

TECHNICAL REPORT SUMMARY

Date
8/31/81

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

(Important - If report is printed on both sides of paper, send two copies to TCC.)

Division Environmental Laboratory (EE & PC)		Dept. Number 0535
Project Commercial Chemicals		Project Number 9970012600
Report Title Chemical Oxygen Demand of CS-2151		Report Number 057
To D. R. Ricker, Commercial Chemicals Division, 53-4N		
Author(s) Eric A. Reiner, Environmental Laboratory/EE & PC, 21-2W-5		Employee Number(s) 47816
Notebook Reference None (See Environmental Lab Request #6260S)		No. of Pages Including Coversheet
SECURITY ►	☒ Open (Company Confidential)	☐ Closed (Special Authorization)
	3M CHEMICAL REGISTRY ►	
	New Chemicals Reported ☐ Yes ☒ No	

KEYWORDS:
(Select terms from 3M
Thesaurus. Suggest other
applicable terms.)

Chemical
Oxygen Demand
(COD)
Degradation
Oxidation
EE&PC Div.
Fluorochemical
Surfactant

CURRENT OBJECTIVE:

To determine the chemical oxygen demand of CS-2151

REPORT ABSTRACT: (200-250 words) This abstract information is distributed by the Technical Communications Center alert 3M'ers to Company R&D. It is Company confidential material.

The chemical oxygen demand (COD) of CS-2151 was determined in accordance with the Standard Methods reflux method and according to the Standard Ampule COD Method of Oceanography International. The reflux protocol gave a COD of 66,000 mg/kg. The ample method gave a COD of 81,000 mg/kg. Experience with a wide variety of perfluorinated organics has shown that the perfluorinated portions are not oxidized under the conditions of the COD test. The potassium salt of the perfluorinated portion of the subject material was previously tested and showed no chemical oxygen demand. Thus the observed COD appears to be due to the diethanol amine portion of the chemical. The theoretical oxygen demand of CS-2151, assuming complete oxidation of only the diethanolamine portion is 77,000 mg/kg.

Information Liaison
Initials: mc

Introduction

The chemical oxygen demand (COD) test measures the oxygen equivalent of a chemical under strong oxidizing conditions. When compared to theoretical oxygen demand, COD can give an indication of the stability of the component to chemical oxidation. Since most organic compounds are completely degraded in the COD test, this test is frequently used for comparison with the biochemical oxygen demand (BOD) test. For those materials degraded by the COD test, the BOD/COD ratio gives an indication of the completeness of biodegradation.

This report describes the test performed on CS-2151 to evaluate its COD. It provides the data generated in this study and compares the chemical oxygen demand to the theoretical oxygen demand.

Methods and Materials

The 3M Environmental Lab received the test substance on 11/4/80. The sample was a light, yellow liquid. It was reported to contain 25% solids in water. Solid portion of this product is designated CS-2070.

Wade Schiel performed the chemical oxygen demand test in accordance with the standard Environmental Laboratory Protocol (attached) this protocol is based on the Standard Methods chemical oxygen demand procedure. The COD was also measured according to the Oceanography International Standard Ampule COD Method (copy attached). For both procedures, COD's were also run in parallel on potassium hydrogen phthalate (KHP) reference samples.

Results and Discussion

Duplicate determinations by the reflux method gave COD for CS-2151 of 67,000 mg/kg and 66,000 mg/kg. A potassium hydrogen phthalate standard run in parallel with a theoretical COD of 405 mg/l was determined to have a COD of 392 mg/l. Duplicate COD measurements on CS-2151 by the ampule protocol were both 81,000 mg/kg. The parallel standard with a theoretical COD of 176 mg/l was determined to have a COD of 170 mg/l.

Previous studies on FC-98, which is the same fluorochemical except that potassium replaces the diethanolamine, showed that FC-98 had no chemical oxygen demand. Therefore, it appears that the chemical oxygen demand of CS-2151 is due only to oxidation of the diethanolamine portion of the molecule. The theoretical COD of the CS-2151 solids (CS-2070), assuming its fluorochemical portion and NH_3 are not oxidized, is 307,000 mg/kg. Thus, the theoretical COD of CS-2151, which is a 25% aqueous solution is 77,000 mg/kg.

