SUMMARY FOR WORK PERFORMED FOR THE GERMAN GOVERNMENT AGENCY FOR MILITARY TECHNOLOGY AND PROCUREMENT ON FIRE EXTINGUISHING FOAM COMPOUNDS FROM MULTIPLE COMPANIES

TEST SUBSTANCE

Identity: A mixture containing Perfluorooctanesulfonate, which may also be referred to as PFOS, FC-95, or as a component of FC-206. (1-Octanesulfonic acid) (CAS # 2795-39-3).

Remarks: The 3M production lot number was not noted. The test sample is FC-206. Current information indicates it is a mixture of 0.67% PFOS, 17.5% diethylene glycol butyl ether, 78.91% water, 1.33% Hydroxy foamer, 1% sodium octyl sulfate, 0.04% sodium lauryl sulfate, 0.5% polyoxyethylene monoctylphenyl ether, and 0.05% tolytriazole.

The following summary applies to a study done by a third party (Dr. H. Hellman and D. Muller) for the German Government Agency For Military Technology and Procurement for purposes of comparing the environmental properties of foam extinguishing agents from multiple companies, including 3M's FC-206. Data may not accurately reflect the environmental properties of the fluorochemical proportion of the test sample.

STUDIES

Zinc, iron, and copper content; surface tension; Chemical Oxygen Demand; 5-Day Biochemical Oxygen Demand; Toxicity to Fish (species not given); Toxicity to Water flea (Daphnia magna); Toxicity to Algae (species not given); Bacteria inhibition (species not given)

Report date: 1977

METHODS:

Chemical Oxygen Demand was measured using potassium permanganate and potassium dichromate.

Biochemical Oxygen Demand evaluated using a Total Organic Carbon degradation test developed by the Bundesanstalt fur Gewasserkunde.

Toxicity to Fish was evaluated according to the German standard process for water testing (DEV) L 15

Toxicity to Daphnia was evaluated according to the German standard process for water testing (DEV) L 11
Toxicity to Algae was evaluated according to the German standard process for water testing (DEV) L 12

The method for evaluating bacterial inhibition was not described.

RESULTS

<table>
<thead>
<tr>
<th></th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish LC$_{50}$</td>
<td>&gt;1000 mg/L</td>
</tr>
<tr>
<td>Daphnia EC$_{50}$</td>
<td>&gt;250 mg/L</td>
</tr>
<tr>
<td>Algae EC$_{50}$</td>
<td>&gt;250 mg/L</td>
</tr>
<tr>
<td>Bacteria inhibition</td>
<td>Inhibited</td>
</tr>
<tr>
<td>BOD21/COD</td>
<td>~7%</td>
</tr>
</tbody>
</table>

Remarks: The above toxicity data did not have test duration information.

DATA QUALITY

Reliability: Klimisch ranking = 4. All study values come from a summary list only. No raw data or method documentation was available. The study summary failed to disclose duration of toxicity testing. It is not clear why such low biodegradability was observed when the products contain materials that are known to readily biodegrade. The sample purity was not properly characterized and the study lacks analytical confirmation of the amount of fluorochemical proportion in the solution.

OTHER

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

Last changed: 6/26/00
Dr. H. Hellman and D. Muler, "Environmental Impact of Fire Extinguishing Foam Compounds." The study was carried out by the West German Department of Water Technology for the West German Agency for Military Technology and Procurement. (Translated by G. Dierssen, March 1, 1980).

This report compares the environmental acceptability of 6 AFFF Agents including FC 3017 (identified in the report as FC-200, freeze protected), FC-206, and FC-200. The researchers measured biodegradability, aquatic toxicity, heavy metal concentration, and surface tension. The report recommends avoiding use of the 3M AFFF products since all were difficult to biodegrade, but the biodegradation results and their interpretation are questionable. Comparisons of BOD₅ and COD showed that the 3M products were more readily degraded than the competitive products, yet the authors chose to give more credence to tests measuring dissolved total organic carbon (TOC) concentration over a 21 day period. These tests gave results that were inconsistent with the BOD results. In these tests 3M products inexplicably did not degrade.
Compliment to Report of
Bundesanstalt für Gewässerkunde
10. April 1979
-Wlb/340.22/2596

Environmental Impact of
Fire Extinguishing Foam Compounds.

