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Orimulsion-400: A Comparative Study

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Orimulsion-400: A Comparative Study

by

P. Jokuty, S. Whiticar, Z. Wang, K. Doe, B. Fieldhouse, and M. Fingas

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ABSTRACT

Orimulsion-400 is a new formulation of Orimulsion containing different surfactants than Orimulsion-100, the currently available commercial product. The physical properties, chemical composition, dispersibility, and aquatic toxicity of Orimulsion-400 were determined and compared to the properties of Orimulsion-100, most of which had been measured previously (Jokuty *et al.*, 1995).

The physical properties of the two types of Orimulsion were very similar, with the most significant difference being a higher viscosity (one order of magnitude) and greater non-Newtonian flow behaviour at 0°C for Orimulsion-400. No significant differences were measured in chemical composition. Under quiescent conditions, spill behaviour of the two formulations was very similar. Under more energetic conditions, however, Orimulsion-400 appeared to be less stable in salt water than Orimulsion-100.

Aquatic toxicity tests were performed with both unfiltered oil-in-water dispersions and filtered water-accommodated fractions. For most of the nine toxicity tests conducted, the toxicity of the two Orimulsion formulations was not significantly different. In two cases, Orimulsion-400 was less toxic than Orimulsion-100, and in one case Orimulsion-400 was more toxic than Orimulsion-100.

RÉSUMÉ

La préparation nouvelle Orimulsion-400 renferme des surfactifs différents de ceux de l'Orimulsion-100, actuellement dans le commerce. Ses propriétés physiques, sa composition chimique, ses caractéristiques de dispersion et sa toxicité dans le milieu aquatique ont fait l'objet de mesures et de comparaisons avec les mêmes propriétés — déjà connues pour la plupart — de l'Orimulsion-100 (Jokuty *et al.*, 1995).

Les propriétés physiques des deux Orimulsion sont très semblables, les différences les plus considérables étant la viscosité plus grande (d'un ordre de grandeur) de l'Orimulsion-400 et son comportement moins newtonien à 0 °C. On n'a pas mesuré d'écart significatif dans la composition chimique des deux préparations. Au repos, après un déversement, leur comportement est très semblable. Soumis à l'agitation, toutefois, l'Orimulsion-400 semble moins stable dans l'eau salée que l'Orimulsion-100.

Les tests toxicologiques (au nombre de neuf) en milieu aquatique ont porté sur des dispersions non filtrées d'huile dans l'eau et des fractions filtrées et adaptées à l'eau. Dans la plupart des cas, la toxicité des deux préparations ne différait pas significativement. Dans deux cas, l'Orimulsion-400 était moins toxique que l'Orimulsion-100 et dans un cas elle était plus toxique.

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1. INTRODUCTION

In 1995, the Emergencies Science Division (ESD) of Environment Canada produced the report titled "Orimulsion: Physical Properties, Chemical Composition, Dispersibility, and Toxicity" (Jokuty *et al.*, 1995). In 1997, ESD was approached by Bitor America Corporation to undertake a similar series of tests on Orimulsion-400, a new formulation of Orimulsion, and to compare its properties to those of Orimulsion-100, the formulation tested previously. A sample of Orimulsion-400, not commercially available at the time, was supplied by Bitor America Corporation, and the tests were completed.

Shortly after the completion and submission of a full report to Bitor America Corporation, the Orimulsion-400 manufacturing process was altered resulting in a product with some physical differences from the sample already tested. A sample of the now commercially available Orimulsion-400 was obtained from New Brunswick Power's Dalhousie plant and some of the key physical properties were measured and included in this report for completeness. However, all other results and conclusions of this report are based solely on the experimental work done with the 1997 sample of Orimulsion-400. As no chemical changes were made in the formulation it is likely that there are no significant differences in the spill behaviour or the toxicity of the currently available Orimulsion-400.

This report is divided into four sections: Physical Properties, Chemical Composition, Spill Behaviour, and Aquatic Toxicity. Each section is self-contained and includes methods, results, discussion, and conclusions.

2. PHYSICAL PROPERTIES

A 20-L plastic container of Orimulsion-400 was received by ESD on August 7, 1997. The sample referred to as Orimulsion-100 (1993) was received by ESD on December 3, 1993. All testing reported by Jokuty *et al.* (1995) was done on this sample. Some physical properties were also measured for another sample, referred to as Orimulsion-100 (1996). This sample was used for those toxicity tests performed in the current round of testing but not done previously, i.e., Microtox and three spine stickleback (acute toxicity). The Orimulsion-100 (1996) sample was sent to the Environment Canada Toxicology Laboratory in Moncton, New Brunswick from Saybolt Canada Ltd. in Dartmouth, Nova Scotia and received on August 25, 1997. After toxicity testing was completed, the remaining sample was forwarded to ESD, where it was received on November 5, 1997. Finally, a second sample of Orimulsion-400 was received in early 1999. This sample is representative of the Orimulsion-400 now being used in the Dalhousie, New Brunswick generating station. All samples were stored at 5°C.

2.1 General Observations

Orimulsion-400 looks very similar to Orimulsion-100. Both are black fluids that flow freely at 15°C. When left undisturbed for 24 hours, however, Orimulsion-400 became obviously lighter in colour at the top, indicating some degree of phase separation. Also, at the storage temperature of 5°C, the higher viscosity of Orimulsion-400 compared to Orimulsion-100, is apparent. For these reasons, before sampling for any test procedure, the Orimulsion-400 was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes to ensure complete homogenization.

The solubility behaviour of Orimulsion-400 in dichloromethane was observed to differ from that of Orimulsion-100. When fresh, the Orimulsion-400 was difficult to clean with dichloromethane and in many cases seemed to spread out more rather than be removed. This behaviour was not observed with Orimulsion-100. On the other hand, the weathered Orimulsion-400 was much more soluble in dichloromethane than the weathered Orimulsion-100. Soaking glassware for a few hours was more than enough to remove Orimulsion-400, while in some cases, Orimulsion-100 glassware had to be placed in a 180°C oven to aid the cleaning process.

2.2 Methods

2.2.1 Water Content

Water contents were determined by Karl Fischer titration, as in ASTM method D 4377 (ASTM, 1999e), with the following modifications. A Metrohm 701 KF automatic titrator was used, and the sample was dissolved in a pre-titrated 1:1:2 volume mixture of methanol/chloroform/toluene. Samples were run in triplicate and the mean water content is reported. This method is different from that prescribed in the Orimulsion Quality Control Manual (Intevep, 1993).

2.2.2 Pour Point

The Orimulsion-400 was poured into test jars meeting the specifications of ASTM method D 97 (ASTM, 1999b). The test jars were fitted with stoppers and ASTM-designated thermometers and

warmed in a water bath to 50°C. The samples were removed from the bath and allowed to cool to room temperature. For additional cooling, the samples were moved sequentially to a cold room maintained at 5°C and a freezer at -25°C. While cooling, the sample was checked periodically as per ASTM method D 97, but not necessarily at multiples of 3°C. When the pour point was reached, 3°C was added to the temperature recorded from the thermometer, as specified in the ASTM method. This value is reported as the pour point. Samples were run in duplicate and the mean pour point is reported. This method differs only slightly from that prescribed in the Orimulsion Quality Control Manual (Intevep, 1993).

2.2.3 Flash Point

A SUR BERLIN TAG 2 automatic flash point tester, which has been modified by adding a stirring mechanism, was used to determine flash points. The stirrer aids in producing more uniform heat transfer to oils that exceed the design viscosity, and in no way interferes with the test mechanism. ASTM method D 56 was followed (ASTM, 1999a). Samples were run in duplicate and the mean flash point is reported.

2.2.4 Density

Density was measured using an Anton Parr DMA 48 digital density meter and following ASTM method D 5002 (ASTM, 1999f). Samples were run in duplicate and the mean density is reported.

2.2.5 Viscosity

Initially, dynamic viscosity of fresh samples was determined using a HAAKE RV20 Rotovisco with the M5 measuring system, SV1 sensor, and HAAKE RC20 Rheocontroller. This method is different from that prescribed in the Orimulsion Quality Control Manual (Intevep, 1993). After some discussion with representatives from Bitor and Intevep, it was agreed to make some additional viscosity measurements that would be more comparable to those made as prescribed in the Orimulsion Quality Control Manual (Intevep, 1993). Some of these measurements were made using the MV2 sensor, at shear rates of 30/s and 100/s.