Conclusion

The measured COD values are consistent with the hypothesis that only the diethanolamine portion of the molecule is degraded in the COD test.

Lab Req. No. 6260 (file)

Environmental Lab Data Sheet

Date analyzed 12/12/80

AMPULE

Analyst W. G. Schind

C.O.D.

OCEANOGRAPHY INTERNATIONAL
COD PROCEDURE

Spec. 20 No. 1-600nm

Blank % T 100

red bulb & red filter

[illegible]

TECHNICAL REPORT SUMMARY

Date
8/31/81

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

(Important - If report is printed on both sides of paper, send two copies to TCC.)

Division Environmental Laboratory (EE & PC)		Dept. Number 0535
Project Commercial Chemicals Division		Project Number 9970012600
Report Title Biodegradation of CS-2151 (CS-2070)		Report Number 058
To Don Ricker, Commercial Chemicals Division, 53-4N		
Author(s) Eric A. Reiner, Environmental Laboratory(EE & PC), 21-2W-5		Employee Number(s) 47816
Notebook Reference None (see Lab Request #6260S)		No. of Pages Including Coversheet
SECURITY ► ☒ Open (Company Confidential) ☐ Closed (Special Authorization)	3M CHEMICAL REGISTRY ►	New Chemicals Reported ☐ Yes ☒ No

KEYWORDS:
(Select terms from 3M
Thesaurus. Suggest other
applicable terms.)

Biodegradation
EE&PC Div.
(Env. Lab)
BOD
Fluorochemical
Surfactant

CURRENT OBJECTIVE:

To evaluate the susceptibility of CS-2151 to
biodegradation.

REPORT ABSTRACT: (200-250 words) This abstract information is distributed by the Technical Communications Center to alert 3M'ers to Company R&D. It is Company confidential material.

A 20-day biochemical oxygen demand (BOD₂₀) test using concentrations of CS-2151 ranging from 68 to 540 mg/l gave a BOD₂₀ for CS-2151 of 69,400 mg/kg (278,000 mg/kg for CS-2070). Oxygen demand is presumed to be due to the diethanolamine portion of the molecule since a previously conducted BOD₂₀ test on the sodium salt of the fluorochemical portion of CS-2151 showed no oxygen uptake. The BOD₂₀ was equivalent to 90% of the theoretical oxygen demand for the diethanolamine portion of the molecule assuming its complete conversion to CO₂, H₂O, and NH₃. The possibility of partial degradation of the fluorochemical portion of CS-2151 cannot be eliminated by this testing. However, experience with a wide variety of similar compound indicates that the perfluorinated portion of this molecule will not biodegrade.

Information Liaison
Initials: WMC

BIOCHEMICAL OXYGEN DEMAND OF CS-2151

Introduction

The objective of this study was to obtain an indication of the biodegradability of CS-2151, which is the diethanolamine salt of perfluoro ethylcyclohexane sulfonic acid. Its intended use is as a surfactant for mist suppression in anodizing, electroplating, and etching baths. As a result of these uses, it will be dragged out with parts and will enter the environment with the water used to rinse these parts. When used in strong-acid, etching systems, the ethanolamine portion of the molecule would likely be partially or completely oxidized prior to its entry into the environment.

Methods and Materials

The Environmental Laboratory received the test sample on 11/4/80. The sample was a light, yellow liquid. It was reported to contain 25% solids in water. W. A. Schiel and M. Roberts performed the 5, 10, and 20-day biochemical oxygen tests according to the attached standard Environmental Laboratory protocol. In this testing, four concentrations were used ranging from 68 to 540 mg of CS-2151 per liter of BOD dilution water. There was little oxygen depletion during the first five days, but at 10 and 20 days only the BOD bottle containing 68 mg/l of CS-2151 contained greater than 0.5 mg/l of oxygen residual. The oxygen depletion due to the samples is shown in Table 1 below:

Table 1 - Oxygen depletion due to CS-2151 (i.e., oxygen depletion in sample bottle corrected for oxygen depletion due to seed and water).

