewater treatment aeration basins. Excessive foaming in an aeration basin can cause a dual problem. First, the suspended activated sludge solids can attach to the foam and be lifted from the aeration basin. This causes clean-up problems at the wastewater treatment plant. Second, the remaining activated sludge mixed liquor is depleted of much of its suspended microbial solids and therefore is not as effective in treating wastewater.

Commonly, excessive foaming is caused by disposal recommendations not being followed. 3M recommends that Light Water™ AFFF waste should first be treated in an oil-water separator followed by metered discharge of the aqueous fraction to a running sewer. If properly metered, Light Water™ AFFF concentrations reaching the aeration basin of a wastewater treatment system will not cause excessive foaming. 3M's AFFF products are designed to be used at either 6% or 3% concentrations in water. For its 6% AFFF concentrates, 3M recommends a discharge rate such that the AFFF concentration in the receiving aeration basin will not exceed 100 mg AFFF concentrate per liter of sewage. Due to its higher surfactant concentration, for its 3% AFFF concentrates 3M recommends a discharge rate such that the AFFF concentration in the receiving aeration basin will not exceed 50 mg AFFF concentrate per liter of sewage. The values for the acceptable concentrations of Light Water™ AFFF have been determined experimentally

and are somewhat conservative; therefore if the AFFF wastes are discharged to a sewer at appropriate levels, they will not cause excessive foaming in the receiving aeration basin.

Some wastewater treatment systems are of an insufficient size to make metered discharge of the collected AFFF wastes practicable. For such sites, 3M recommends one of two disposal alternatives: 1) transporting collected waste materials by tank trucks for metered discharge into a larger waste treatment facility; or 2) discharging the waste at a higher rate (up to 800 mg/L vs. 50 or 100 mg/L) with appropriate concentrations of an antifoam agent added to the waste system to suppress foaming.

Consequently, there is a need to identify the most effective antifoam agents to be used in cases of improper disposal of AFFF waste or when the AFFF waste must be discharged at higher rates. To achieve this goal, a two phased study was completed to evaluate the effectiveness of several commercially available antifoam agents on current Light Water ™ AFFF products. Similar studies conducted in the 3M Environmental Laboratory between 1982 and 1987[1], found SWS-214 supplied by SWS Silicones Corporation and WB-209 supplied by Diamond Shamrock to be the most effective. Therefore, care was taken to include these products in this study. SWS-214 is now produced by Wacker Silicones Corporation and WB-209 is now produced by Henkel Corporation.

Phase one of this study was a survey of antifoam manufacturers. Eleven companies were contacted and asked to run independent tests to evaluate the effectiveness of their antifoams on Light Water™ AFFF solutions. Of the eleven manufacturers contacted, nine supplied samples and three completed evaluations of their products. The three manufacturers that completed evaluations were Henkel, Dow Corning, and Wacker Silicones. These evaluations were completed using two Light Water ™ AFFF products. The products used were FC-203CF and FC-600.

Henkel ran tests of their products and sent their three top performers: Defoamer WB-209, Foammaster™ DS, and Foammaster™ SZU. Of the three, Defoamer WB-209 received the highest recommendation from Henkel not only because of its effectiveness, but also because of its low price. This agreed with the results of the previous 3M Environmental studies and the present work.

Dow Corning sent two product samples after completing their testing. Their two products were 1510-US Food Grade Antifoam Emulsion and FG10 Antifoam Emulsion. Their first recommendation was the 1510-US Food Grade Antifoam Emulsion. In the tests done for this study, neither of the Dow Corning products were found to be effective.

Wacker Silicones also conducted independent tests to determine their most effective antifoams. Although SWS-214 has been recommended by 3M to our customers in the past, Wacker found three of their other products to be more effective than SWS-214. The three Wacker products were Antifoam Agent SE-36, Antifoam Emulsion SE-39, and

Antifoam Emulsion SRE. This study concurred with Wacker's results and found SE-36 and SRE to be effective. When considering cost-effectiveness, Wacker Silicones SWS-214 is also acceptable.

The objectives of the second phase of the study were threefold. The first was to evaluate the relative effectiveness of the 31 antifoam products that the nine companies submitted and to identify the top performers. The second was to find the antifoam concentrations of the top performers that could suppress foaming caused by AFFF concentrations greater than the recommended disposal concentrations. The final objective was a cost analysis of the top performers to determine the most cost-effective antifoams.

MATERIALS AND METHODS

PRODUCTS TESTED

Light Water Brand AFFF products used in the evaluation were FC-203CF, FC-206CF, FC-600, and FC-600F.

Thirty-one samples were received from the antifoam manufacturers. The products were:

Air Products	SURFYNOL™ 104A Surfactant SURFYNOL™ DF110L Defoamer SURFYNOL™ DF-75 Defoamer SURFYNOL™ 420 Surfactant
BASF	PLURONIC™ L61 PLURONIC™ L101 PLURONIC™ L121 PLURONIC™ 31R1
Dow Corning	1510-US Food Grade Antifoamer Emulsion FG10 Antifoam Emulsion
GE Silicones	Antifoam Emulsion AF-60 Antifoam Emulsion AF-72 Antifoam Emulsion AF-75 Antifoam Emulsion AF-93 Antifoam Emulsion AF-9020
Henkel	Defoamer WB-209 Foammaster™ DS Foammaster™ SZU

6	Nalco	7455 Antifoam 7460 Antifoam 7470 Antifoam 7471 Antifoam 7472 Antifoam
7	Union Carbide	SAG 2001 Organosilicone Emulsion
8	Wacker Silicones	Antifoam Agent SE-36 Antifoam Agent SWS-214 Antifoam Emulsion SE-39 Antifoam Emulsion SRE
9	Witco	Bubble Breaker™ 776P Bubble Breaker™ 3056A Bubble Breaker™ 913

PROCEDURE

Tests were done using a modified J. J. Bikerman foam control test [2].