Although this type of instrument is widely used in industry, there are no ASTM standard methods for determining viscosity using concentric cylinder rotational viscometers. The following procedure was used. An aliquot of Orimulsion was obtained using a disposable syringe body (no needle). The excess was wiped from the outside of the syringe and the sample cup was carefully filled. For the initial set of measurements (Orimulsion-400, SV1 sensor) the sample was allowed to equilibrate 45 minutes at 0°C, and 30 minutes at 15 and 20°C. All measurements made with the MV2 sensor, and measurements made with the SV1 sensor on the Orimulsion-100 (1996) sample, were allowed to equilibrate for approximately 5 minutes. At 15 or 20°C, samples were only slightly non-Newtonian and were measured at a single shear rate of 100/s. The shear rate was ramped up 5 minutes, held 5 minutes, and ramped down 5 minutes. Samples were run in duplicate and the mean viscosity is reported except for measurements made on Orimulsion-400 and Orimulsion-100 (1996) with the MV2 sensor at 0 and 15°C. To conserve both sample and time, these measurements were made only once.

The evaporated Orimulsion samples have an extremely high viscosity, exceeding the capabilities of the RV20. For these samples, the RS100 Rheostress rheometer was used. A 20-mm plate/plate

system was chosen, to allow measurement of the highest possible viscosity values. The sample was warmed to room temperature, then sampled with a spatula, scooping the evaporated Orimulsion onto the 20-mm base plate. The base plate was then raised to the rotary plate leaving a gap height of 2 mm. The excess Orimulsion was removed from the base plate. The sample was allowed to equilibrate for 30 minutes before measurement. Viscosity was measured using a controlled shear rate from 0.1/s to 10/s, at 0 and 15°C, with logarithmic distribution. Duplicate measurements were taken at each shear rate and the mean viscosity is reported.

2.2.6 Surface Tension

Surface tension was measured using a Kruss K10ST automatic Du Nuoy ring tensiometer. The instrument was operated according to the manufacturers instructions, with one modification. Ordinary 100-mL Pyrex beakers were used instead of the special sample containers supplied by Kruss. The beakers were prepared for use by rinsing with dichloromethane, followed by soaking and washing with a commercial cleaner (Decon 75), and thorough rinsing with water purified by reverse osmosis. The beakers were then oven-dried at 160°C, cooled to room temperature, and stored at the desired measurement temperature. Calculation of the surface tension was done as described in ASTM method D 971 (ASTM, 1999c). Samples were run in duplicate and the mean surface tension is reported.

2.2.7 Evaporation Rate

Evaporation rate was measured using a pan evaporation technique. Measurements were conducted in a controlled-temperature chamber at 15°C. A 139-mm diameter standard glass petri dish was tared and then loaded with 20 g of oil. Data acquisition was started and continued until the desired time had elapsed. The weight was recorded at regular intervals using a data acquisition system consisting of a computer, software, and serial links to the balance. The balance used was a Mettler PM4000, (minimum measurement value 0.01 g). At the end of each experiment, the evaporation dish was cleaned and rinsed with dichloromethane. The evaporation data were then analyzed and curve fitting was performed using the software program *TableCurve* from Jandel Scientific Corporation.

2.2.8 Particle Size Distribution

Particle size distribution was determined using a Coulter Counter Multisizer with AccuComp software. This method is different from that prescribed in the Orimulsion Quality Control Manual (Intevp, 1993). The Coulter Counter determines particle size by measuring the increase in voltage as a particle passes through a small aperture between two electrodes. The particles are suspended in an electrolytic solution that is drawn by vacuum suction through a small aperture separating two electrodes under applied current. As a particle passes through the aperture, there is an increase in resistance between the electrodes that results in a voltage pulse. The magnitude of the voltage pulse is proportional to the volume of the particle passing through the aperture. The voltage pulses are scaled and counted by the AccuComp^R software package, which can then mathematically manipulate the data to provide particle size distribution information. The mean volume diameter [D(4,3)] is reported.

2.3 Results and Discussion

Figure 1 shows the results of two evaporation experiments with Orimulsion-400 and one done previously with Orimulsion-100 (1993). All three curves are essentially the same, allowing the calculation of a single "best fit" curve, which is also shown. The equation of this curve is:

$$\%Ev = (3.12 + 0.045T) \ln(t),$$

where %Ev is weight percent lost, T is surface temperature in °C, and t is time in minutes.

Table 1 summarizes the physical properties of Orimulsion-400. For comparison, the properties of Orimulsion-100 are also included. All of the Orimulsion-100 (1993) data is taken from Jokuty *et al.*, 1995, with the exception of the viscosity of the 26% evaporated sample, which was measured for this study using the RS100 instrument as described in Section 2.2.6.

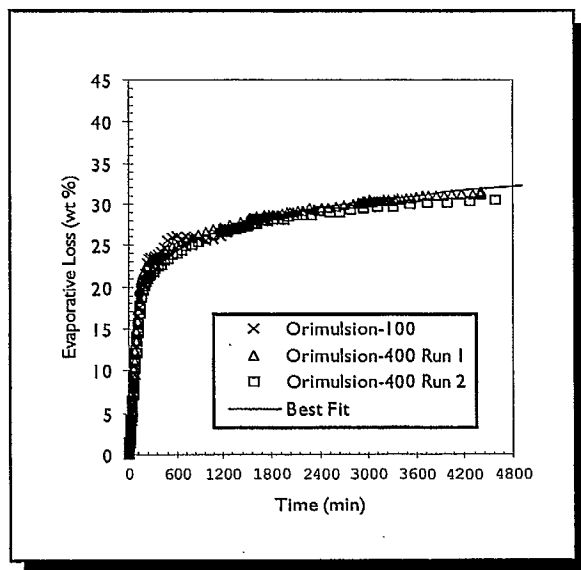


Figure 1 Orimulsion Evaporation

Most physical properties of Orimulsion-400 are not very different than those of Orimulsion-100. Physical properties that were not significantly different for the two formulations include particle size, flash point, pour point, and surface tension. Although the water content of both Orimulsion-100 samples was 27%, and the water content of the Orimulsion-400 sample was 30%, both of these values fall within the 27 to 31% range stated in the water content section of the Orimulsion Quality Control Manual (Intevep, 1993). The Karl Fischer method for the determination of water content has been used for many years at ESD, with both crude oils and water-in-oil emulsions, and found to provide accurate and reproducible results. Water contents measured by other methods, e.g., distillation, may give slightly different results. The slight differences in the densities of the two Orimulsion formulations may be directly related to their water contents.

The most notable physical difference between Orimulsion-400 and Orimulsion-100 is the viscosity, especially at 0°C. Initially, all the viscosity measurements on fresh (not evaporated) Orimulsion-400 and Orimulsion-100 (1993) were made using the SV1 sensor at a shear rate of 100/s. After reviewing the viscosity measurement method described in the Orimulsion Quality Control Manual (Intevep, 1993), additional measurements were made using the MV2 sensor. As shown in Table 1, measurements with the MV2 sensor were made at a shear rate of 100/s at all temperatures, and also at a shear rate of 30/s at 30°C. The Orimulsion Quality Control Manual (Intevep, 1993) specifies the use of the MV1 sensor, shear rates of 20/s and 100/s, and a temperature of 30°C.