CS-2151 Conc.(mg/l)	Oxygen Depletion Due to Sample(mg/l)		
	Day 5	Day 10	Day 20
68	0.06	4.17	4.69
140	0.16	>7.65	--
270	0.20	>7.65	--
540	0.31	>7.6	--

When there is less than 2 mg/l oxygen depletion, the Environmental Laboratory Protocol calls for reporting BOD as less than the BOD value which would have been calculated if the highest test material concentration had shown an oxygen depletion of 2 mg/l. The 5-day BOD was thus reported to be less than 3,700 mg/kg. The BOD at 5 and 10 days was calculated based on the oxygen depletion of the 68 mg/l culture in accordance with the attached protocol. The reported BOD values are, therefore:

BOD₅ - <3,700 mg/kg

BOD₁₀ - 62,000 mg/kg

BOD₂₀ - 69,000 mg/kg

BOD tests have also been done on the potassium salt of perfluoro ethylcyclohexane sulfonic acid. The 20-day BOD was found to be less than 3,800 mg/l. These results indicate that under these conditions that the perfluorinated portion of the molecule is unlikely to degrade. Assuming no nitrification and no biodegradation of perfluorinated portion of the molecule, the theoretical biochemical oxygen demand would be 77,000 mg/kg (307 mg/kg for the 100% solids material). The observed BOD value was, thus, 90% of the theoretical assuming that only the diethanolamine was biodegraded. Since BOD values rarely reach theoretical oxygen demand, these results indicate essentially complete degradation of the diethanolamine portion of the molecule.

Discussion

The results of this testing when evaluated in conjunction with BOD results on the potassium salt of the fluorochemical portion of this molecule indicate that the fluorochemical portion of the molecule would not biodegrade under the test conditions, while the diethanolamine portion would be completely degraded. The 20-day biochemical oxygen demand test (BOD₂₀) is a test for ready biodegradability. This test alone cannot exclude the possibility that the fluorochemical portion of the molecule may biodegrade after longer periods of acclimation or under more favorable conditions. Such degradation is, however, very unlikely. Literature studies conducted on an ongoing basis for several years have not uncovered articles that describe the biodegradation of a completely perfluorinated organic material. The 3M Environmental Laboratory has also not seen the biodegradation of any 3M perfluorinated organic materials.

Sample Description		11-18-80 W.G. Schul CS2151, LIQUID FORM
Initial Dilution	2.03 grams of Sample diluted to 100 ml with DI water	
Initial Dilution Factor	(Dilution factor = 1 if undiluted)	

[illegible]

Notes:

1. Conc. = Concentration of sample (ml/l or mg/l) in BOD bottles.
2. Sample Size = ml or g of sample or diluted sample added to BOD Bottle.

[illegible]

Sample Description	
11-18-80 W.G. Schul CS2151, LIQUID FORM	
Initial Dilution	2.03 grams of Sample diluted to 100 ml with DI water
Initial Dilution Factor	(Dilution factor = 1 if undiluted)

[illegible]

Comments

SAVE BOTTLES IF THERE IS ANY
SIGNS OF DEGRADATION.

* After taken the 10-day DO readings, the DO of each
of these bottles was raised to 4.4.

Sample Description		11-18-80 W.A. Schul CS2151, LIQUID FORM
Initial Dilution	2.03 grams	of Sample diluted to 100 ml with DI water
Initial Dilution Factor	(Dilution factor = 1 if undiluted)	

[illegible]

Comments

SAVE BOTTLES IF THERE IS ANY
SIGNS OF DEGRADATION.

After the 20-day readings, all of the dilutions were poured into a clean glass jug (1 gal). The jug was shaken vigorously for ~15 sec. to aerate and then incubated @ $20 \pm 1^\circ\text{C}$.