Study carried out for
Bundesamt für Wehrtechnik und Beschaffung
(Government Agency for Military Technology and Procurement)


Reporter:
Oberregierungsrat Dr. H. Hellmann
Oberregierungsrat Dr. Müller

Koblenz 1979
Table of Contents

1. Introduction 3
2. Definition of Problem and Task 4
3. Test Results 5
   3.1 Physical Chemical Tests 5
   3.2 Tests for Biochemical Degradation 7
   3.3 Toxicology Tests 12
4. Evaluation of Results and Conclusion 15
5. Recommendations for Technical Ordering Specifications 18
6. Conclusion 19

Enclosures:

- Literature list
- Additions
1. INTRODUCTION

For fire extinguishing foam compounds one can distinguish six application regions:

1. General application (local fire protection)
2. Solvent industry
3. Fighting of carbonhydride fires for instance in refineries (closed systems)
4. Electrical equipment, high voltage
5. Applications in airports.
6. Applications on ships.

In the present study it will appear that airport fires take on preferred importance (1). It is obvious, that a few seconds in time can make important difference for saving human lives, and that the question of environmental endangering especially of waters and streams does assume some what less importance. But water safety need not be completely overlooked especially because most of the actually used fire extinguishing compounds are used in training.

The Bundesanstalt fur Gewasserkunde (Dept. of Water Technology) in 1975 got the task from the Ministeriums fur Ernährung, Landwirtschaft und Forsten (Ministry of Food Agriculture and Forestry of Nordrhein-Westfalen) to evaluate the impact of foam extinguishing compounds on the water quality. Thirty eight foam extinguishing compounds from 8 suppliers were evaluated chemically, physically and biochemically for possible endangering of water. Different brands did vary in degradation and toxicity. Especially the 5% foam extinguishing solutions used can result in the following damage:
- Poisoning of natural water purification (in streams)
- Poisoning or damage to fish and fish food animals.
- Reduction of oxygen contact by metabolic processes (surface or ground water)
- Reduction of water quality by organic compounds (general)
- Undesirable reduction processes in the ground-water.

This report was published in parts 1 and 2 and received attention from the parties involved, such as the manufacturers of foam extinguishing compounds and the authorities responsible for water purity. Among others, these considerations were taken into account in the DIN-standards.

2. DEFINITION OF PROBLEM AND TASK

After several discourses in 1977 between representatives of the Bundesamt für Wehrtechnik and Beschaffung and the Bundesanstalt für Gewässerkunde (BFG), the BFG was authorized on Oct. 12, 1977 to carry out a special study. This study should only cover the products used by the Bundeswehr (W. German military) and also products which are considered for possible new introduction.

As a first objective, the environmental influence of the following six extinguishing compounds should be determined:
The two types of Light-Water are offered as being "especially safe to the environment" (According to BWB). Light Water FC 200 is reported to be out of production, but should be evaluated for comparison. The test for environmental impact should, if possible, be tested for 5% solutions as used (for Light Water 6%) and encompass the following parameters:

- Surface tension activity
- Toxicity
- Biochemical degradation
- Content of heavy metals
- Flame point.

The final report should also contain recommendations for the technical procurement specifications (TL).

The final report was scheduled for completion in Sept 1978. Due to sickness of one of the investigators it was delayed for some months.
3. TEST RESULTS

3.1 Physical-Chemical Tests

The first test result gives the heavy metal content which was determined by X-ray fluorescence.

Evaluating the figures of Table 1 listing the heavy metal content, the two compounds Fluorprotein (No 1) and Protein foam compound (No 5) stand out. For Fluorprotein the zinc and iron content of the application solution (mixtures) with 40 and 55 mg/l respectively, is relatively high. For the second compound the iron content of 50 mg/l stands out. All other heavy metal concentrations such as the especially recorded levels for copper are unimportant.

Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Original Products</th>
<th>5 % Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>780</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>970</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>9</td>
</tr>
</tbody>
</table>

1) Determined by Dipl. Chem. U. Schleichert
When the flame point is determined, the water content of the sample must be considered. Flame points above 100°C, the boiling point of water, could not be determined. As could be expected none of the tested samples did have a flame point below 100°C. It should be obvious that none of the products would contain flammable solvents.