Table 1a Summary of Physical Properties of Fresh Orimulsion Samples

| | Orimulsion-400 (1997 Fresh) | Orimulsion-400 (1999 Fresh) | Orimulsion-100 (1993 Fresh) | Orimulsion-100 (1996 Fresh) |
|---|---------------------------------------|-------------------------------------|--------------------------------|-------------------------------------|
| Water Content (wt %) | 30 | 28 | 27 | 27 |
| Mean Volume Diameter (μm) | 19 | 15 | 17 | |
| Flash Point ($^{\circ}\text{C}$) | >95 | | >95 | |
| Pour Point ($^{\circ}\text{C}$) | 0 | | 3 | |
| Density at 0°C (g/mL) | 1.0162 | 1.0158 | 1.0200 | 1.0159 |
| Density at 15°C (g/mL) | 1.0095 | 1.0084 | 1.0123 | 1.0070 |
| Viscosity at 0°C (mPa·s) @ 100/s | 1065 ^a , 1294 ^b | 636 ^a , 568 ^b | 788 ^a | 217 ^a , 478 ^b |
| @ 10/s | 2,754 ^a | 2,355 ^a | | |
| @ 1/s | 5,501 ^a | 4,894 ^a | | |
| Viscosity at 15°C (mPa·s) @ 100/s | 450 ^a , 657 ^b | 380 ^a , 404 ^b | 622 ^a | 250 ^a , 211 ^b |
| Viscosity at 20°C (mPa·s) @ 100/s | 518 ^a , 647 ^b | 414 ^a , 340 ^b | 548 ^a | NM ^a , 253 ^b |
| Viscosity at 30°C (mPa·s) @ 100/s | 554 ^a , 615 ^b | 371 ^a , 334 ^b | 515 ^a | 418 ^a , 465 ^b |
| Viscosity at 30°C (mPa·s) @ 30/s | 778 ^a , 882 ^b | 501 ^a , 391 ^b | | 700 ^a , 800 ^b |
| Surface Tension at 15°C (mN/m) | 35.4 | | 34.6 | |

^aSV1 sensor; ^bMV2 sensor; NM=not measurable (too much variability); DNF=does not flow;
Gray shading indicates bad measurements due to insufficient sample

Table 1b Summary of Physical Properties of Bitumen Samples

| | Orimulsion-400 (1997 Evap. 29%) | Orimulsion-100 (1993 Evap. 26%) |
|---|------------------------------------|------------------------------------|
| Water Content (wt %) | 0.1 | 1.7 |
| Flash Point ($^{\circ}\text{C}$) | >95 | >95 |
| Pour Point ($^{\circ}\text{C}$) | 33 | 39 |
| Density at 0°C (g/mL) | 1.0220 | 1.0269 |
| Density at 15°C (g/mL) | 1.0202 | 1.0190 |
| Viscosity at 0°C (mPa·s) @ 1/s | 2.2×10^8 | 1.0×10^8 |
| Viscosity at 15°C (mPa·s) @ 1/s | 9.0×10^6 | 5.5×10^6 |
| Surface Tension at 15°C (mN/m) | DNF | DNF |

DNF=does not flow

The MV1 and MV2 sensors have similar measuring ranges. At a shear rate of 20/s, the basic measurement range of the MV1 is 1,500 to 15,000 mPa·s. Similarly, at a shear rate of 30/s, the basic measurement range of the MV2 is 1,330 to 13,300 mPa·s. At temperatures of 15 to 30°C , the viscosity of Orimulsion was in the range 600 to 900 mPa·s. Therefore, these lower shear rates are not suitable for measurements at these temperatures. At a shear rate of 100/s, the viscosity of Orimulsion falls within the basic measurement range of both sensors, as defined by the instrument manufacturer (Haake). For the MV1, the range is 300 to 3,000 mPa·s and for the MV2, the range is 400 to 4000 mPa·s.

The SV1 sensor is best suited to high viscosity fluids (1,000 to 1,000,000 mPa·s at shear rates of 1/s to 100/s). For Orimulsion viscosity measurements at 0°C , the SV1 was an appropriate sensor. One important advantage of the SV1 sensor over the MV sensors is a much smaller sample volume. The SV1 requires only 9 mL of sample, compared to 40 mL and 55 mL for the MV1 and MV2 sensors, respectively. As a result of the large amount of sample required for the MV2 sensor and the need to run duplicate samples, insufficient Orimulsion-100 (1996) sample was available when making the measurements at 0, 15, and 20°C .

The extremely high viscosities of the bitumen remaining after evaporation of Orimulsion-400 and Orimulsion-100 are of the same order of magnitude and the approximately two-fold difference between them is probably not significant.

2.4 Conclusions

The physical properties of the Orimulsion-100 and Orimulsion-400 samples were very similar, with the following exceptions.

- a) The water content of the Orimulsion-400 was 30% compared to 27% for both Orimulsion-100 samples.
- b) The density of the fresh Orimulsion-400 was slightly lower than that of both Orimulsion-100 samples, although this is consistent with its higher water content.
- c) Orimulsion-400 displays greater non-Newtonian flow behaviour at 0°C than does Orimulsion-100. The viscosity of Orimulsion-400 at this temperature is approximately one order of magnitude greater than that of Orimulsion-100.

3. CHEMICAL COMPOSITION

3.1 Methods

3.1.1 Sulphur

Sulphur contents were determined using a Horiba MESA 200 sulphur and chlorine analyzer. Duplicate samples were run twice and the mean of the four measurements is reported. The method used is ASTM method D 4294 (ASTM, 1996a). This method is different from that prescribed in the Orimulsion Quality Control Manual (Intevep, 1993).

3.1.2 Hydrocarbon Groups

Asphaltenes were precipitated from n-pentane. To separate saturates, aromatics, and resins, deasphalted oil (maltenes) were placed on an open silica column and eluted sequentially with hexane, hexane/benzene, dichloromethane, and methanol (Jokuty *et al.*, 1996).

3.1.3 Volatile Organic Compounds (VOCs)

Approximately 0.2 g of oil is made up to 10.00 mL in n-pentane. To 0.100 mL of this solution is added 0.200 mL of 10 ppm d10-ethylbenzene as internal standard and 0.700 mL of n-pentane. Benzene, toluene, ethylbenzene, xylenes (BTEX), and C₃-substituted benzenes are determined directly from a 1.0 µL injection volume, using gas chromatography with mass spectrometric detection (GC/MSD) (Wang *et al.*, 1995).

3.1.4 Petroleum Hydrocarbons Analysis

The complete method is too lengthy to repeat here (Wang *et al.*, 1994; Wang and Fingas, 1996). In summary, a microcolumn fractionation technique was used for sample cleanup and fractionation of the Orimulsion samples. Polar compounds (resins and asphaltenes) were retained on the silica column, while saturates and aromatics were separated and collected as F1 and F2 respectively. The distribution of alkylated polyaromatic hydrocarbons (PAH) was determined by GC/MSD analysis of F2.

3.2 Results

Table 2 summarizes the chemical composition of Orimulsion-400. For comparison, the data for Orimulsion-100 are also included, where available. All of the Orimulsion-100 data is taken from Jokuty *et al.*, 1995, with the exception of the sulphur content of the 26% evaporated sample, which was calculated from the data for fresh Orimulsion-100, by assuming a 26% increase.

3.3 Conclusions

There were no significant differences observed in the chemical composition of Orimulsion-400 and Orimulsion-100 on the basis of the tests completed. It should be noted that no analysis of metals was done. According to the manufacturer, unlike Orimulsion-100, magnesium nitrate is not added to Orimulsion-400 during the manufacturing process. It is unlikely that this difference in composition would produce any significant difference in the behaviour of Orimulsion-400 spills.

Table 2 Chemical Composition

| | Orimulsion-400 (Fresh) | Orimulsion-100 (Fresh) | Orimulsion-400 (Evap. 29%) | Orimulsion-100 (Evap. 26%) |
|---|-----------------------------------|-----------------------------------|---------------------------------------|---------------------------------------|
| Sulphur (wt %) | 2.02 | 2.32 | 3.47 | 3.14 (calculated) |
| Hydrocarbon Groups (wt %) | | | | |
| Saturates | | | 14 | 17 |
| Aromatics | | | 47 | 47 |
| Resins | | | 22 | 16 |
| Asphaltenes | | | 17 | 20 |
| VOCs (ppm) | | | | |
| Benzene | 0 | | | |
| Toluene | 4 | | | |
| Ethylbenzene | 19 | | | |
| Xylenes | 13 | | | |
| C ₃ -benzenes | 54 | | | |
| Total BTEX | 37 | | | |
| Total BTEX+C ₃ -benzenes | 90 | | 0 | 0 |
| Alkyl PAHs (µg/g bitumen) | | | | |
| C ₀ -C ₄ Naphthalenes | 774 | 1,084 | | |
| C ₀ -C ₄ Phenanthrenes | 1,140 | 1,197 | | |
| C ₀ -C ₄ Dibenzo thiophenes | 671 | 805 | | |
| C ₀ -C ₄ Fluorenes | 310 | 353 | | |
| C ₀ -C ₄ Chrysenes | 145 | 183 | | |
| Total C ₀ -C ₄ PAH | 3,040 | 3,622 | | |

4. SPILL BEHAVIOUR

To determine the range of spill behaviours to be expected from Orimulsion, three types of tests were conducted, with each test using a different level of energy.

