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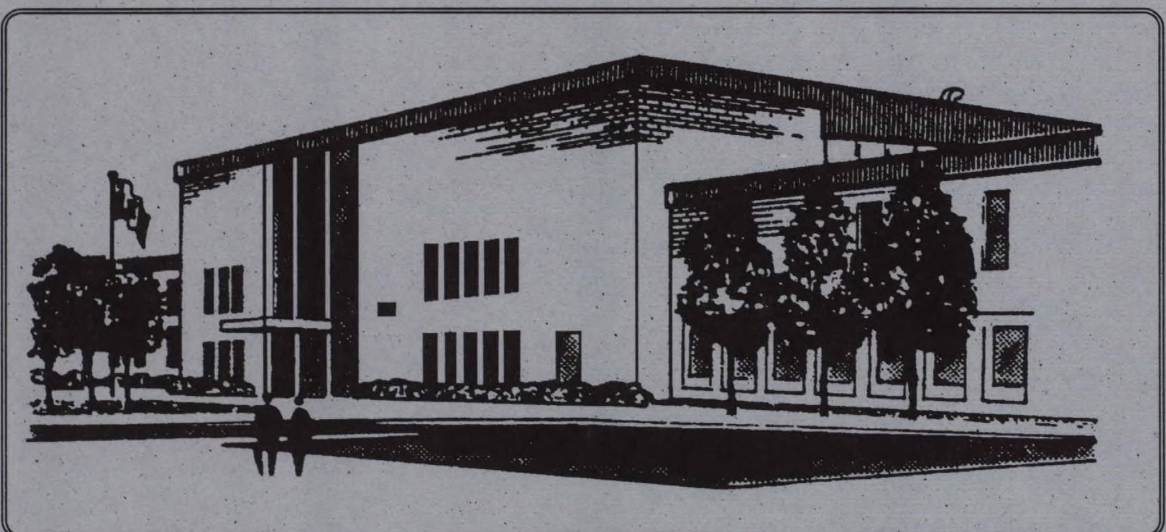
Shoreline Studies Program
Removal of Stranded Bitumen from Intertidal Sediments Using Chemical Agents

Phase I: Screening of Chemical Agents



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Orimulsion Shoreline Studies Program
Removal of Stranded Bitumen from Intertidal Sediments Using Chemical Agents

Phase I: Screening of Chemical Agents

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PREFACE

This report presents the findings from a preliminary study on the use of chemical agents to enhance the removal of stranded bitumen from shorelines in the event of an accidental spill of Orimulsion. This study is part of the ongoing "Orimulsion Shoreline Studies Program" for spill preparedness. The objective of the Program is to develop scientific/technical information and direction on the behaviour and cleanup of Orimulsion on different types of shorelines and under different conditions. The goal is to deliver both operational guidance and scientific information of a quality required to provide spill planning and response teams with more informed technical support for decisions regarding shoreline treatment activities. The program consists of staged component studies that address issues related to Orimulsion on shorelines. Current outputs will feed into a comprehensive shoreline response guidance manual.

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ABSTRACT

This project was carried out to determine the potential of commercial beach cleaning products and dispersants for enhanced removal of weathered bitumen coatings from shoreline sediments. Six surface washing agents, which are also called beach cleaners, and five dispersants were selected for testing. A simple laboratory test was developed to quantify the removal of weathered bitumen from hard surfaces by commercial chemical agents. The test was based on a standard test procedure for surface washing agents ('Surface Washing Test'), developed and currently used by Environment Canada. The selected surface washing agents and dispersants were tested to determine their comparative effectiveness at removing weathered bitumen from a solid surface. Tests were carried out at 5 and 22°C. The effectiveness of the chemical agents was also tested with Bunker C for comparison purposes. The general conclusions were that surface washing agents enhanced the removal of weathered bitumen by 23 to 36% at room temperature, whereas dispersants and salt water alone had no effect. The surface washing agents were more effective on Bunker C than on bitumen.