The surface, or interphase tensions can be seen from Table 2. The surface tension water/air generally drops some for concentrations from 50 mg/l to 500 mg/l. The surface tension is least affected for No5 (Protein-foam extinguisher), most affected for two Light-Water types of FC-206-type. The reason for this is found in the chemical composition of the extinguishing compounds. Protein foam agents can be expected to be generally inactive to the water/air interphase; while tensides and also so called "synthetic" products are interphase active. The interphase activity is less a product specific, but rather a group specific characteristic.

Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Interphase activity at 20°C (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>62</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>67</td>
</tr>
</tbody>
</table>

2) Determined according to Abel-Pensky in closed vessel; DIN 51 755, Ed. 966
3) Interphase-Tensiometer, according to Nooy, Firm. A. Kross, Hamburg
3.2 Test for Biochemical Degradation

To evaluate the water pollution characteristics of compounds, it is of interest to sum up the chemical parameters, potassium permanganate and oxygen demands \( C_{\text{COD}} \) and potassium dichromate uptake, \( \text{CSB} \). The biochemical oxygen uptake \( \text{BSB} \), \( \text{COD} \) of DEV (4)) can be used especially in combination with CSB to preliminarily evaluate the degradation. When the CSB analytical test gives reliable results (this, for instance, is not always true when hydrophobic compounds are being tested) one must consider positive result derived from the CSB/BSB ratio as useful, while negative results can not be counted, since the 3 day incubation period for the BSB-test under same conditions does not encompass sufficient time for adaptation of the organisms active in the biological breakdown. It is not certain that toxic inhibitions can be excluded in the standard BSB (5). To better insure results concerning the degradation than is possible by evaluating the CSB/BSB ratio, one must carry out extensive degradation tests, where the incubation time, the inoculation material and other parameters are determined, so that further breakdown than for the five day BSB-test can be evaluated.

At present there are international efforts underway to standardize degradation tests. For this investigation of breakdown of fire extinguishing foam compounds a new T.O.C. degradation test (6) developed by the Bundesanstalt fur Gewasserkunde was used. Its test criteria is the complete breakdown of the total organic carbon (TOC).

For the test procedure the test compound serves as the only source of carbon. Inorganic mineral salts are added in advance. The incubation takes place in a screw-cap flask with air space, placed in a shaker. The degradation tests for the fire extinguishing foam compounds were carried out at 20°C in the dark, in deviation from the stated test procedures.
When the percentage breakdown according to the TOC-test is compared to results from other degradation tests, it must be taken into account, that the disappearance of one material from the solution is often considered as degradation. Under certain circumstances a high degradation can be simulated which actually is based upon physical processes such as, for instance, absorption of solids which has no relation to complete biological breakdown and mineralization.

According to the experiences gathered by participation in a round test, the TOC results for completely soluble compounds are somewhat lower than when the breakdown is measured by the "modified OECD-screening test" (7). This "modified OECD-screening test" was tested by international round tests. It has some disadvantages compared to the TOC-degradation test and cannot be used for testing of emulsions and suspensions.

Since the products tested here are mixtures the results of the degradation test is only well defined when a total breakdown is recorded. In cases where particle breakdown is observed, this can be due to the fact that only part of the product can be broken down, while other parts can not. The breakdown of mixture can then be manipulated by the manufacturer by addition of compounds which are easily broken down, but otherwise without function.

Even though, it is useful to test the breakdown of the present mixture products, because it gives a preliminary ranking of the products. For future tests, which could be carried out after a period of a few years of use, it should be attempted to test the breakdown of the single components of the products.
RESULTS:

Table 3 does list the measurement results obtained for the original products, to evaluate the potential for endangering of the water. Table 4 lists the percentage of degradation of the application solutions after a period of 5 days together with other degradation parameters of interest. The specific TOC-degradation curves are incorporated in attachments 1-6.

The values obtained from Table 3 show that the different products contain varying amounts of organic compounds. Of course one should count a low content of organic materials and of organic carbon found in products 1, 4 and 5 as positive factors when water endangering is to be judged.

For the application solutions (Table 4) the CSB and BSB5 are listed together with the ratio between these two factors and can be used in addition to the TOC-degradation results for the evaluations. According to the ratio the product No 6 should be considered easy to degrade. For the products 1 and 5, which according to the TOC-degradation test appear medium degradable (as also established from the metabolism test), the unfavorable CSB/BSB5 ratio could possibly be due to the chemical oxidation of iron salts present in the products. The iron salts would increase the CSB without increasing the BSB5. The degradation of each product, separately, is evaluated as follows:

1. Foam extinguishing compound No 8 shows a favorable ratio of K2MnO4 consumption / K2Cr2O7 consumption, and shows good bacteria action in the metabolism test, together with a 47% TOC-degradation. It must be rated as medium degradable.