4.1 Methods

4.1.1 Natural Dispersibility (High Energy Test)

A tank, approximately 30 cm in each dimension, was filled with 5 L of water. Two emulsion-to-water ratios were tested: 1:1,200 (4.2 mL Orimulsion) and 1:20,000 (250 μ L Orimulsion). The Orimulsion was added to the water. The vessel was then covered and shaken at 300 RPM on a table shaker. Shaking was continued for 20 minutes. After a 10-minute settling time, 120 mL of water was taken from the middle of the water layer and extracted with dichloromethane. The extracts were compared to a 1% Orimulsion-400 in dichloromethane solution as a reference.

4.1.2 Oscillating Hoop

The oscillating hoop test is a medium energy test that uses an oil:water ratio of 1:20,000. The apparatus consists of a cylindrical tank 90 cm in diameter and 106 cm in height, and a vertically oscillating, flat, stainless steel hoop. Concentric wave patterns are produced by the oscillating hoop. These waves tend to minimize wall effects by keeping the oil centred in the tank. The large surface area and low oil-to-water ratio ensures that this centring does not significantly reduce the free spreading of the oil.

For each test, the tank was filled to a depth of approximately 60 cm. Salt was added as appropriate to obtain the desired salinity, nominally 0%, 2%, and 3.3%. Salinity was checked with a Horiba U-10 water quality tester. The temperature of the water was between 15 and 17°C for all three tests. With the hoop in motion, 25 mL of Orimulsion (17.5 mL bitumen) was added to the water surface by syringe. Agitation was continued for two hours. Bitumen was then collected from the water surface and vessel floor separately, and weighed. The percentage of bitumen recovered was calculated by assuming 17.5 g bitumen initially, and recovery efficiencies of 75% for the fresh water test and 80% for the brackish and salt water tests.

4.1.3 Carboy Test

This test was used to determine the rising or sinking behaviour of Orimulsion spills under static conditions. The test was designed to be similar to the Teflon jar test described in Jokuty *et al.*, 1995, but it was necessary to use a different method of quantitation to avoid the use of carbon tetrachloride, an ozone-depleting substance (ODS) banned under the Montreal Protocol. To ensure that there would be sufficient bitumen for gravimetric determination, the oil:water ratio was approximately doubled to 1:465.

Each of three 20-L carboys was fitted with two sampling ports. When filled with 20 L of water, the upper port was 7 cm below the surface. The lower port was 11 cm from the bottom. The two ports were approximately 16.5 cm apart. Each carboy was filled with 20 L of tap water. Salt (sodium chloride) was added to two of the vessels to produce brackish water (2%) and salt water (3.3%). Salinity was checked with a Horiba U-10 water quality tester. 60 mL of Orimulsion-400

was added at the surface of the water and briefly stirred to ensure an initial uniform distribution in the water column. The carboy was then left to stand, undisturbed, for the duration of the test. From the fresh water carboy, samples (60 mL) were drawn from each sampling port at 10 min, 20 min, 30 min, 1 hr, 2 hr, 4 hr, 6 hr, 12 hr, 24 hr, and 48 hr. From the brackish and salt water carboys, samples were drawn at 20 min, 40 min, 1 hr, 2 hr, 4 hr, 6 hr, 12 hr, 24 hr, and 48 hr. Each water sample was extracted with three 25 mL portions of dichloromethane. The solvent was then evaporated and the remaining bitumen was weighed.

4.2 Observations and Results

4.2.1 Natural Dispersibility (High Energy Test)

In both experiments (1:1,200 and 1:20,000), the addition of Orimulsion-400 resulted in a resurfacing of lightly coloured material that spread across the water surface. After agitation, bitumen was observed adhering to the vessel walls right up to the lid and there was a sheen on the surface of the water. Dichloromethane extraction of water from the 1:1,200 test produced a very lightly coloured extract, much lighter than the reference 1% solution. The extract from the 1:20,000 test was completely colourless, indicating no dispersion.

4.2.2 Oscillating Hoop Test

Fresh Water - Within 30 seconds of its addition to the water, the inky string of Orimulsion-400 from the syringe dispersed into a black cloud, darkening the water in the vessel. Within one minute, a sheen formed on the surface. Part of the sheen thickened to form particulate bitumen that adhered to the hoop and vessel water line. This process continued throughout the test, with bitumen accumulating on the surface, hoop, and waterline, while the water became progressively lighter. After two hours (end of test), the water was still coloured, but an accumulation of bitumen was visible on the bottom of the vessel. The following amounts of bitumen were recovered: 7.1640 g (54%) from the hoop and walls and 1.2508 g (10%) from the bottom of the vessel, for a total of 8.4148 g (64%).

Brackish Water (2%) - The initial behaviour of the Orimulsion-400 in brackish water was very similar to the fresh water, including the initial dispersal, sheen formation, and thickening of the sheen into particulate bitumen that accumulated on the surface, hoop, and waterline. The main differences were that the water became more clear, more quickly and there was no accumulation of bitumen on the bottom of the vessel. The total amount of bitumen recovered from the hoop and walls was 10.1564 g (73%).

Salt Water (3.3%) - Upon addition to salt water, Orimulsion-400 dispersed into a black cloud, but within 30 seconds, a heavy sheen formed on the surface and particulate bitumen began to accumulate. After 1 minute, the bitumen began to form larger mats in the middle of the vessel. This behaviour continued and by 90 minutes the water was virtually clear, with most of the bitumen contained in mats 4 to 8 cm across, and the remainder as particulate bitumen on the surface, with only a small amount on the hoop and walls. The mats were easily recovered from the surface for weighing. A total of 11.8255 g (84%) of bitumen was recovered.

4.2.3 Carboy Test

The results of the carboy tests are summarized in Figures 2, 3, and 4. The data sheets for these experiments can be found in the Appendix.

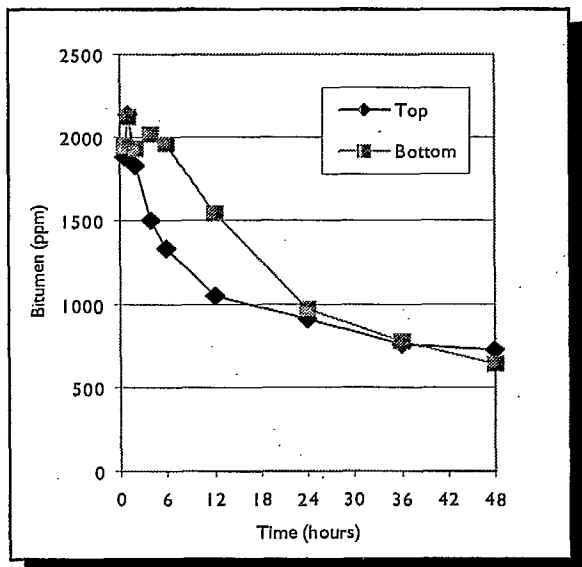


Figure 2 Fresh Water Carboy Test

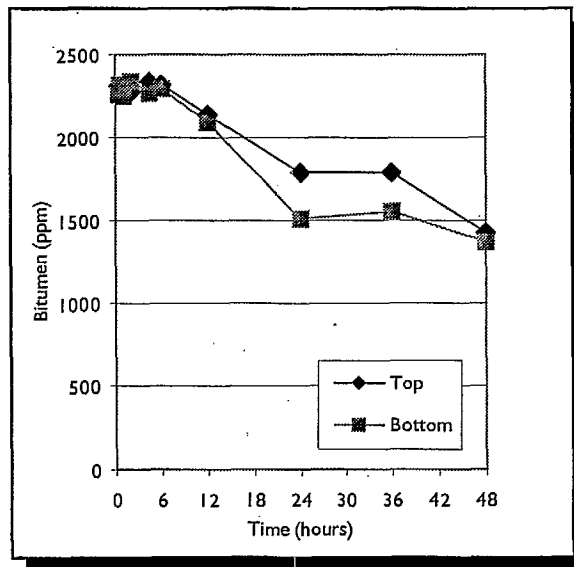


Figure 3 Brackish Water Carboy Test

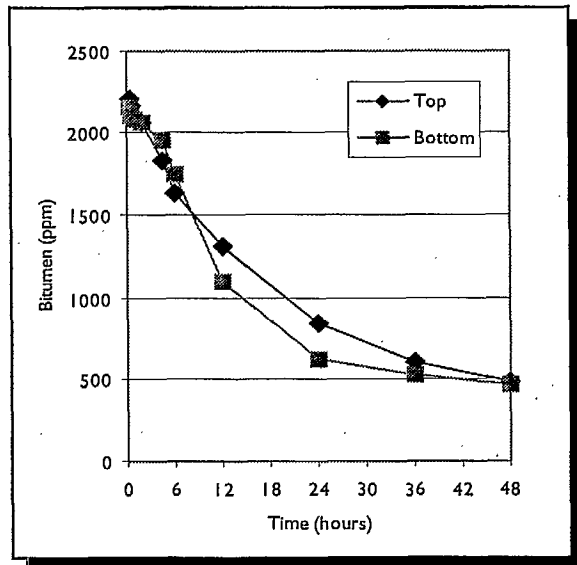


Figure 4 Salt Water Carboy Test

4.3 Discussion

Assuming that approximately 17.5 g of bitumen were used in each oscillating hoop experiment with Orimulsion-400, and that the efficiency of bitumen recovery was 75% for the fresh water test and 80% for the brackish and salt water tests, the amount of bitumen dispersed in the water column was estimated. The results are summarized and compared with similar calculations for Orimulsion-100 (1993) tests in Table 3.