RÉSUMÉ

On a effectué ce travail pour déterminer la capacité de produits nettoyants et de dispersants du commerce de déloger davantage les enduits de bitume altéré que l'on trouve sur les sédiments de plages. On a retenu pour les essais six agents nettoyants de surface dits également « nettoyants de plages » *(beach cleaners)* et cinq dispersants. On a mis au point un test simple de laboratoire pour quantifier l'enlèvement du bitume altéré des surfaces dures par les agents chimiques du commerce. Le test se fondait sur un mode opératoire uniformisé, élaboré pour les agents de nettoyage des surfaces (test de lavage des surfaces) et actuellement utilisé par Environnement Canada. On a déterminé l'efficacité comparative des agents et dispersants retenus à l'égard du bitume altéré d'une surface solide. Les tests ont été réalisés à 5 et à 20 °C. Pour comparaison, on a aussi testé l'efficacité des agents chimiques à l'égard du mazout brut. Les conclusions générales sont que les agents de lavage en surface ont augmenté le taux d'élimination du bitume altéré de 23 à 36 %, à la température ambiante, tandis que les dispersants et l'eau salée employés seuls n'ont eu aucun effet. Les agents de lavage en surface ont été plus efficaces à l'égard du mazout brut que du bitume.

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1. INTRODUCTION

1.1 Background

Orimulsion is the trade name of a Venezuelan petroleum product that can be used as a substitute for coal or fuel oil in power generating plants. The product consists of approximately 70% Orinoco bitumen, 30% water, and 0.2% surfactant to maintain the stability of this oil-in-water emulsion. The product is currently exported to a number of countries worldwide including Canada. The need for shoreline response preparedness in the event of an accidental spill of Orimulsion at sea has led to the development of a long-term series of investigations under the umbrella program "Orimulsion Shoreline Studies".

The project outlined in this report addresses the potential use of chemical agents for the removal of bitumen coatings as a result of an Orimulsion spill on surface or in subsurface sediments of the intertidal zone. The issues concerning the use of chemical agents relate to the removal/recovery effectiveness of the technique and to the resultant changes to the fate of the oil/bitumen, both of which have a bearing on the suitability of this technique as a shoreline cleanup option.

It should be noted that oil or bitumen in the subsurface intertidal sediments still presents one of the more difficult situations for shoreline cleanup. In low to moderate wave environments, the persistence of subsurface oil can be relatively long, i.e., years, and as such, may present an unacceptable long-term chronic source of contamination. Removal of subsurface oil/bitumen, especially in coarse sediments, can be difficult, requiring either invasive techniques (e.g., sediment removal) or in-situ techniques. In the interest of spill response preparedness, investigations were therefore suggested to determine whether, how, and under what conditions, chemical agents are a suitable cleanup response for the removal of bitumen from shorelines.

1.2 Oil Spill Treating Agents

Many chemical agents have been developed and promoted over the years for the treatment of oil spills including solidifiers, demulsifying agents, surface-washing agents, and dispersants. Those agents that would be most likely considered for use in a shoreline cleanup operation are surface-washing agents, also known as beach cleaners, and dispersants.

Dispersants have approximately the same solubility in water as in oil and cause the oil to be dispersed into the water column in the form of fine droplets. Dispersants can be applied from boats or low-flying aircrafts, although aircraft application has been favoured in recent years as a greater area can be treated. Dispersants used for oil spill response have been specifically designed to operate on oil on open waters. Dispersant effectiveness is dependent on oil type and sea state. Lighter crude oils disperse more readily than heavier ones, and a minimum sea energy is required for dispersants to be effective. During laboratory tests and field trials, dispersant effectiveness has been recorded on light and medium oils as 30% and 20% respectively. Dispersants are known to have little or no effectiveness on residual fuels (Fingas and Mansfield, 1994).

Surface-washing agents or beach cleaners are agents that remove oil from solid surfaces such as beach sediment by the mechanism known as detergency (Fingas and Mansfield, 1994). Unlike dispersants, which cause the oil to disperse into the water column, oil removed by beach cleaners refloats to the water's surface where it can be collected. Because the properties of surface washing and dispersancy are orthogonal, good surface washing agents are generally poor dispersants, and vice versa. When using surface washing agents to clean oil shorelines, the goal is (i) to remove oil the from the contaminated surface and (ii) to be able to recover that oil as it is refloated on the water surface.

Chemical agents have been used or tested during cleanup operations for a number of spills. Corexit 9580 and PES-51 were tested after the *Morris J. Berman* spill in January,1994 when a No. 6 Fuel Oil was released and contaminated Puerto Rican shorelines (Michel and Benggio, 1995). The chemical agents used in conjunction with high pressure washing were found to be more effective than high pressure washing alone. Studies conducted with Bunker C and South Louisiana crude demonstrated the potential of using Corexit 9580 to remove oil from marsh vegetation and thereby reduce the toxic effect of spilled oil (Pezeshki *et al.*, 1995).