2. Product No 2 shows a favorable CSB/BSB5 - ratio, but since the other tests do not indicate a good degradation rate it is classified as difficult to degrade.

3. The degradation of product 3 is even less than that of product 2, so it is classified as difficult to degrade.

Even though the degradation during the TOC-test was further advanced.
Potential for endangering of waters by original products

<table>
<thead>
<tr>
<th>No</th>
<th>KMnO₄ used</th>
<th>K₂CrO₇ used</th>
<th>Org. C content</th>
<th>H₂O content a)</th>
<th>Organic part b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/l</td>
<td>kg/l</td>
<td>kg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.203</td>
<td>1.525</td>
<td>0.15</td>
<td>89</td>
<td>10.7</td>
</tr>
<tr>
<td>2</td>
<td>0.988</td>
<td>1.438</td>
<td>0.24</td>
<td>53</td>
<td>46.7</td>
</tr>
<tr>
<td>3</td>
<td>0.085</td>
<td>2.930</td>
<td>0.22</td>
<td>77</td>
<td>23.8</td>
</tr>
<tr>
<td>4</td>
<td>0.030</td>
<td>1.973</td>
<td>0.30</td>
<td>80</td>
<td>20.6</td>
</tr>
<tr>
<td>5</td>
<td>0.415</td>
<td>2.392</td>
<td>0.88</td>
<td>94</td>
<td>15.1</td>
</tr>
<tr>
<td>6</td>
<td>0.101</td>
<td>4.164</td>
<td>0.31</td>
<td>66</td>
<td>8.8</td>
</tr>
</tbody>
</table>

a) only approximate values

b) only approximate values, burnoff values at 600°C and variable duration

Table 4

Biochemical degradation of application ready solutions (5%)

<table>
<thead>
<tr>
<th>No</th>
<th>Rate of KMnO₄ (m. K₂CrO₇)</th>
<th>C₅₀</th>
<th>ΔC₀</th>
<th>C₂₀</th>
<th>ΔC₂₀</th>
<th>Degrad. in methabol. TOC</th>
<th>Degrad. in TOC test</th>
<th>Final eval.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg O₃/l</td>
<td>mg O₃/l</td>
<td>mg O₃/l</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.000</td>
<td>12.300</td>
<td>4.000</td>
<td>3.1</td>
<td>0.3</td>
<td>+</td>
<td>47</td>
<td>medium</td>
</tr>
<tr>
<td>2</td>
<td>2.500</td>
<td>20.800</td>
<td>13.000</td>
<td>1.9</td>
<td>0.5</td>
<td>-</td>
<td>6</td>
<td>difficult</td>
</tr>
<tr>
<td>3</td>
<td>2.100</td>
<td>24.000</td>
<td>10.000</td>
<td>3.3</td>
<td>0.4</td>
<td>-</td>
<td>6</td>
<td>difficult</td>
</tr>
<tr>
<td>4</td>
<td>1.250</td>
<td>16.500</td>
<td>4.450</td>
<td>3.4</td>
<td>0.3</td>
<td>-</td>
<td>12</td>
<td>difficult</td>
</tr>
<tr>
<td>5</td>
<td>1.100</td>
<td>20.000</td>
<td>3.250</td>
<td>6.1</td>
<td>0.2</td>
<td>+</td>
<td>37</td>
<td>medium</td>
</tr>
<tr>
<td>6</td>
<td>2.500</td>
<td>36.000</td>
<td>41.000</td>
<td>0.9</td>
<td>1.1</td>
<td>+</td>
<td>62</td>
<td>easy to</td>
</tr>
</tbody>
</table>

x) Evaluation of biochemical degradation in TOC-test (at standard temperature of 25°C)

0 - 20% difficult to degrade
20 - 40% slightly degradable
40 - 75% medium degradable
75 - 100% very degradable
for product 4 than for products 2 and 3, it was classified as difficult to degrade.