Table 3 Distribution of Bitumen After Two-Hour Oscillating Hoop Test

| | % Dispersed | |
|----------------|----------------|-----------------------|
| | Orimulsion-400 | Orimulsion-100 (1993) |
| Fresh Water | 36 | 42 |
| Brackish Water | 27 | |
| Salt Water | 16 | 46 |

After the two-hour test, only 16% of the bitumen from the Orimulsion-400 salt water test remained dispersed, compared to 46% of the bitumen from the Orimulsion-100 (1993) salt water test. In fresh water, similar amounts of Orimulsion-400 (36%) and Orimulsion-100 (42%) remained dispersed. In brackish water, the amount of Orimulsion-400 bitumen remaining dispersed after 2 hours was intermediate between that of fresh and salt water. This quantity was not determined for the Orimulsion-100 (1993) brackish water test.

The results of the carboy tests with Orimulsion-400 were very similar to the results of the Teflon jar tests run previously with Orimulsion-100 (1993). In both tests, the fresh water and salt water bitumen concentrations had decreased to similar concentrations after 48 hours. For the tests with Orimulsion-100 (1993), this level was about 100 ppm and with Orimulsion-400 it was about 500 ppm. Similarly, in brackish water the bitumen concentration decreased more slowly to 450 ppm after 48 hours for Orimulsion-100 (1993) and to 1,400 ppm for Orimulsion-400 after 48 hours. It must be noted, however, that the initial oil:water ratio was about twice as high for the Orimulsion-400 experiments.

4.4 Conclusions

Based on these results, it appears that the spill behaviour of Orimulsion-400 and Orimulsion-100 is very similar under quiescent conditions (carboy test). Under more energetic conditions (oscillating hoop test), Orimulsion-400 appears to be less stable in salt water than Orimulsion-100.

5. AQUATIC TOXICITY

5.1 Introduction

A 1-gal. sample labeled "*Orimulsion from BITOR received at ESD on August 7, 1997*" was received by Environment Canada's Toxicology Laboratory in Moncton, New Brunswick from the Emergencies Science Division (ESD) of Environment Canada's Environmental Technology Centre (ETC) in Ottawa, Ontario on August 22, 1997. This sample is referred to as Orimulsion-400 in this report. The sample was stored at 4°C until used in toxicity testing between September 17 and September 22, 1997. This sample contained approximately 0.17% surfactant composed of ethanol amine and alcohol ethoxylate (P. Jokuty, Environment Canada and I. Johnson, Golder Associates, personal communication).

The sample was sent to the Environment Canada Toxicology Laboratory for toxicity testing with fish, invertebrates, and bacteria, since these tests had not yet been performed on this formulation of Orimulsion. The methods were to duplicate as far as possible those used to test an earlier Orimulsion sample as reported in Jokuty *et al.* (1995). Since additional toxicity tests were performed on this sample of Orimulsion-400, it was decided to test a sample of the older Orimulsion formulation using these tests as well, for comparison purposes. Therefore, a second Orimulsion sample was sent to the Moncton lab from Saybolt Canada Ltd., Dartmouth, Nova Scotia and received on August 25, 1997. This sample was also stored at 4°C until used in toxicity testing between September 17 and September 22, 1997. The sample was labeled "*Orimulsion. Composite; Source: Ship; Sampling Date: March/96*" and is referred to as Orimulsion-100 (1996) in this report. This sample contained 0.2% nonyl phenol ethoxylate as a surfactant (P. Jokuty, Environment Canada and I. Johnson, Golder Associates, personal communication).

5.2 Methods

5.2.1 Sea Urchin Fertilization

Preparation of Water-Accommodated Fraction - The water-accommodated fraction (WAF) was prepared in a 1-L Erlenmeyer flask with a stopcock near the bottom. One litre of seawater and 26.66 g of Orimulsion-400 were placed in the flask (oil:water ratio was approximately 1:40). The target concentration of 25,000 mg/L was slightly exceeded because of the viscous nature of the test material. A 1-in Teflon-coated magnetic stir bar was added to the flask and stirring commenced. The flask was sealed with a Teflon-lined cap and covered with aluminum foil. The mixture was stirred for 33.5 hours. Stirring was ceased and the mixture was allowed to settle for approximately 4 hours. The mixture was drained from the stopcock at the bottom of the flask. A portion of this sample was analyzed directly using the sea urchin fertilization test. The remainder of the sample was treated by filtration through a PreSep 1.0 µm glass prefilter before analysis with the sea urchin fertilization. Aliquots of the WAF before and after filtration, as well as the control/dilution water, were taken for chemical analysis, cooled to 4°C, and shipped to ESD for determination of total solvent-extractable material.

Test Protocol - The sea urchin fertilization test was performed as per Environment Canada's standard protocol EPS 1/RM/27 (Environment Canada, 1992a). The species used was *Lytechinus pictus* and testing was performed at $20 \pm 1^\circ\text{C}$. Concentrations of the test WAF were prepared by dilution with clean seawater. Samples were exposed to sperm for ten minutes; eggs were added and exposure continued for an additional ten minutes. The test was terminated by adding formalin to the test vessels. Each test vessel was enumerated by counting 100 eggs and determining the percent fertilization. IC_{50} (inhibition concentration - calculated concentration for 50% inhibition of fertilization) was estimated at the end of the test. Controls, blanks, and reference toxicant were used to monitor the reproducibility of the protocol. Each test treatment, including controls, blanks and reference toxicant, was set up in quadruplicate.

5.2.2 Microtox

Preparation of Oil-in-Water Dispersions - Oil-in-water dispersions (OWDs) of Orimulsion-100 (1996) and Orimulsion-400 were prepared by mixing 10.25 g and 11.80 g, respectively, with 1 L of seawater in volumetric flasks. The target concentration of 10,000 mg/L was slightly exceeded because of the viscous nature of the test material. A portion of each solution was treated by passing through a PreSep 1.0 μm glass prefilter. Before and after filtration, aliquots of each OWD were sampled for chemical analysis, cooled to 4°C , and shipped to ESD for analysis of total solvent-extractable material.

Test Protocol - The analysis followed the Environment Canada standard protocol EPS 1/RM/24 (Environment Canada, 1992b). Two protocols were used: the Microtox basic protocol and the Microtox 100% test. The basic protocol has a top concentration of 50%, while the 100% protocol has a top concentration of 99%. All samples were first analyzed by the basic protocol. Any samples found to be non-toxic using this protocol were analyzed using the 100% test. Both protocols involve exposure of the test concentrations to the bacterium, *Vibrio fischeri* (previously called *Photobacterium phosphoreum*) for 15 minutes. The Microtox analyzer records the light output from the bacteria. A decrease in light output is interpreted as a toxic response. An EC_{50} (median effective concentration - calculated concentration estimated to cause 50% decrease in light output or bioluminescence) was estimated using the Microtox software. Controls and reference toxicants were used to monitor test reproducibility.