Equipment used:

Ministatic™ pump, Manostat Inc.
flow meter, Gilmont Instruments
1000 mL graduated cylinder, Fisherbrand
gas dispersion tube, Ace Glass Inc. ASTM 70-100 μ

The pump was used to produce an adjustable airflow that was bubbled through the test solution in the graduated cylinder. This airflow was measured by the flow meter and delivered into the test solution through the gas dispersion tube. To better simulate an aeration basin and for consistency, the Ministatic™ pump was adjusted to maintain a constant air flow rate of 2000 mL/min. This rate simulated the agitation and turbulent conditions in an activated sludge aeration basin. Results were derived from the presence and amount of foam that built up in the graduated cylinder. The measurement of the amount of foam was somewhat subjective and was determined by a combination of the height and density of the foam. For improved objectivity between experimental runs, results were recorded by taking photographs of the tests at predetermined times for side by side comparisons at a later time.

RESULTS

First objective: To evaluate the relative effectiveness of the 31 antifoam products, thereby identifying the top performers.

For the initial screen, the 31 antifoam agents were tested using a 100 ppm antifoam concentration to control a 500 mg/L concentration of AFFF in a deionized water solution. The AFFF solution was prepared by diluting weighed amounts of AFFF, and the antifoamer was dispensed into the AFFF solution by micropipette and then mixed. The Light Water™ AFFF products used for this test were FC-203CF, FC-600, and FC-600F. Results were recorded at three and ten minutes. Antifoam products were rated for their effectiveness on a scale of "A" to "F", with "A" being the best and "F" for failing. This initial screen reduced the field of 31 to 12 effective antifoams.

During this screen, it was also determined that the antifoams were essentially equally effective on each of the three Light Water™ AFFF products. Therefore, all remaining tests were preformed using only FC-203CF.

The twelve antifoams that passed the first set of tests are:

Air Products	SURFYNOL™ DF-75 Defoamer
GE Silicones	Antifoam Emulsion AF-60 Antifoam Emulsion AF-72 Antifoam Emulsion AF-93 Antifoam Emulsion AF-9020
Henkel	Defoamer WB-209 Foammaster™ DS
Union Carbide	SAG 2001 Organosilicone Emulsion
Wacker Silicones	Antifoam Agent SE-36 Antifoam Agent SWS-214 Antifoam Emulsion SE-39 Antifoam Emulsion SRE

The next set of tests was completed using a revised procedure. Instead of each experiment having a set concentration of AFFF and antifoamer from beginning to end, the amount of antifoamer in the test solution remained constant while additions of Light Water™ AFFF stock solution were added at 10 minute intervals. The total volume of the test solution began at 100 mL with the antifoam concentration at 100 mg/L. The AFFF stock solution contained 2 grams of FC-203CF per liter of solution. While aerating the test

solution, 10 mL of AFFF stock solution was added at 10 minute intervals. The aeration rate used was 1100 mL/min instead of the 2000 mL/min used for the initial screen. This lower rate produced sufficient aeration and reduced the strain on the air pumps.

The additions of AFFF solution increased the concentration of AFFF while reducing the concentration of antifoamer. The additions of AFFF were continued until the antifoams could no longer control excessive foaming. Results were photographed at each interval. The photographs were used to identify the maximum additions of AFFF at which the antifoamer could suppress foaming to acceptable levels. The number of additions of AFFF, the starting volume, and the initial concentration of antifoamer were used to calculate the antifoam and AFFF concentrations. Based on the results of this test the field of twelve antifoams was reduced to the final field of the top nine.

The top nine antifoams are:

GE Silicones	Antifoam Emulsion AF-72 Antifoam Emulsion AF-93 Antifoam Emulsion AF-9020
Henkel	Defoamer WB-209 Foammaster™ DS
Union Carbide	SAG 2001 Organosilicone Emulsion
Wacker Silicones	Antifoam Agent SE-36 Antifoam Agent SWS-214 Antifoam Emulsion SRE

Second objective: To determine the concentrations of the top antifoams that can suppress foaming caused by AFFF concentrations greater than the recommended disposal concentrations.

The procedure used was the same procedure used to find the top nine antifoams with one exception. To more accurately simulate a wastewater treatment aeration basin, fresh sludge was used for all of the remaining tests. The sludge was obtained from Metropolitan Wastewater Treatment Plant in Saint Paul, Minnesota. During the weeks of testing, the MLSS of sludge ranged from 2.4 to 3.5 g/L, and the pH ranged from 6.1 to 7.9. Using this sludge, data were collected for each of the nine remaining antifoams at four initial antifoam concentrations. To get a range of data, four initial antifoam concentrations in the sludge were evaluated: 300, 600, 1000 and 5000 mg/L. The study found the maximum

concentration of FC-203CF at which each concentration of the top nine antifoams could suppress excessive foaming. Results are presented graphically in Figure 1 and tabulated at the end of the report.

If the AFFF concentration in the aeration basin is known, the appropriate amount of antifoamer can be determined from Figure 1. This information is useful for minimizing the amount of antifoam. This is an important consideration for reducing treatment cost and avoiding foaming caused by the addition of excessive antifoam. The possibility of foaming due to excessive antifoam can best be seen in the abnormal shape of the graph of Henkel WB-209 in Figure 1. The graph shows that above about 300 mg/L of WB-209 the antifoam becomes increasingly ineffective at suppressing AFFF foam and may actually cause foaming.

Third objective: To perform a cost analysis of the top nine antifoams.

The cost analysis was based on the price and the amount of antifoam needed to suppress excessive foaming caused by AFFF concentrations greater than 50 mg/L. The antifoam unit cost used in this analysis was the cost per pound when purchasing one to seven barrels. Antifoam prices are tabulated at the end of this report. Although the prices are subject to change and vary based on location and purchase volume, the graphs from this analysis can be useful when comparing relative cost of different products. Figure 2 illustrates the relationship between AFFF concentration and the cost to suppress foaming in 1000 gallons of sewage. Figure 3 is an expanded scale of the same data given in Figure 2.