For fire extinguishing foam compound 5, the metabolism test indicates that it can be broken down. A finding which is confirmed by the results of the TOC-test. The product is classified as medium degradable.

For product 6 one finds a complicated degradation behavior which might originate from the high toxic effect of this product. After 7 days degradation already 10% of the TOC is broken down. Further degradation does result only after 14 testing days, but then an intensive degradation leading to breakdown of 60% of the starting TOC does take place. The slow down in breakdown after 7 test days can be evaluated as an adaptation period for the microorganism involved.

3.3 Toxicology testing

METHOD

In the "Evaluation of the Water Endangering by Foam Extinguishing Compounds" (2), the results concerning toxic effects towards algae and bacteria were discussed.

In this evaluation which is concerned with tests for products that possibly could be used in large amounts, the toxicology tests were intensified. In addition to the incorporation-metabolism tests, also tests with small crabs and fish were carried out. This way the previous results could be further confirmed.

The toxicology test is carried out according to the German standard process for water testing (DEV) (4) L 11, L 12, and L 15. For these, the latest test procedures were used as published by the responsible working committees.

For fish-tests the concentrations used were from 0 to 10,000 mg/l, where
a large gradation of dilutions was used. The further toxicological test were carried out with smaller gradations from 0 to 210 mg/l to ensure, that the products could be differentiated as well as possible.

RESULTS:

In the enclosures 1 to 6, the results of the toxicology tests are presented as dose-reaction curves and the results are calculated and presented in Table 5.

Product No 1, "Fluoreschumgeist (Enclosure 1) is as toxic at concentrations of 10,000 mg/l that all test animals did die (EC_{100} = 10000 mg/l). But for the concentration 1000 mg/l the product is not detrimental (EC_{0} = 1000 mg/l). (EC = effective concentration with respect to the corresponding test. EC_{100} is the lowest tested concentration for which a 100% result with respect to the test criteria is recorded. For the fish test, this is the concentration at which all animals die; EC_{0} is the highest tested concentration at which no significant reaction is observed with respect to the test criteria).

Towards the small crab, Daphnia magna (water flea), the product is not detrimental at the highest concentrations tested (EC_{0} = 250 mg/l).

The photosynthesis activity of algae is easily affected by Fluoreschumgeist. The effect is still below the critical limit at concentrations of 50 mg/l; but at 100 mg/l it is significant.

The bacteria oxygen uptake during break down of peptone is increased by the product. This makes the biochemical break down of the product itself plausible. This result is also confirmed by the TOC - degradation test (sec. 3.2).

The product No2, Light Water, FC 206, frost-insured (enclosure 2), reacts similar to product No 1 in the fish and daphnia tests. Also the result of the incorporation test is similar to the first product. But the inhibition of the photosynthesis activity is less and becomes significant only at the highest concentration 250 mg/l. The result of the metabolism rate test is
definitely different than for the first product: There is no metabolic increase which could be interpreted as a sign of breakdown. The TOC degradation test also does show a breakdown of less than 10%.

The results of the biological tests carried out concerning product No. 3 "Light Water, FC 206, normal," are nearly identical to the results obtained for product No. 2 Light Water, frost protected. The only difference is; that the toxic effects towards algae indicated for product 2 are not found for product No. 3.

Product No. 4, "Light Water, FC 200, normal," is different from the other foam agents discussed previously by having a definite toxic effect towards fish, small crabs, and algae. For fish, the test animals die already at 1000 mg/l (EC0 = 100 mg/l, EC100 = 1000 mg/l). In the daphnia test, 33% of the animals died within 24 hours at 100 mg/l, at 250 mg/l about 75% of the animals died (EC0 = 50 mg/l, EC100 = 500 mg/l).

The incorporation test for this product is already surpassed at concentrations of 5 mg/l; at 250 mg/l a complete inhibition of algae activity is recorded (EC0 = 2 mg/l, EC = 250 mg/l).

Product No. 5, Protein Foam Agent, in all biological tests is equal to product No. 1. No significant toxic effects were found towards algae at concentration of about 250 mg/l. For the metabolism test an increase in bacteria oxygen consumption was recorded, but it was less than for product No. 1. The result of the metabolism test corresponds to a relatively positive reaction towards the breakdown test.