1.3 Objective

The objective of the project **Phase I: Screening of Chemical Agents** was to determine the potential for enhanced removal of weathered bitumen coatings from shoreline sediments by use of commercial beach cleaning products and dispersants.

This was the first step in assessing the role of chemical agents as a shoreline cleanup response option.

2. EXPERIMENTAL DESIGN

2.1 Project Overview

There are three potential phases of this project, as outlined below. The scope of the second and third phases will depend on the outcome of the previous phases.

Phase 1: Screening of Chemical Agents

This component consists of testing existing products for effectiveness potential and includes the following tasks.

- Developing a simple laboratory test to quantify the removal of weathered bitumen from hard surfaces by commercial chemical agents. A standard test procedure for testing surface washing agents, developed and currently used by Environment Canada, was used as the basis, and modified as required.
- Testing of selected surface washing agents and dispersants to determine the comparative effectiveness of these products for removing weathered bitumen from a solid surface.

Phase II: Sediment Column Testing of Chemical Agents

This component of the project would test promising products from Phase I in sediment columns, using a similar methodology to that used in previous sediment column experiments conducted with a variety of oils and Orimulsion (Harper and Kory, 1997).

A number of variables likely to affect bitumen penetration and retention, bitumen and water movement, and the effectiveness of the chemical agent will be investigated including sediment grain size, loading, type of chemical agent, temperature, and turbulence/flushing level. In addition to the above sediment column tests, a similar study will be conducted to focus on surface coatings only, using larger sediments.

Phase III: Full-scale Testing

The ultimate test of the effectiveness of any spill response option is full-scale testing preferably under realistic environmental conditions. Such testing could be performed in large-scale beach basins, where some control of parameters is possible, and in the field under realistic conditions. In addition to effectiveness testing, field trials could also include studies related to ecological impact on treated and untreated shoreline contaminated with bitumen.

2.2 Terminology

Harper and Kory, 1997 developed a provisional terminology for the different phases of Orimulsion following observations made during laboratory testing. Orimulsion only exists as Orimulsion when it consists of its original components, 70% bitumen and 30% water. Once Orimulsion is spilled on water, it quickly separates and changes into the following possible forms: dispersed bitumen and weathered bitumen (Harper and Kory, 1997). These are described in Table 1.

Table 1 Provisional Terminology of Orimulsion Phases

PHASE	DESCRIPTION
Orimulsion[1]	Orimulsion is a synthetic product consisting of approximately 70% Orinoco bitumen, 30% water, and < 0.2% surfactant.
Dispersed Bitumen[1]	Appears as a dark chocolate colour, opaque and floats as a distinct layer on top of a container; it is not sticky and pours easily. Partitioning of this layer was observed over time with gentle mixing resulting in a 'sub-phase' of *diluted bitumen*.
Weathered Bitumen[1] (on water)	Black, highly opaque, very viscous, sticky, often a "tarry", "ropey" or "lumpy" consistency; very buoyant; often incorporates air bubbles (possibly due to the artificial mixing technique) and forms a "skin" on the water surface; requires vigorous mixing and air to form.
Weathered Bitumen Coating[1] (on sediments)	Hard, "tarry" coating on grains and within small pore spaces of the sediments; forms when dispersed bitumen is in contact with air.
Weathered Orimulsion[2]	Simular in properties to *weathered bitumen*, but obtained through evaporation of water from Orimulsion. Contains the emulsifying surfactant.

1. From Harper and Kory, 1997
2. From Jokuty *et al.*, 1995

For the purposes of this study, an additional term, "weathered Orimulsion", is suggested for Orimulsion prepared for the various physical-chemical properties analysis. Typically, oils undergoing physical-chemical analysis are 'weathered' in a rotovap which removes the lighter components of the oil, simulating the evaporation of spilled oil at sea for predetermined periods of time (Jokuty *et al.,* 1995). Heavy fuel oils and bitumen contain very little of these lighter components and therefore do not weather to any great extent. In the case of Orimulsion, weathering this product in the rotovap results in the removal of the water fraction. Therefore, the term "weathered Orimulsion" in this case will refer to the bitumen remaining after evaporation of the Orimulsion (water fraction) by the rotovap technique.