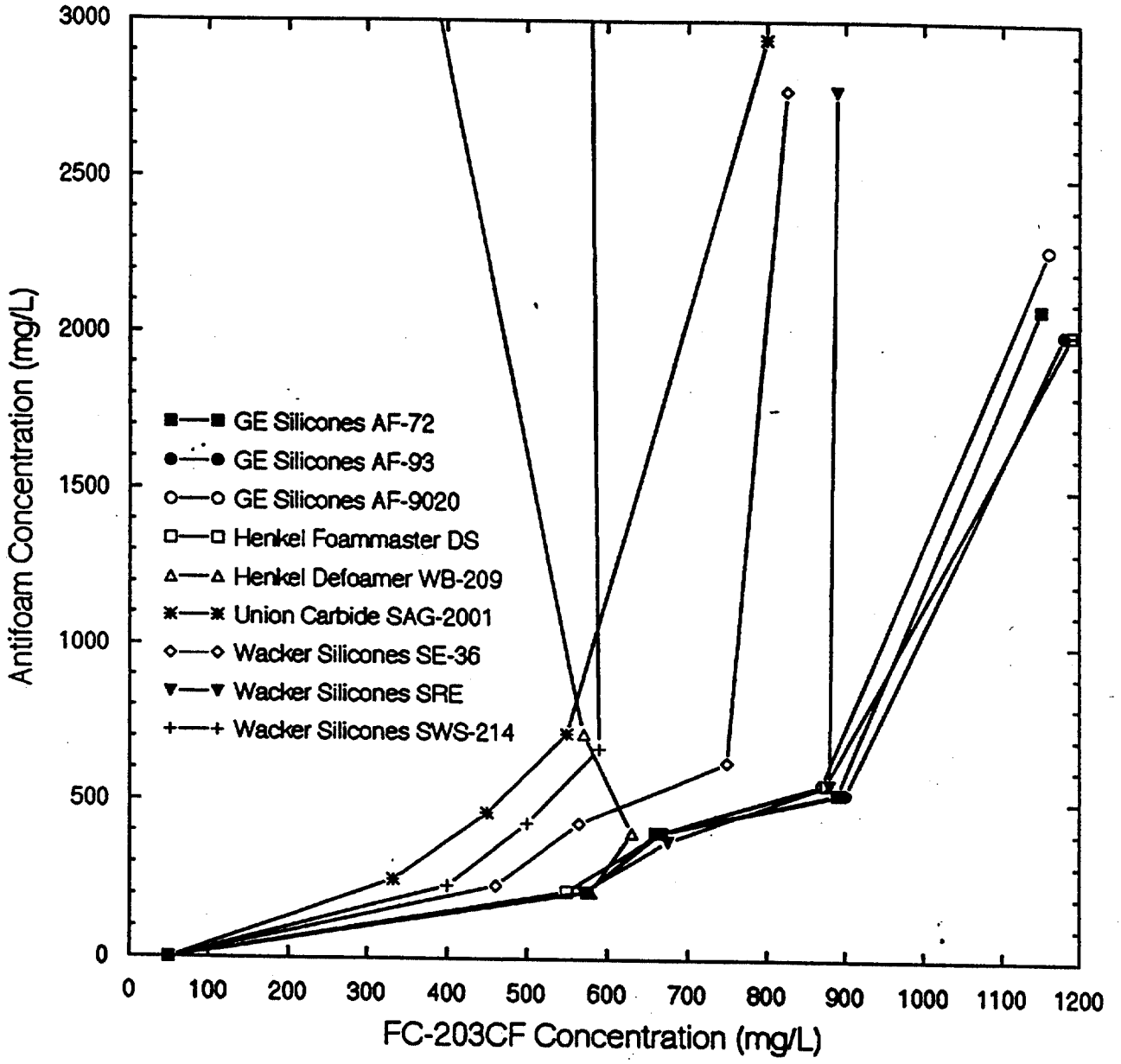


Figure 1. Antifoam concentration required to control foaming from FC-203CF.