Product No. 6, Expyrol, is exceptionally high in toxicity and in delay of breakdown. The toxicity against fish is as high as for product No. 4 (EC0 = 1000 mg/l and EC100 = 1000 mg/l). For small crabs this product is especially toxic. For -

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1716.0017
especially toxic (EC₁₀₀ = 25 mg/l and EC₁₀₀₀ = 500 mg/l).

The incorporation test shows an inhibition at 10% concentrations above 10 mg/l. For 250 mg/l there is a 65% inhibition.

The metabolism curve of this product indicates that it contains metabolic active as well as toxic compounds.

Table 5
Results of toxicology test (expressed in order of poison classes)

<table>
<thead>
<tr>
<th>No</th>
<th>Fish (DEVL 15)</th>
<th>Daphne (DEVL 11)</th>
<th>Algae (DEVL 12) inhibit</th>
<th>Bacteria (DEVL 12) enhance</th>
<th>Total evaluation x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>III</td>
<td>III</td>
<td>II</td>
<td>III</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
<td>III</td>
<td>III</td>
<td>II/III</td>
<td>III</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>-</td>
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<tr>
<td>4</td>
<td>II</td>
<td>II</td>
<td>I</td>
<td>III</td>
<td>+</td>
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<td>III</td>
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<td>+</td>
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<tr>
<td>6</td>
<td>II</td>
<td>II</td>
<td>III</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

Poison class I: Proven inhibition on test animals at concentrations below 5 mg/l

Poison class II: As in I, region 5 to 250 mg/l

Poison class III: No damage at concentrations below 250 mg/l

x) Total evaluation: Calculated by weighted average. The test result with lowest critical limit of concentration is multiplied by 5.

4. Evaluation of Results and Conclusions

Summarizing the single criteria of the test, one can obtain different results, depending upon what importance is given to the different criteria.

The original products constitute a threat to biological systems such as the life in streams and biological systems of purification plants, due to their high toxic level to which the surface tension, and for product 1,
the content of zinc is added. The drinking water supply could be endangered by the content of just the organic material in the original compounds.

Also the application strength 5-6 % solutions of all products tested can lead to danger for biological systems due to their physical, chemical and toxic characteristics.

By the further dilution by a factor of 20 to 80, which is active in the application of foam fire-extinguishing compounds the toxic level of zinc (2 mg/l for bacteria, 10 - 25 mg/l for fish) is not exceeded and also the surface tension activity can loose its importance.

It then seems reasonable to evaluate the water danger by the products according to their toxicity at the concentrations which can be reached during application, and according to their biochemical degradation, even though there at present are only degradation results available for the finished mixed products.

For none of the compounds the degradation is so easy as to classify them as environmentally friendly compounds. In the selection one then must differentiate relatively better products from relatively worse products.

When fire-extinguishing foam compounds are applied, the about 5 % solutions are as previously stated diluted by a factor of 20 to 80. They then are in a region of concentration between 125 to 500 mg/l. At this concentration the compounds of product No. 3 and No. 5 are without acute detriment to the test organism. Product No. 1 and No. 2 lose their toxic effect after further dilution by a factor of 2 to 5. Such dilution is to be expected in the pre-flood tank of the purification systems. For the very toxic products No. 4 and No. 6, an additional dilution by a factor of between 50 and 200 is necessary to get below the toxic level. Such dilutions
are not certain in practice. Product No. 4 shows in addition a low degree of degradation and should not be used for that reason.

The products 2 and 3 are of little concern when toxic properties are taken into account. But both products are difficult to degrade and could thus disturb and impair the drinking water supply, and the use of these products therefore should be avoided.

Of the remaining products the foam compound No. 1 has a relatively high toxic level towards algae due to the high content of zinc. But since these properties are lost to a large extent due to the dilution during usage, and since the product is relatively easy to degrade, the endangering of the waters due to this product appears to be of little importance.

The grouping of the 6 products proposed here does take biological and chemical results into account, but does not consider application technical characteristics. If it is not possible, due to application technical reasons to avoid the use of products which are difficult to degrade or are especially toxic, then it would be advisable to test their single components for degradation and toxic effects. Further it should be attempted to replace components especially biologically damaging by less damaging materials of similar effect. Such approach has been successful for other materials of environmental concern.

5. Recommendations for technical ordering specifications

Based upon the investigations as discussed, the following requirements can be made of the manufacture of foam fire-extinguishing compounds:

- The biological degradation characteristics of the organic components present in foam compounds should be well established.