2.3 Test Variables

These tests were intended as a preliminary assessment of the effectiveness of various chemical agents at removing weathered bitumen from solid surfaces. Tests with Bunker C were also included for comparison. All tests with surface washing agents were carried out in triplicate, while the tests with dispersants were done in duplicate. The following is a summary of the test parameters.

Oils: weathered bitumen and Bunker C
Temperature: 5 and 22.5 ±1°C
Rinse water: salt water (3.3%)
Chemical agents: six surface washing agents, five dispersants, and one blank (water)

3. MATERIALS AND METHODS

3.1 Test Oils

The test oils used in the project were:

- weathered bitumen; and
- Bunker C.

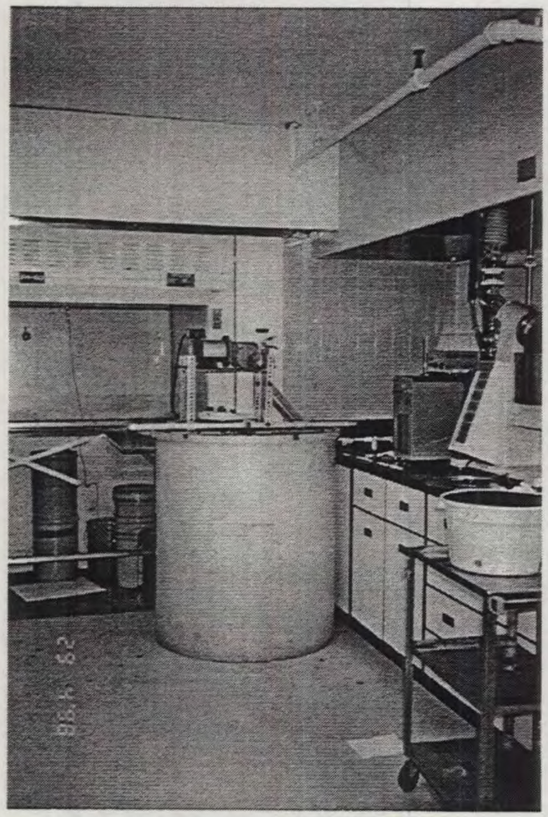
A summary of some of the physical properties of these oils is given in Table 2. More extensive information can be found in the *Catalogue of Crude Oil Properties* (Environment Canada, 1998) and in Jokuty *et al.*, 1995, 1998, and 1999.

Of the various derivative forms of Orimulsion that could result following a marine spill, weathered bitumen is the most likely one to impact a shoreline (Harper and Kory, 1997). Weathered bitumen was therefore selected for this preliminary study.

Table 2 Physical Properties of Orimulsion-400 and Bunker C

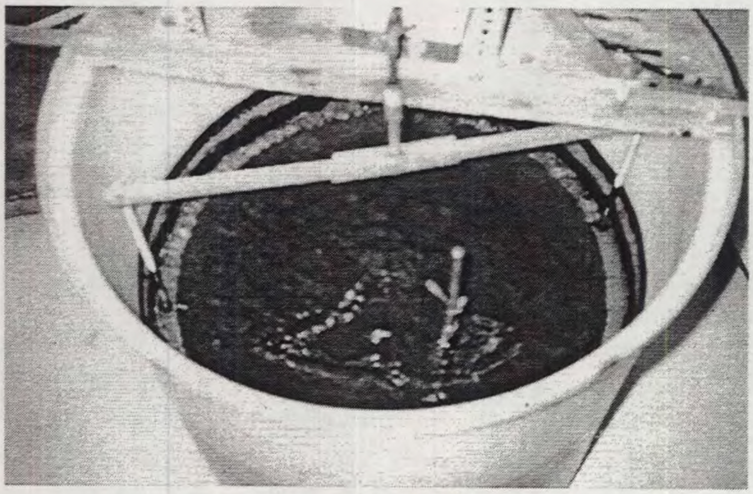
Property	Orimulsion-400 (Fresh)	Orimulsion-400 (Evap. 29%)	Bunker C (Fresh)
Appearance (at 15°C)	Black; flows easily	Black; solid	Black; barely flows
Water content (wt%)	30	0.1	0.1
Pour point (°C)	0	33	15
Density at 0°C (g/cm³)	1.0162	1.0222	0.9941
Density at 15°C (g/cm³)	1.0095	1.0202	0.983
Viscosity at 0°C (mPa•s)	1065 @ 100/s	2.2×10^8 @ 1/s	1.04×10^6
Viscosity at 0°C (mPa•s)	450 @ 100/s	9.0×10^6 @ 1/s	4.5×10^4