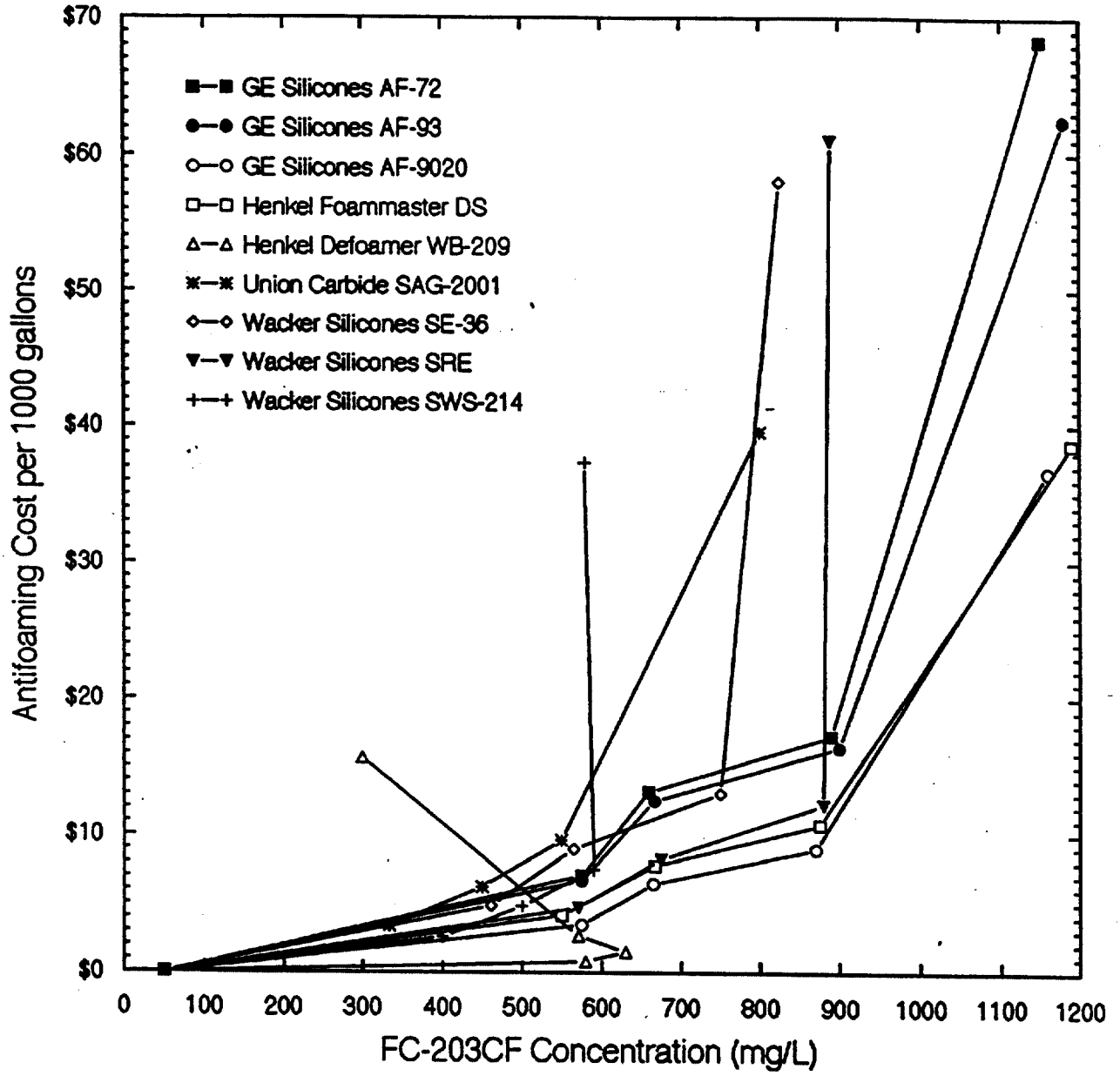


Figure 2. Cost comparison for antifoaming 1000 gallons of solution containing various concentrations of FC-203CF.

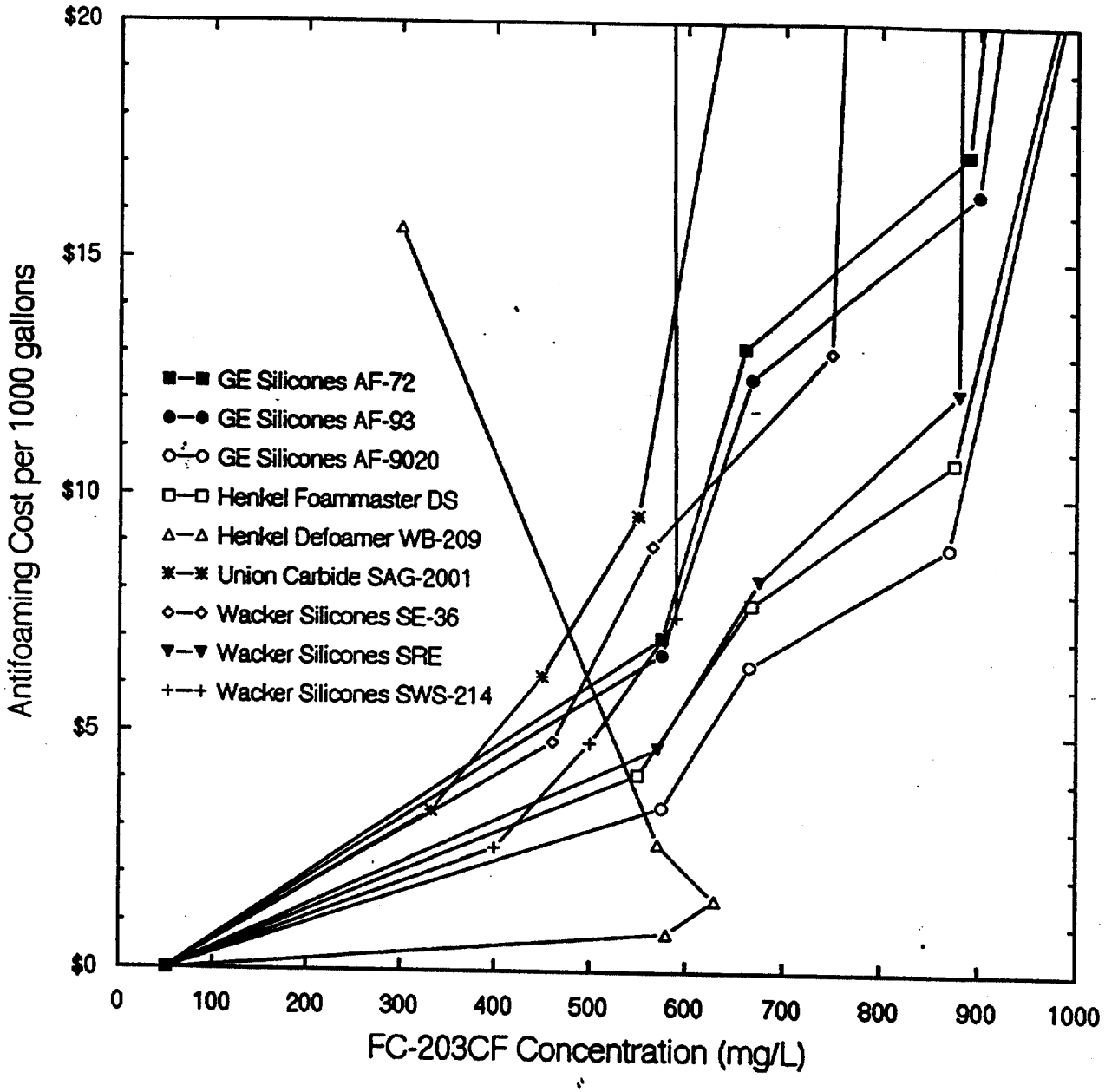


Figure 3. Cost comparison for antifoaming 1000 gallons of solution containing various concentrations of FC-203CF. (Expanded scale.)