Environmental Laboratory
BOD Work Sheet - Blanks,
Controls, and Standards

6262 S
6259 S
6260 S
6261 S
6258 S
6263 S

3M

Lab Request No. 6210 S (original)		BOD Run No. 8-37	
Analyst H. A. Scheil, H. Roberts		Date Started 11-14-80	5 - Day BOD Readings
Seed Type & Source State Sewage Chemolite	Seed Concentration 6 ml/l	Analyst M. Roberts	Date 11/17/80

Nonseeded Dilution - Water Blank

Bottle No.	Initial D.O. (A ₁)	Present D.O. (A ₂)	D.O. Depletion (A ₁ - A ₂)	Average D.O. Depletion ($\bar{A}_1 - \bar{A}_2$)
69	8.80	8.80	0.00	0.05
73	8.80	8.75	0.05	
22	8.85	8.75	0.10	

Seeded Dilution - Water Blank (optional)

Bottle No.	Initial D.O. (C ₁)	Present D.O. (C ₂)	D.O. Depletion (C ₁ - C ₂)	Average D.O. Depletion ($\bar{C}_1 - \bar{C}_2$)
55	8.85	8.75	0.10	0.08
25	8.80	8.70	0.10	
71	8.80	8.75	0.05	

Seed Controls

Bottle No.	Sample Size	Initial D.O. (B ₁)	Present D.O. (B ₂)	D.O. Depletion (B ₁ - B ₂)
839	20	8.70	7.65	1.05
78	40	8.50	6.40	2.10
21	80	8.00	3.75	4.25
3	160	7.20	<0.5	

Glucose - Glutamic Acid Standard

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	Total D.O. Depletion (D ₁ - D ₂)	Depletion Due To Standard	5 - Day BOD		5 Average Day BOD	
					#4 #5	#4 #5	#4 #5	#4 #5	
99	3.0	8.70	6.45	2.25	2.11 2.17	211 217	211 217	211 217	
68	5.0	8.80	5.05	3.75	3.61 3.67	216 220	216 220	216 220	
21	7.0	8.70	3.35	5.35	5.21 5.27	220 223	220 223	220 223	

Potassium Hydrogen Phthalate Standard (optional) (LR# 6260-2)

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	Total D.O. Depletion (D ₁ - D ₂)	Depletion Due To Standard	5 - Day BOD		5 Average Day BOD	
					#4 #5	#4 #5	#4 #5	#4 #5	
88	3.0	8.75	5.60	3.15	3.01 3.07	301 307	301 307	301 307	
13	5.0	8.75	3.55	5.20	5.06 5.12	304 307	304 307	304 307	
54 (LR)	7.0	8.75	1.30	7.45	7.31 7.37	313 316	313 316	313 316	

Other Requests - 6262 S
6259 S
6260 S
6261 S
6258 S
6263 S

Environmental Laboratory
BOD Work Sheet - Blanks,
Controls, and Standards

3M

Lab Request No. $\blacklozenge$ 6210 S (original)		BOD Run No. $\blacklozenge$ 8-37	
Analyst W.A. Schmit, H. Roberts		Date Started 11-14-80	
Seed Type & Source Stale Sewage - Chemolite		Seed Concentration 6 ml/l	
Analyst W.A. Schmit		Date 11-24-80	

Nonseeded Dilution - Water Blank

Bottle No.	Initial D.O. (A ₁)	Present D.O. (A ₂)	D.O. Depletion (A ₁ - A ₂)	Average D.O. Depletion ($\bar{A}_1 - \bar{A}_2$)
69	8.80	8.30	0.50	0.517
73	8.80	8.30	0.50	
22	8.85	8.30	0.55	

Seeded Dilution - Water Blank (optional)

Bottle No.	Initial D.O. (C ₁)	Present D.O. (C ₂)	D.O. Depletion (C ₁ - C ₂)	Average D.O. Depletion ($\bar{C}_1 - \bar{C}_2$)
55	8.95	8.25	0.60	0.567
25	8.80	8.25	0.55	
71	8.80	8.25	0.55	