5.2.3 *Daphnia magna*

Preparation of Water-Accommodated Fraction - The water-accommodated fraction (WAF) was prepared in a 2-L Erlenmeyer flask with a stopcock near the bottom, to which 2 L of moderately hard EPA water and 50.25 g of Orimulsion-400 were added (oil:water ratio was approximately 1:40). The target concentration of 25,000 mg/L was slightly exceeded because of the viscous nature of the test material. A 1-in Teflon-coated magnetic stir bar was added to the flask and stirring commenced. The flask was sealed with a Teflon-lined cap and covered with aluminum foil. The mixture was stirred for 33.5 hours. Stirring was ceased and the mixture was allowed to settle for approximately 30 hours. The mixture was drained from the stopcock at the bottom of the flask. A portion of this sample was analyzed directly using the *Daphnia magna* toxicity test. The remainder of the sample was treated by filtration through a PreSep 1.0 μm glass prefilter before analysis with *Daphnia magna*. Aliquots of the WAF before and after filtration, as well as

the control/dilution water, were taken for chemical analysis, cooled to 4°C, and shipped to ESD for analysis of total solvent extractable material.

It should be noted that, according to Blenkinsopp *et al.* (1996), WAFs prepared by this method *should* be used within 24 hours. The 30-hour "settling time" described above essentially represents a one-day storage due to a delay in obtaining the test organisms. In retrospect, this criterion should not be applied to Orimulsion WAFs, as significant changes in concentration can occur during this period, especially in fresh water. In this case, the determination of total solvent- extractable material in the test solution obviates the problem by providing an accurate measure of the actual bitumen concentration.

Test Protocol - Testing for *Daphnia magna* was performed as per Environment Canada's standard protocol EPS 1/RM/11 (Environment Canada, 1990a). Concentrations of the test WAF were prepared by diluting the Orimulsion-400 WAF preparation with moderately hard EPA water. Ten Clone 5 *Daphnia magna* neonates (< 24 hours old) were transferred to the test solutions in 200-mL glass beakers. The beakers were covered with Parafilm. Exposure time was 48 hours at 20±1°C. A photoperiod of 16 hours of light and 8 hours of dark was provided by fluorescent lighting. At test termination, animals were observed for immobility (failure to swim during a 15 second observation period) and death (lack of movement of the heart as observed under a dissecting microscope). An LC₅₀ (median lethal concentration - calculated concentration estimated to cause 50% mortality of the test organisms) and EC₅₀ (median effective concentration - calculated concentration estimated to cause 50% immobilization of the test organisms) are estimated at the end of the test.

5.2.4 Fish Tests

Preparation of Oil-in-Water Dispersions - Oil-in-water dispersions (OWDs) for the fish tests were prepared by adding control water to test containers. Weighed aliquots of the test materials were added to the water while vigorously stirring to prepare the desired test concentrations. For *Onchorynchus mykiss* (rainbow trout), the control water was dechlorinated Moncton municipal water; for *Gasterosteus aculeatus* (threespine stickleback), the control water was Pointe du Chêne seawater. For each separate fish test, aliquots of high, medium, and low concentrations of OWDs, as well as the control/dilution water, were taken at the start and termination of the test for chemical analysis, cooled to 4°C, and shipped to ESD for analysis of total solvent-extractable material.

Test Protocols - Testing for rainbow trout was performed as per Environment Canada's standard protocol EPS 1/RM/9 (Environment Canada, 1990b). Fingerling rainbow trout weighing from 0.2 to 0.5 g were exposed to a series of concentrations of the fresh OWD. Testing was performed at 15±1°C with a photoperiod of 16 hours of light and 8 hours of dark provided by overhead fluorescent lighting. Test duration was 96 hours. At the termination of the test, fish were observed for mortality by lack of opercular activity. An LC₅₀ was estimated from the data. The controls and reference toxicants are used to monitor test reproducibility.

Testing for threespine stickleback was performed as per Environment Canada's standard protocol EPS 1/RM/10 (Environment Canada, 1990c). Fish of 0.17 and 0.18 g weight (mean wet weights for the two tests conducted) were exposed to a series of concentrations of the fresh

OWD. Testing was performed at $10 \pm 1^\circ\text{C}$ with a photoperiod of 16 hours of light and 8 hours of dark provided by overhead fluorescent lighting. Test duration was 96 hours. At the termination of the test, fish were observed for mortality by lack of opercular activity. An LC_{50} was estimated from the data. The controls and reference toxicants are used to monitor test reproducibility.

5.2.5 Total Solvent-Extractable Materials (TSEM)

For each of the tests, samples of the OWDs or WAFs were solvent-extracted to determine the actual oil concentration compared to the nominal concentration. Each sample was serially extracted three times with 50 mL of dichloromethane (DCM). Each sample jar was rinsed three times with DCM and the solvent was added to the extraction solvent. The extracts were combined, dried by filtering through sodium sulphate, and then concentrated to appropriate volumes using a rotary evaporator. The concentrated extracts were quantitatively transferred to volumetric cylinders or precalibrated centrifuge and then made up to appropriate volumes (2 or 10 mL) depending on their concentration.

For most samples, an aliquot of the concentrated extract (1 or 3 mL) was blown down with nitrogen to a residue and weighed three times at two-hour intervals on a microbalance to obtain the mean weight of TSEM for each sample. For some samples with extremely low concentrations of TSEM, such as control water and filtered test solutions, the concentrated extracts were analyzed using a gas chromatography with flame ionization (GC/FID) technique, to determine total GC-detectable petroleum hydrocarbons (Wang *et al.*, 1994).

5.3 Results

The results of the toxicity tests performed on Orimulsion-400 are summarized in Table 4. The additional tests performed on Orimulsion-100 (1996) are provided in Table 5. A summary of the results of chemical analyses conducted on the aliquots of the test solutions by ESD is provided in Table 6.

The results provided in Table 6 show that WAFs contain far less TSEM than nominal (added) concentrations (10% or less). Measured TSEM in OWDs, on the other hand, ranged between 36 and 81% of nominal values (mean value = 63%, $N = 11$) at time zero (start of the tests). These values for OWDs dropped after 96 hours to about 10% of nominal values (fresh water OWDs) and to slightly below 1% of nominal values (salt water OWDs). This decrease in TSEM in the water column in the toxicity tests resulted in floating slicks of viscous tar-like material. Filtering the OWDs and the WAFs through $1\text{-}\mu\text{m}$ filters resulted in a decrease in TSEM ranging from 54 to 98.5% for WAFs and a decrease of greater than 99.7% for OWDs.

A comparison of the toxicity of Orimulsion-400 with that of Orimulsion-100 is provided in Table 7. For *L. pictus* fertilization assay, the values for the WAFs of Orimulsion-400 and Orimulsion-100 were not significantly different.

Table 4 Results of Toxicity Tests on Orimulsion-400

| Test Organism | Test Type and Duration | Sample Type | Results Based on Nominal Conc'n (mg/L) | Results Based on TSEM ¹ (mg/L) |
|-----------------------------------|------------------------------|-------------------------------|---|---|
| <i>Lytechinus pictus</i> | 20 minute fertilization test | WAF ² , unfiltered | IC ₅₀ =21.5%=5,730 | IC ₅₀ =21.5%=21.1 |
| <i>Lytechinus pictus</i> | 20 minute fertilization test | WAF filtered | IC ₅₀ =21.3%=5.6 (as surfactant) ⁴ | |
| <i>Daphnia magna</i> | 48 hour acute test | WAF unfiltered | LC ₅₀ =19.3%=4,850 EC ₅₀ =0.56%=140 | LC ₅₀ =488 EC ₅₀ =14.2 |
| <i>Daphnia magna</i> | 48 hour acute test | WAF filtered | NOT ACUTELY TOXIC LC ₅₀ >100%>24.8 (as surfactant) ⁴ EC ₅₀ >100%>24.8 (as surfactant) ⁴ | |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute basic test | OWD ³ unfiltered | EC ₅₀ =2,800 | EC ₅₀ =2,060 |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute basic test | OWD filtered | EC ₅₀ >5.8 (as surfactant) ⁴ | |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute 100% test | OWD filtered | EC ₅₀ =11.0 (as surfactant) ⁴ | |
| <i>Gasterosteus acculeatus</i> | 96 hour acute test | OWD unfiltered | LC ₅₀ =3,200 | LC ₅₀ =1,330 |
| <i>Onchorhynchus mykiss</i> | 96 hour acute test | OWD unfiltered | LC ₅₀ =301 | LC ₅₀ =192 |

¹TSEM = Total Solvent Extractable Material

²WAF = Water-Accommodated Fraction

³OWD = Oil-in-Water Dispersion

⁴Toxicity expressed as nominal surfactant concentration, assuming 67% of surfactant present was dissolved in the aqueous phase.