CONCLUSIONS

In case of improper disposal of Light Water™ AFFF wastes or when the wastes must be discharged at a higher rate than optimally recommended, the most cost-effective antifoam agents are Henkel WB-209, GE Silicones AF-9020, Henkel Foammaster™ DS, and Wacker Silicones SRE. If the AFFF concentration is 600 mg/L or less, WB-209 is the most cost-effective antifoam. Note that when using WB-209 care should be taken not to use too much, because concentrations of WB-209 greater then about 300 mg/L have a greatly reduced efficacy and may actually cause foaming.

If the AFFF concentration is greater than 600 mg/L, or WB-209 is not readily available, GE Silicones AF-9020 is recommended. AF-9020 is effective over a much larger range than WB-209 and is the second most cost efficient antifoam. The second choice for a large range antifoam is Henkel Foammaster™ DS. Foammaster™ DS gave results comparable to the GE AF-9020 but was slightly more expensive. Another antifoam that preformed very well over a large range and was only moderately more expensive to use, was Wacker SRE. Although all four of the recommended antifoams are available for export, a consideration for SRE is that it is produced in Europe and therefore may be more readily available for the European market. The recommended concentrations to control concentrations of AFFF can be found for each of the recommended products by using Figure 1 or the data tabulated at the end of the report. Also, to find the approximate cost of suppressing foam at various AFFF concentrations can be found using Figure 2 or Figure 3 for an expanded scale.

REFERENCES

1. Environmental Laboratory Lab Request No. D1629.

2. Bikerman, J. J. *Foams* Springer-Verlag: New York 1973.

Antifoam concentration required to suppress AFFF at varying concentration for the top nine antifoam products. All concentrations are in mg/L.

GE Silicones AF-72	FC-203CF
50	0
575	214
660	400
890	526
1150	2083

GE Silicones AF-93	FC-203CF
50	0
575	214
667	400
900	526
1180	2000

GE Silicones AF-9020	FC-203CF
50	0
575	214
665	400
870	556
1160	2273

Henkel Foammaster™ DS	FC-203CF
50	0
550	214
667	400
875	556
1190	2000

Henkel WB-209	FC-203CF
50	0
580	214
630	400
571	714
300	4167

Union Carbide SAG 2001	FC-203CF
50	0
333	250
450	461
550	714
800	2941

Wacker SE-36	FC-203CF
50	0
461	231
565	429
750	625
825	2778

Wacker SRE	FC-203CF
50	0
571	214
675	375
880	556
889	2778

Wacker SWS-214	FC-203CF
50	0
400	231
500	429
590	667
580	3333

Antifoam prices used in the cost analysis. The prices were obtained by telephone from the manufacturers during the month of July, 1992.

GE Silicones	1-800-332-3390	
	Antifoam Emulsion AF-72	$3.93/lb
	Antifoam Emulsion AF-93	3.74
	Antifoam Emulsion AF-9020	1.93
Henkel	1-800-922-0605	
	Defoamer WB-209	0.45
	Foammaster™ DS	2.315
Union Carbide	1-800-523-5862	
	SAG 2001 Organosilicone Emulsion	1.61
Wacker Silicones	1-800-248-0063	
	Antifoam Agent SE-36	2.50
	Antifoam Agent SWS-214	1.34
	Antifoam Emulsion SRE	2.63

AFFF Foaming Study

FC 203

Diluents used:

Millipore Milli-Q water - ultra pure deionized water (Hardness <0.04 mg/L as $CaCO_3$)

Carbon-filtered Well Water - 3M Well #2, St. Paul, Mn (Hardness 255 mg/L as $CaCO_3$)

St Paul City Water - (Hardness 96 mg/L as $CaCO_3$)

- 5 mL / 15 mL centrifuge tube
- Shake 5 seconds
- No foam formed in any of the diluents

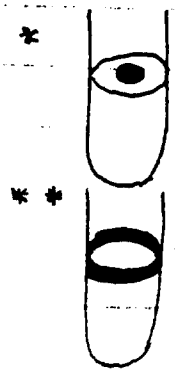
Chemicals tested

- FC-203 Lot 503 100 ppm solution (0.10 mL/L, verified by weight on Ohaus balance 0.10 mL = 0.1000
- FC-203CF Lot 501 100 ppm solution (0.10 mL/L)
- FC-95 Lot 171, 1.0% solution (tested at 100 ppm)
- Acrylic foamer (L4140 solids from F8362 Lot 502 (5/1/91), 2.75% solution (tested at 100 ppm)