Seed Controls

Bottle No.	Sample Size	Initial D.O. (B ₁)	Present D.O. (B ₂)	D.O. Depletion (B ₁ - B ₂)
839	20	8.70	7.40	1.30
78	40	8.50	5.65	2.85
21	80	8.00	2.30	5.70
3	160	7.20	—	—

Glucose - Glutamic Acid Standard

207 $\pm$ 20 mg/l

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	Total D.O. Depletion (D ₁ - D ₂)	Depletion Due To Standard	$\frac{10}{\text{BOD}}$ - Day		Average $\frac{10}{\text{BOD}}$ - Day
99	3.0	8.70	5.90	2.80	2.17	2.24	217	224
68	5.0	8.80	4.75	4.05	3.43	3.49	206	210
21	7.0	8.70	reading revised was 4.1				mg/l	mg/l

Potassium Hydrogen Phthalate Standard (optional) (LR# 6260-2)

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	Total D.O. Depletion (D ₁ - D ₂)	Depletion Due To Standard	$\frac{10}{\text{BOD}}$ - Day		Average $\frac{10}{\text{BOD}}$ - Day
88	3.0	8.75	5.20	3.55	2.92	2.99	292	299
13	5.0	8.75	3.05	5.70	5.08	5.14	305	309
54 (10)	7.0	8.75	0.90	7.85	7.23	7.30	310	313

Environmental Laboratory
BOD Work Sheet - Blanks,
Controls, and Standards

Other requests - 6268.5
0258.5
6260.5
6201.8
6258.5
6268.5

3M

Lab Request No. 6210 S (original)		BOD Run No. 8-37	
Analyst W.A. Schiel, H. Roberts		Date Started 11-14-80	
Seed Type & Source Stale Sewage - Chemelite		Seed Concentration 6 ml/l	
Analyst W.A. Schiel		Date 12-4-80	

Nonseeded Dilution - Water Blank

Bottle No.	Initial D.O. (A ₁)	Present D.O. (A ₂)	D.O. Depletion (A ₁ - A ₂)	Average D.O. Depletion (A ₁ - A ₂)
69	8.80	8.10	0.70	0.70
73	8.80	8.10	0.70	
22	8.85	8.15	0.70	

Seeded Dilution - Water Blank (optional)

Bottle No.	Initial D.O. (C ₁)	Present D.O. (C ₂)	D.O. Depletion (C ₁ - C ₂)	Average D.O. Depletion (C ₁ - C ₂)
55	8.85	7.80	1.05	0.883
25	8.80	8.00	0.80	
71	8.80	8.00	0.80	

Seed Controls

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	D.O. Depletion (D ₁ - D ₂)
839	20	8.70	2.90	5.80 ← <i>used for calc</i>
78	40	8.50	< 0.5	
21	80	8.00	< 0.5	
3	160	7.20		

Glucose - Glutamic Acid Standard

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	Total D.O. Depletion (D ₁ - D ₂)	Depletion Due To Standard	207 ± 20 mg/l 20 - Day BOD		Average 20 - Day BOD	
99	3.0	8.70	5.50	3.20	2.05	2.33	205	233	*4
68	5.0	8.80	2.40	6.40	5.26	5.53	316	332	250
21	7.0	8.70	2.00	6.70	5.57	5.84	235	247	mg/l

Potassium Hydrogen Phthalate Standard (optional) (LR# 6260-2)

Bottle No.	Sample Size	Initial D.O. (D ₁)	Present D.O. (D ₂)	Total D.O. Depletion (D ₁ - D ₂)	Depletion Due To Standard	20 - Day BOD		Average 20 - Day BOD	
88	3.0	8.75	3.20	5.55	4.40	4.68	440	468	
13	5.0	8.75	2.25	6.50	5.36	5.63	322	338	360
54	7.0	8.75	—	—	—	—	—	—	400