The breakdown should be as easy as possible, right now it is considered
as fair, when a 50 % break down is recorded in the modified OECD-Screening-
Test (7). For a test which records complete chemical degradation such as
the TOC-degradation test (6), a 40 % break down should be the minimum required.
Other tests can be used in replacement of the abovementioned, if it has been
proven, that equal results are obtained as for the tests according to (6)
and (7), when these products are tested.

The toxic effects of the foam compounds towards water organisms, especially
bacteria, algae, small crabs and fish should be as small as possible. A
sufficiently nontoxic range can be set if the EC50 for bacteria, algae,
daphnia and fish is above 1500 mg/l foam agent in water.

For toxicology test, L 11, L 12, and L'15 ofDEV (4), or similar
procedure for which equal type results can be proven, are to be used.
The heavy metal content should not exceed 1 % zinc, or for other metal
an amount for which a corresponding degree of bacteria toxic effects is
recorded.

6. Conclusion

According to the task the following six foam compounds, determined
by the "Bundesamt für Wehrtechnik und Beschaffung" in Koblenz, were evaluated
with relation to possible endangering of waters: Fluorprotein; Light Water
≤<2×17
FC 206, normal; Light Water FC 206, Frost protected; ; Light Water FC 200, normal;
Proteinschaummittel; Expyrol F 15. The test includes interphase activity,
toxicology, biochemical degradation, heavy metal content and flame point.
The results were presented and discussed and a conclusion reached. The
products Fluorprotein and Proteinschaummittel were recommended due to
relatively favorable biologic characteristics. The final conclusions were
given as recommendations for technical delivery terms (TL) to be used by
the contract agency.
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the E.C. as recommended process. (21.2.1978).

Enclosures

Toxicology - concentration/reaction curves and degradation curves. 1 to 6.

Translated G. Dinsen
March 1, 1980.
**Nr. 1 Fluorprotein**

**TOXICOLOGY TEST**
- A = Incorporation test DEVL 12
- Z = Metabolism test DEVL 12
- D = Daphne test DEVL 11
- F = Fish test DEVL 15

**Test of TOC degradation**

**Degradation time, Days**

**Concentration mg/l**

**Inhibition in %**

**Increase in %**

**TOC in % of initial TOC**
 Nr. 2 Light water, FC 206, frostgeschützt

TOXICOLOGY TEST
A = Incorporation test DEVL 12
Z = Metabolism test DEVL 12
D = Daphne test DEVL 11
F = Fish test DEVI. 15

Concentration mg/l

Inhibition in %

Increase in %

TOC in % of initial TOC

Test of TOC - degradation

Degradation time, Days
Nr. 3 Light water, FC 206, normal

TOXICOLOGY TEST
A= Incorporation test DEVLO 12  Z= Metabolism test DEVLO 12
B= Dupline test DEVLO 11  F= Fish test DEVLO 15

Inhibition in %

Increase in %

Concentration mg/l

Degradation time, Days

Test of TOC- degradation

TOC in % of initial TOC

0  7  14  21

0  20  40  60  80  100

100  1000  10000

(bar concentration mg/l)

80  60  40  20  0
Nr. 4 Light water, FC 200, normal

TOXICOLOGY TEST
A = Incorporation test DEV 12  
Z = Metabolism test DEV 12  
D = Daphne test DEV 11  
F = Fish test DEV 15

INHIBITION in %

CONCENTRATION mg/l

TOC in % of initial TOC

Degradation time, Days

Test of TOC degradation
Nr. 5 Proteinschaummittel

TOXICOLOGY TEST
A = Incorporation test D.WL. 12
D = Daphnia test DSVI. 11
F = Fish test D.WL. 13
Z = Lethality test D.WL. 17

Inhibition in %

Concentration mg/l

Test of TOC - degradation

Degradation time, Days

TOC in % of initial TOC

100
80
60
40
20
0

0 7 14 21

1716.0027
Nr. 6 Expyrol F 15

Graph showing toxicology tests:
- A: Incorporation test DEVL 12
- D: Daphne test DEVL 11
- E: Fish test DEVL 15

Graph showing TOC degradation:
- Time in days: 0, 7, 14, 21
- TOC in % of initial: 80, 60, 40, 20, 0

Concentration mg/l

Test of TOC degradation

Degradation time, Days

1716.0028