1/27/94

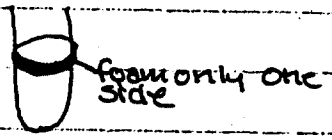
FC 203 Lot 503
Foam Formation

Concentration (ppm)	Diluents: CFW (Carbon-Filtered Well Water)	Milli-Q	St. Paul City Water
1	None formed	None formed	None formed
5	None formed	None formed	None formed
10	None formed	Slight disc* of foam in center 2 mm diameter persists for 2 minutes	None formed
25	Slight ring around tube formed 1 mm size persist for 1 min 2 sec	Disc of foam in center 6 mm diameter at 2.5 minutes reduced to half size, 3 mm at 5 min still persists at 3 mm size	Slight ring around tube formed 1 mm size, persist for 2 min 20 sec
50	1.5 mm layer of foam at 2 min 45 sec reduced to slight ring around tube, gone at 3 min	0.75 mm layer of foam, 1 min to moderate ring around tube, at 5 min slight ring persist	1.5 mm layer of foam at 30 sec. to 1.5 mm ring around tube at 5 min 1.5 mm ring persists
75	3 mm layer of foam, at 1 min to solid ring around tube 1.5 mm size, at 2 min 30 sec 5 min. 1.5 mm solid ring**	1.5 mm layer of foam, at 30 sec to solid ring around tube 1.5 mm size, at 5 min 1.5 mm ring persists**	1.5 mm layer of foam at 30 sec to solid ring around tube 1.5 mm size, at 5 min 1.5 mm ring persists**
100	3 mm layer of foam formed and persists passed 5 min	3 mm layer of foam formed and persists passed 5 min.	3 mm layer of foam formed and persists pass 5 min



FC 203CF Lot 501

Foam Formation

Concentration ppm	Diluent Milli-Q
1	None formed
5	None formed
10	None formed
25	~0.75mm slight ring formed, gone in 10 seconds
50	1.5mm layer of foam at 12 secs to moderate ring ~.75mm size, gone at 2min 10sec.
75	2mm layer of foam at 20 secs to 2mm ring of foam around tube at 5 min only half of ring remains 
100	3mm layer of foam formed and persists passed 5 min.

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Report Summary must be typewritten. Guidelines are on reverse side.

3M

Document Number:	Department Number: 0222	Project Number	Report Number (Place additional D.N.s in Abstract area)
To: D. L. BACON			Date Typed: 03/20/95
Author(s): R. D. HOWELL			Employee Number(s): 295864
Division/Department: ENVIRONMENTAL TECHNOLOGY & SERVICES	CC: 01	Loc: 089	Organization Code
Project Description: AFFF WASTE TREATMENT			
Report Title: PRECIPITATION AND ULTRAFILITRATION EXPERIMENTS WITH 3M FC-203CF			Period Covered: 1/94 - 12/94

Keywords

AFFF; WASTEWATER TREATMENT; LIGHTWATER BRAND; FLOCCULANT; SURFACTANT, FLUOROCHEMICAL; AQUEOUS FILM FORMING FOAM; COAGULANT; PRECIPITATION

Project Objective & Report Abstract

AFFF usage waste disposal is often a problem for 3M customers after actual fires, testing extinguishment systems or after training exercises. 3M recommends metered discharge of AFFF usage wastes to a municipal or industrial wastewater treatment system so that biodegradable components will be mineralized. Often, this is not practical because of the small capacity of the waste treatment system, regulatory limits, or because of excessive foaming. We have been investigating new methods for waste treatment, including surfactant precipitation with polycationic surfactants and inorganic salts (see Technical Report by Kimberly Bekes, 7/30/93) and ultrafiltration. This report includes results of precipitation and precipitation coupled with ultrafiltration. Both methods show promise as AFFF usage waste treatment processes, but the ultrafiltration method is much more costly both in terms of capital and operating expense. We are continuing to develop a solution to the AFFF disposal problem and we are seeking a third party wastewater treatment firm to perform a full-scale demonstration.

Report Type

- ☒ R & D Research and Development
- ☐ PILot Plant
- ☐ MANufacturing
- ☐ Management SUMmary
- ☐ TRP Trip or Field Report
- ☐ FACtory Experiment
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- ☐ ROI Record of Invention
- ☐ TECh. Service
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☒ Open Report and Summary ☐ Closed Report - Open Summary

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003091

Precipitation and Ultrafiltration

Experiments with 3M FC 203-CF

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Norman, OK 73072

December 8, 1994

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Experiments with 3M AFFF

Two types of experiments were performed with aqueous solutions of AFFF. The first type was precipitation of the fluorinated surfactants FC-95 and L4640 with an added cationic polyelectrolyte. The second type was ultrafiltration treatment with an excess concentration of the cationic polyelectrolyte to produce a treated water (permeate) stream with reduced fluorinated surfactant content and a concentrated waste stream containing fluorinated surfactants.

Precipitation Measurements

The hypothesis in the precipitation measurements was that, by adding a stoichiometric amount of a positively charged polymer to an aqueous solution of AFFF, negatively charged surfactant ions (including FC-95 and perhaps the amphoteric FC-1240) could be precipitated as an electrically neutral complex. Calculation suggested that the anionic charge equivalence in the original AFFF solution was ca. 0.003 M (when diluted to working concentration). Solutions were made up so that the polymer concentration would range from 0.001M to 0.005M in solution (initially) at a working concentration of AFFF (3 parts concentrate to 97 parts water). The cationic polymer used for these experiments was Merquat 100 which is a high molecular weight (ca. 200K Daltons) quaternary amine polymer (polydiallyldimethylammonium chloride). The polymer was a product of Calgon (Merck) and was supplied as a 40% by weight aqueous solution. The concentrations referred to above are in terms of monomolarity. For example, if the repeat unit of the polymer has a molecular fragment weight of 163, then a 1 M solution would consist of 163 grams of polymer in one liter of water. Table 1 below reports analytical results by Jim Wolter of 3M for the precipitate samples sent to 3M on 9-6-94

Table 1: Results of AFFF Precipitation with Cationic Polyelectrolyte

Sample #	[FC-95] ppm	[L4640] ppm	[Cat][1] M
0[2]	28.39	720.5	0
1	22.86	295.1	0.001
2	1.63	115.9	0.002
3	0.36	102.3	0.003
4	0.08	73.5	0.004
5	5.27	163.54	0.005

[1] Total (mono)molar concentration of cationic polymer in the solution. [2] Sample 0 represents the composition (in ppm of fluorinated components) of a blank sample containing only AFFF and deionized water. The total or formal concentrations of FC-95 and L4640 should be the same as this for samples 1-5.