Table 5 Results of New Toxicity Tests on Orimulsion-100 (1996)

| Test Organism | Test Type and Duration | Sample Type | Results Based on Nominal Conc'n (mg/L) | Results Based on TSEM ¹ (mg/L) |
|-----------------------------------|------------------------|-------------------------------|---|---|
| <i>Vibrio fischeri</i> (Microtox) | 15 minute basic test | OWD ² , unfiltered | EC ₅₀ =540 | EC ₅₀ =420 |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute basic test | OWD, filtered | EC ₅₀ >6.8 (as surfactant) ³ | |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute 100% test | OWD, filtered | EC ₅₀ =15.6 (as surfactant) ³ | |
| <i>Gasterosteus acculeatus</i> | 96 hour acute test | OWD, unfiltered | LC ₅₀ =2,270 | LC ₅₀ =1,711 |

¹TSEM = Total Solvent Extractable Material

²OWD = Oil-in-Water Dispersion

³Toxicity expressed as nominal surfactant concentration, assuming 67% of surfactant present was dissolved in the aqueous phase.

Table 6 Results of Analysis of Orimulsion-400 and Orimulsion-100 (1996) Test Solutions

| Test Organism | Orimulsion Formulation | Sample Type | Nominal Concentration (mg/L) | Measured Concentration (mg/L) | | |
|-----------------------------------|------------------------|-----------------------------|------------------------------|-------------------------------|----------|----------|
| | | | | 0 hours | 24 hours | 96 hours |
| <i>Lytechinus pictus</i> | Orimulsion-400 | WAF ¹ unfiltered | 26,660 | 98 | | |
| <i>Lytechinus pictus</i> | Orimulsion-400 | WAF filtered | 26,660 | 45 | | |
| <i>Lytechinus pictus</i> | Orimulsion-400 | Control | 0 | 2 | | |
| <i>Daphnia magna</i> | Orimulsion-400 | WAF unfiltered | 25,175 | 2,527 | | |
| <i>Daphnia magna</i> | Orimulsion-400 | WAF filtered | 25,175 | 39 | | |
| <i>Daphnia magna</i> | Orimulsion-400 | Control | 0 | 2 | | |
| <i>Vibrio fischeri</i> (Microtox) | Orimulsion-400 | OWD ² unfiltered | 11,800 | 8,699 | | |
| <i>Vibrio fischeri</i> (Microtox) | Orimulsion-400 | OWD filtered | 11,800 | 17 | | |
| <i>Vibrio fischeri</i> (Microtox) | Orimulsion-100 | OWD unfiltered | 10,250 | 7,969 | | |
| <i>Vibrio fischeri</i> (Microtox) | Orimulsion-100 | OWD filtered | 10,250 | 20 | | |
| <i>Onchorhynchus mykiss</i> | Orimulsion-400 | OWD unfiltered | 3,750 | 2,177 | 1,795 | 424 |
| <i>Onchorhynchus mykiss</i> | Orimulsion-400 | OWD unfiltered | 938 | 627 | 379 | 23 |
| <i>Onchorhynchus mykiss</i> | Orimulsion-400 | OWD unfiltered | 200 | 133 | | 23 |
| <i>Onchorhynchus mykiss</i> | Orimulsion-400 | Control | Control | 2 | | |
| <i>Gasterosteus acculeatus</i> | Both | Control | | 2 | | 3 |
| <i>Gasterosteus acculeatus</i> | Orimulsion-400 | OWD unfiltered | 10,000 | 4,577 | | |
| <i>Gasterosteus acculeatus</i> | Orimulsion-400 | OWD unfiltered | 2,500 | 887 | | 19 |
| <i>Gasterosteus acculeatus</i> | Orimulsion-400 | OWD unfiltered | 500 | 216 | | |
| <i>Gasterosteus acculeatus</i> | Orimulsion-100 | OWD unfiltered | 10,000 | 8,138 | | |
| <i>Gasterosteus acculeatus</i> | Orimulsion-100 | OWD unfiltered | 2,500 | 1,578 | | 16 |
| <i>Gasterosteus acculeatus</i> | Orimulsion-100 | OWD unfiltered | 500 | 408 | | |

¹WAF = Water-Accommodated Fraction

²OWD = Oil-in-Water Dispersion

Table 7 Comparison of Toxicity Tests on Orimulsion-400 and Orimulsion-100

| Test Organism | Test Type | Sample Type | Orimulsion-400 Toxicity ³ (mg/L) | Orimulsion-100 Toxicity ³ (mg/L) |
|--------------------------------------|------------------------------|--------------------------------|--|---|
| <i>Lytechinus pictus</i> | 20 minute fertilization test | WAF ¹ unfiltered | IC ₅₀ =5,730 P _{0.95} = (5,550-5,870) | IC ₅₀ =5,220* |
| <i>Lytechinus pictus</i> | 20 minute fertilization test | WAF filtered | IC ₅₀ =21.3%=5.6 (as surfactant) ³ | IC ₅₀ =21.6%=7.4* (as surfactant) ³ |
| <i>Daphnia magna</i> | 48 hour acute test | WAF unfiltered | LC ₅₀ =4,850 P _{0.95} = (2,100-6,380) | LC ₅₀ =2,370* P _{0.95} = (1,590-3,425) |
| <i>Daphnia magna</i> | 48 hour acute test | WAF filtered | NOT ACUTELY TOXIC LC ₅₀ >100%>24.8 (as surfactant) ³ | LC ₅₀ =69.9%=23.5* (as surfactant) |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute basic test | OWD ² unfiltered | EC ₅₀ =2,800 P _{0.95} = (1,850-4,220) | EC ₅₀ =540 P _{0.95} = (450-640) |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute basic test | OWD filtered | EC ₅₀ >5.8 (as surfactant) ³ | EC ₅₀ >5.1 (as surfactant) |
| <i>Vibrio fischeri</i> (Microtox) | 15 minute 100% test | OWD filtered | EC ₅₀ =11.0 mg/L (as surfactant) | EC ₅₀ >15.6 (as surfactant) |
| <i>Gasterosteus aculeatus</i> | 96 hour acute test | OWD unfiltered | LC ₅₀ =3,200 P _{0.95} = (2,750-3,720) | LC ₅₀ =2,270 P _{0.95} = (1,620-3210) |
| <i>Onchorhynchus mykiss</i> | 96 hour acute test | OWD unfiltered | LC ₅₀ =301 P _{0.95} = (231-417) | LC ₅₀ =754* P _{0.95} = (469-1,880) |

¹WAF = Water-Accommodated Fraction

²OWD = Oil-in-Water Dispersion

³Toxicity expressed as nominal concentration of Orimulsion, or as nominal surfactant concentration, assuming 67% of surfactant present was dissolved in the aqueous phase.

*Orimulsion (1993); data from Jokuty *et al.* (1995)

For *D. magna*, the unfiltered WAF of Orimulsion-100 was not statistically different than the unfiltered WAF of Orimulsion-400, but the filtered WAF of Orimulsion-100 was more toxic than the filtered WAF of Orimulsion-400 (which was completely non-toxic).

For *G. aculeatus*, the toxicity of the OWDs of Orimulsion-400 and Orimulsion-100 were not significantly different.

For Microtox (*V. fischeri*), the unfiltered WAF of Orimulsion-100 was significantly more toxic than the unfiltered WAF of Orimulsion-400, while the filtered WAFs of both formulations were not toxic at approximately 10,000 mg/L (nominal concentration added), the highest concentration tested. The colour correction protocol was not required, as interfering amounts of colour/turbidity occurred at concentrations higher than the EC₅₀ values.

For *O. mykiss* (rainbow trout), the OWD of Orimulsion-100 (LC₅₀ = 754 [P_{0.95} = 469-1,880]) was significantly less toxic than that of Orimulsion-400 (LC₅₀ = 301 [P_{0.95} = 231-417]). It was found that filtering the test solutions made them clear and that the majority of the TSEM were removed, probably as oil droplets (Table 6). These filtered test solutions contain some residual TSEM (Table 6), dissolved surfactant, parts per billion levels of benzene, toluene, ethylbenzene, and xylene (BTEX), naphthalenes, and PAHs (Potter *et al.*, 1997), and possibly polar oxygenated compounds (Guard *et al.*, 1975).