The analytical results for AFFF fluorinated components in the supernatant solutions generally conform to expectations. There is a continuous decrease in FC-95 and L4640 concentrations in solution as the cationic polymer concentration in solution increases up to a point estimated as near charge equivalence. This decrease is presumed to occur through precipitation of a fraction of the polymer and anionic solution constituents as a neutral solid. At the highest concentration of Merquat 100 (sample #5), the solution concentrations of FC-95 and L4640 appear to increase. This increase is expected because an excess of cationic polymer will tend to keep the anionic constituents in solution. In previous work (with the samples sent to 3M on 3-20-94) utilizing a range of polymer concentrations from 0.003 to 0.03 M to investigate precipitation in AFFF solutions, it was found that no visible precipitate appeared in solutions with polymer concentrations above 0.006 M. This indicates that a charge excess of more than 100%, i.e., a polymer to AFFF anionic constituents ratio of 2:1 or higher, is sufficient to keep the AFFF fluorinated components in solution. On this basis, a concentration of 0.01 M polymer was chosen for use in the ultrafiltration experiments (see below).

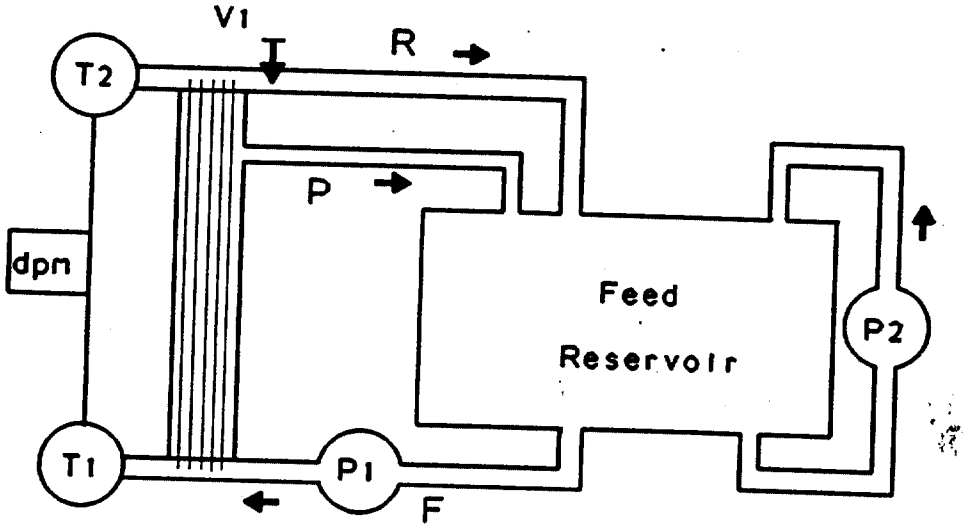
Conditions for the precipitation experiments were as follows: A stock solution of AFFF was made by delivering 3 mL of AFFF concentrate into a 50 mL volumetric flask. The flask was then filled to the mark with deionized water. This solution contains AFFF at twice the normal working concentration of 3 parts AFFF concentrate to 97 parts water. 5 ml of the AFFF stock solution was placed in each of six 20 mL screw cap vials. 5 mL of deionized water was added to vial #0 as a control sample. A stock solution of 0.01 M cationic polymer in water was prepared by diluting a weighed amount of polymer concentrate (40% by weight in water). Volumes of stock polymer of 1, 2, 3, 4, and 5 mL, respectively, were added to vials numbered 1 through 5 containing 5 mL of AFFF stock. Deionized water in volumes of 4, 3, 3, 1, and 0 mL, respectively, was added to vials 1 through 5, respectively. All vials then contained 10 mL of AFFF at a working concentration ratio of 3 parts AFFF to 97 parts water. Vials 1 through 5 also contained 0.001 to 0.005 M polymer in numerical sequence. All vials were shaken briefly by hand to mix the contents.

All samples showed visible precipitation of tan colored particles within at least a few minutes. Some qualitative observations are that the samples below and above the charge equivalence point appeared to produce more finely divided precipitates. Samples near the equivalence point (#3 and #4) produced some larger particulate matter on the order of 1-2 mm in diameter. These larger particles did not settle rapidly and appeared to adhere to the glass walls of the vial.

Ultrafiltration Measurements

The figure below gives a schematic of a simple ultrafiltration (UF) setup. The column depicted in this figure is a hollow fiber column. This type of column was used in the previous UF experiment on AFFF (3-20-94). For the current experimental results, a so-called spiral wound UF column was employed. The hollow fiber column is constructed of a number of membrane tubules potted with adhesive in a configuration quite similar to an ordinary laboratory condenser. The Feed UF solution flows into one end of the fiber lumen and Permeate liquid exits the fiber at right angles through the membrane pores. The remaining solution in the fiber (Retentate) exits at the top end of the fiber lumen. The spiral wound column consists of a dual-face membrane envelope concentrically wound with flow spacers separating each winding. Feed solution is pumped into one end of the column. Liquid (Permeate) which penetrates the membrane circulates in a spiral fashion to a center tube for withdrawal. The remaining solution which does not penetrate the membrane exits as Retentate at the column end opposite to the Feed entrance.

Figure 1. Hollow Fiber Ultrafiltration Apparatus



The feed reservoir is a 5 gallon polyethylene tank. The tank contents are internally recirculated at a 300 gal./hr. rate by pump P2. Feed solution is forced into the hollow fibers by pump P1, which has an accurately controlled pumping rate up to 2 L/min. The fibers are represented by the thin vertical lines. Retentate exits at the top of the column and permeate exits the fibers horizontally, flowing out through the tube marked P. The column is a Harp 18 inch, polysulfone membrane hollow fiber cartridge with 2 ft² area and a 10K mol. wt. cut-off (MWCO). T1 and T2 are pressure transducers measuring input and output (back) pressures, respectively, up to 50 psig for the column and displaying readings on the digital panel meter (dpm). Variable volume splitting of feed into retentate and permeate fractions is accomplished by opening or closing valve V1 which modifies column back pressure. Restriction of retentate flow by partially closing valve V1 increases the fraction of feed exiting horizontally (through the fiber walls) to the column as permeate. The apparatus is operated in steady state mode with both retentate and permeate being recycled to the feed reservoir. Sampling points for feed, retentate, and permeate flow are not shown. Withdrawal of samples for analysis leads to a slight decrease in feed concentration over the course of an experiment. In addition to the composition of the feed solution, the two interdependent factors of feed pumping rate and retentate flow restriction may be modified to change separation conditions.

The ultrafiltration experiment was initiated by mixing 240 mL of AFFF concentrate with 8L of aqueous cationic polymer solution at a concentration of 0.01 M. One sample from this mixture was taken to provide a reference point. Conditions were then adjusted in the UF system to produce ca. 30% of the flow through the column as permeate liquid with the remaining 70% existing as retentate. Samples of retentate and permeate liquids were taken at this point. Two further sets of samples of permeate and retentate were taken at conditions near 40 and 80% flow as permeate liquid, respectively. Total liquid flow through the column ranged from a high of ca. 600 mL/min at 30% permeate (Recovery) to a low of ca. 120 mL/min at 80% recovery. Table 2 gives analytical results for these several samples as well as the Recovery percentages and the applied pressure at the column entrance.

Table 2: Results of UF Experiment on AFFF with Cationic Polyelectrolyte

Sample #	[FC-95] P,ppm	[FC-95] R,ppm	[L4640] P,ppm	[L4640] R,ppm	Recov. %	Pres. psi
0*	--	39.7	--	1261.9	--	--
1	0.04	47.6	106.9	1497.5	31.7	26.4
2	1.12	48.6	125.8	1497.1	40.3	33.5
3	5.29	111.0	199.2	1419.4	82.7	41.8

* *Sample 0 represents the composition (in ppm of fluorinated components) of the original Feed solution prior to commencing the UF experiment. This sample was marked as F1 in the analytical results provided by Jim Wolter of 3M. Results are arbitrarily placed in the retentate (R) column for Sample 0 even though the composition of the feed solution is measured here.*

To examine the effectiveness of the UF process in removing fluorinated AFFF components we can look at the Recovery (percentage of liquid flow passing through the membrane as permeate) and the level of the components in this liquid. For sample #2, 40.3% of the feed liquid appears as permeate water. Relative to the composition of Sample #0 (Feed), the fraction of FC-95 remaining in the permeate is 1.12/39.7 or 0.028. This means that 97.2% of FC-95 has been removed from this liquid. Likewise, the fraction of L4640 remaining in the permeate for Sample #2 is 125.8/1261.9 or 0.0996. This means that 90% of L4640 has been removed from the permeate liquid, relative to the Feed under the conditions for Sample #2.

As the pressure is increased on the system and more liquid is forced through the membrane as permeate for Sample #3, the quality of the separation becomes somewhat worse. At this point, 82.7% of the feed liquid is being produced as

permeate. The removal of FC-95 from the permeate is 5.29/39.7 or 0.133 for fraction remaining (86.7% of FC-95 has been removed from the permeate). The removal of L4640 from the permeate is 199.2/1261.9 or 0.158 for fraction remaining (84.2% of L4640 has been removed from the permeate liquid). The removal percentages for FC-95 and L4640 are comparable at this point. However, the retentate concentration of L4640 (1419.4 ppm) in the retentate does not appear reasonable. Just as the retentate concentration of FC-95 increased for Sample #2 to Sample #3 (i.e., 48.6 to 111.0) the retentate concentration of L4640 should have increased by a substantial amount, instead of the slight decrease shown.

In summary, the removal of FC-95 and L4640 from aqueous solution by ultrafiltration with an excess of cationic polyelectrolyte appears to be reasonably successful. There are three specific points, however, which deserve comment:

1). It is disturbing that the analytical results show that the initial concentration in the Feed sample (Marked 0 in the Table above) for ultrafiltration is some 50% higher than the concentration of the AFFF stock solution which was used for the precipitation studies. The initial intent was to use the same concentration of AFFF in both studies; i.e., 3 parts by volume of AFFF contained in 100 volumes of solution. The only known difference in the two solutions is that the zeroth solution for precipitation contained only distilled water and AFFF while the zeroth (F1) solution for UF experimentation contained distilled water, cationic polyelectrolyte, and AFFF. If one assumes that the analytical results are correct, then it is likely that a repeat of the UF experiment (at the lower AFFF concentrations apparent in the precipitation experiment) would show improved results. That is, the removal of AFFF fluorinated components should be better than the results shown in Table 2 above.

2). With reference to Table 2 above, it is in principle possible to check the mass balance of a particular component in the system. Because the total flow in the UF system is recycled (both permeate and retentate fluids are returned to the feed tank), the following relationship should apply:

$$[\text{Feed}] = \text{Recovery}\,[\text{Permeate}] + (1\text{-Recovery})\,[\text{Retentate}] \qquad \{1\}$$

where [Feed], [Permeate], and [Retentate] are analytical concentrations of a particular component in the feed, permeate, and retentate solutions, respectively, and Recovery is the fraction of the total liquid Feed in the system which appears as permeate. Taking data from Sample #0 (Feed concentration) and for Sample #1 above for FC-95, the following relationship should be an identity:

$$[39.7] = 0.317\,[0.04] + 0.683\,[47.6]$$

$$\text{however, } [39.7] \neq [32.5]$$

3099

(295a & 2193a) + 003097 2
3099