The cause of any observed toxicity remains unproven. Therefore, there is no single best way to express the toxicity of the filtered solutions. It is unlikely that the low levels of BTEX and naphthalenes found in these solutions are the direct cause of toxicity observed, since they are several orders of magnitude below levels found lethal to *Daphnia magna* and *Artemia sp.* (MacLean and Doe, 1989). The theoretical concentrations of surfactants found in filter-clarified test solutions (Tables 4, 5, and 7) are at and often above levels of a wide variety of surfactants found to have toxic effects on a variety of aquatic organisms (e.g., Abel, 1974; Patoczka and Pulliam, 1990; Wildish, 1974; Lewis, 1991; Lewis and Suprenant, 1983; Johnson *et al.*, 1997), and so surfactants are one possible cause of the observed toxicity.

We have therefore chosen to express the toxicity of filter-clarified test solutions in two ways, as a nominal concentration (usually a percentage of the original filtered solution) and as nominal surfactant concentration. We assumed that 56 to 78% (for calculations we use 67%) of the surfactant dissolves in the water (Calabrese *et al.*, 1997) and so we can express toxicity in terms of nominal surfactant concentration. These calculations have been done and are provided in Tables 4, 5, and 7.

A toxicity identification evaluation of the filtered or water-soluble fractions of Orimulsion would be required to determine the cause(s) of observed toxicity in these solutions. A determination of the toxicity of the surfactants used in both formulations to a variety of aquatic organisms would assist in the Toxicity Identification Evaluation process.

5.4 Conclusions

For most of the toxicity tests conducted, the toxicity of the two Orimulsion formulations was not significantly different. In two cases, Orimulsion-400 was less toxic than Orimulsion-100 (*D. magna*, filtered WAF in fresh water and *V. fischeri*, OWD in salt water). For rainbow trout in fresh water, the OWD of Orimulsion-400 was more toxic than the OWD of Orimulsion-100.

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APPENDIX

Data from Carboy Experiments

| Water Type | Sample Location | Time (hrs) | Beaker Wt. (g) | Beaker + Oil (g) | Oil (g/60 mL) | Oil (ppm) |
|------------|-----------------|------------|----------------|------------------|---------------|-----------|
| Fresh | Top | 0.17 | 129.866 | 129.984 | 0.118 | 1967 |
| Fresh | Top | 0.33 | 128.948 | 129.065 | 0.117 | 1950 |
| Fresh | Top | 0.5 | 129.134 | 129.247 | 0.113 | 1883 |
| Fresh | Top | 1 | 50.4338 | 50.5617 | 0.1279 | 2132 |
| Fresh | Top | 2 | 50.7054 | 50.8150 | 0.1096 | 1827 |
| Fresh | Top | 4 | 50.3600 | 50.4500 | 0.0900 | 1500 |
| Fresh | Top | 6 | 50.3024 | 50.3824 | 0.0800 | 1333 |
| Fresh | Top | 12 | 50.3951 | 50.4581 | 0.0630 | 1050 |
| Fresh | Top | 24 | 50.4544 | 50.5092 | 0.0548 | 913 |
| Fresh | Top | 36 | 53.7110 | 53.7568 | 0.0458 | 763 |
| Fresh | Top | 48 | 52.6068 | 52.6503 | 0.0435 | 725 |
| Fresh | Bottom | 0.17 | 129.993 | 130.101 | 0.108 | 1800 |
| Fresh | Bottom | 0.33 | 130.104 | 130.219 | 0.115 | 1917 |
| Fresh | Bottom | 0.5 | 129.584 | 129.701 | 0.117 | 1950 |
| Fresh | Bottom | 1 | 50.5920 | 50.7189 | 0.1269 | 2115 |
| Fresh | Bottom | 2 | 50.3599 | 50.4758 | 0.1159 | 1932 |
| Fresh | Bottom | 4 | 50.8619 | 50.9831 | 0.1212 | 2020 |
| Fresh | Bottom | 6 | 50.3334 | 50.4508 | 0.1174 | 1957 |
| Fresh | Bottom | 12 | 50.6455 | 50.7382 | 0.0927 | 1545 |
| Fresh | Bottom | 24 | 50.7219 | 50.7804 | 0.0585 | 975 |
| Fresh | Bottom | 36 | 48.8779 | 48.9246 | 0.0467 | 778 |
| Fresh | Bottom | 48 | 50.4596 | 50.4980 | 0.0384 | 640 |
| | | | | | | |
| Brackish | Top | 0.33 | 50.3762 | 50.5147 | 0.1385 | 2308 |
| Brackish | Top | 0.67 | 50.2411 | 50.3762 | 0.1351 | 2252 |
| Brackish | Top | 1 | 49.9731 | 50.1115 | 0.1384 | 2307 |
| Brackish | Top | 2 | 50.3953 | 50.5318 | 0.1365 | 2275 |
| Brackish | Top | 4.5 | 50.3948 | 50.5351 | 0.1403 | 2338 |
| Brackish | Top | 6 | 50.6452 | 50.7844 | 0.1392 | 2320 |
| Brackish | Top | 12 | 50.3333 | 50.4616 | 0.1283 | 2138 |
| Brackish | Top | 24 | 53.2612 | 53.3685 | 0.1073 | 1788 |
| Brackish | Top | 36 | 53.7105 | 53.8177 | 0.1072 | 1787 |
| Brackish | Top | 48 | 50.4615 | 50.5470 | 0.0855 | 1425 |
| Brackish | Bottom | 0.33 | 53.2596 | 53.3948 | 0.1352 | 2253 |
| Brackish | Bottom | 0.67 | 50.4302 | 50.5694 | 0.1392 | 2320 |
| Brackish | Bottom | 1 | 50.4569 | 50.5917 | 0.1348 | 2247 |
| Brackish | Bottom | 2 | 53.5358 | 53.6761 | 0.1403 | 2338 |
| Brackish | Bottom | 4.5 | 50.7217 | 50.8572 | 0.1355 | 2258 |
| Brackish | Bottom | 6 | 50.4338 | 50.5712 | 0.1374 | 2290 |
| Brackish | Bottom | 12 | 50.3597 | 50.4853 | 0.1256 | 2093 |
| Brackish | Bottom | 24 | 48.8778 | 48.9681 | 0.0903 | 1505 |
| Brackish | Bottom | 36 | 52.6068 | 52.6996 | 0.0928 | 1547 |
| Brackish | Bottom | 48 | 50.5924 | 50.6744 | 0.0820 | 1367 |

| Water Type | Sample Location | Time (hrs) | Beaker Wt. (g) | Beaker + Oil (g) | Oil (g/60 mL) | Oil (ppm) |
|------------|-----------------|------------|----------------|------------------|---------------|-----------|
| Salt | Top | 0.33 | 50.3917 | 50.5242 | 0.1325 | 2208 |
| Salt | Top | 0.67 | 50.3819 | 50.5118 | 0.1299 | 2165 |
| Salt | Top | 1 | 50.5298 | 50.6559 | 0.1261 | 2102 |
| Salt | Top | 2 | 50.3818 | 50.5054 | 0.1236 | 2060 |
| Salt | Top | 4.5 | 50.3020 | 50.4118 | 0.1098 | 1830 |
| Salt | Top | 6 | 50.8617 | 50.9594 | 0.0977 | 1628 |
| Salt | Top | 12 | 50.4543 | 50.5334 | 0.0791 | 1318 |
| Salt | Top | 24 | 50.4596 | 50.5099 | 0.0503 | 838 |
| Salt | Top | 36 | 50.3919 | 50.4282 | 0.0363 | 605 |
| Salt | Top | 48 | 50.4362 | 50.4652 | 0.0290 | 483 |
| Salt | Bottom | 0.33 | 49.8944 | 50.0238 | 0.1294 | 2157 |
| Salt | Bottom | 0.67 | 49.4956 | 49.6221 | 0.1265 | 2108 |
| Salt | Bottom | 1 | 50.5335 | 50.6582 | 0.1247 | 2078 |
| Salt | Bottom | 2 | 49.4705 | 49.5942 | 0.1237 | 2062 |
| Salt | Bottom | 4.5 | 50.7055 | 50.8226 | 0.1171 | 1952 |
| Salt | Bottom | 6 | 50.5914 | 50.6961 | 0.1047 | 1745 |
| Salt | Bottom | 12 | 50.3549 | 50.4208 | 0.0659 | 1098 |
| Salt | Bottom | 24 | 50.3352 | 50.3724 | 0.0372 | 620 |
| Salt | Bottom | 36 | 49.8965 | 49.9277 | 0.0312 | 520 |
| Salt | Bottom | 48 | 50.8626 | 50.8904 | 0.0278 | 463 |

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