The weathered bitumen used for the Surface Washing Agent Tests was obtained following dispersibility tests with Orimulsion using the 'Oscillating Hoop' method (Jokuty *et al*, 1998). The apparatus, shown in Figure 1, consists of a cylindrical tank measuring 90 cm in diameter and 106 cm in height. The tank is filled with water to a depth of approximately 60 cm. Concentric wave patterns are produced by a vertically oscillating flat stainless steel hoop located along the inside perimeter of the tank. Orimulsion-400 is added to the tank containing salt water (3.3%) at a ratio of 1:1000 bitumen to water. The dispersibility test lasted approximately two hours, during which the bitumen particles of the Orimulsion initially were dispersed into the water column, then floated to the water surface. It is this bitumen, which had resurfaced and adhered to the tank



a) Oscillating Hoop apparatus for preparation of weathered bitumen

b) Rotovap apparatus for preparation of weathered Orimulsion®



c) Resurfaced weathered bitumen

Figure 1: Set-up for the Preparation of Weathered Bitumen and Orimulsion®

walls, that was collected for the Surface Washing Tests.

Chemical analysis has revealed that when bitumen is prepared using the rotovap evaporation technique, the surfactant, used to maintain the bitumen-in-water emulsion, remains with the bitumen (Wang, 1998). The surfactant does not evaporate at the temperatures reached during the weathering procedure. Studies have shown that the surfactant, which is water-soluble, enters into the water phase when Orimulsion is added to a volume of water. Studies of the fate of the surfactant in Orimulsion-100 have demonstrated that with a dilution ratio of 1:100 (Orimulsion: salt water) approximately 56 and 78% the surfactant is transferred to the aqueous phase (Potter *et al.,* 1997).

Weathered bitumen, rather than evaporated Orimulsion,was used for the Surface Washing Test to reduce the effect of the surfactant remaining in the bitumen. The bitumen used in this project was derived from Orimulsion-400, which contains a different surfactant than Orimulsion-100. Although the fate of the surfactant in the Orimulsion-400 formulation has not been studied as extensively as the previous formulation, it is assumed that the weathered bitumen obtained by the dilution method would more realistically represent weathered bitumen formed at sea.

3.2 Test Spill Treating Agents

A number of agents were selected from the list of surface washing agents and dispersants that have been tested by Environment Canada. Of the several hundred agents tested, only a limited number are currently available. Few surface washing agents meet the toxicity limits established by Environment Canada (96-hour Rainbow Trout LC-50 of greater than 1000 mg/L for surface washing agents and 100 mg/L for dispersants). Only the Corexit products appear on the Environment Canada 'Approved Treating Agents' list for oil spill response applications. Other agents were also selected for testing for comparison purposes and because some may perform differently with weathered bitumen than with the standard test oil (Bunker C) used for the Surface Washing Test. These chemicals were selected based on effectiveness and toxicity.

Six surface washing agents, or beach cleaners, and five dispersants were selected for testing using the 'Surface Washing Test'. The Corexit dispersants were developed specifically for dispersing crude oil on water, while the other dispersant products on this list are industrial or household cleaning products. All of the surface washing agents selected for this test were specifically designed for oil spill cleanup.

Surface washing agents:

- Corexit 9580
- D-Limonene
- Oriclean
- Tesoro Pes 51
- BP1100X
- Champion JS10-232

Dispersants:

- Corexit 9500
- Corexit 9527
- Citrikleen 1850
- Palmolive (dish soap)
- Simple Green

3.3 Surface Washing Test Method

The beach cleaners and dispersants were tested using the Environment Canada standard 'Surface Washing Test' (Appendix A). This test is a comparative test which measures the amount of oil removed from a solid surface when a chemical agent is allowed to soak into the oil and then rinsed with water (Fingas *et al.*, 1995). The following are the main steps in the procedure.

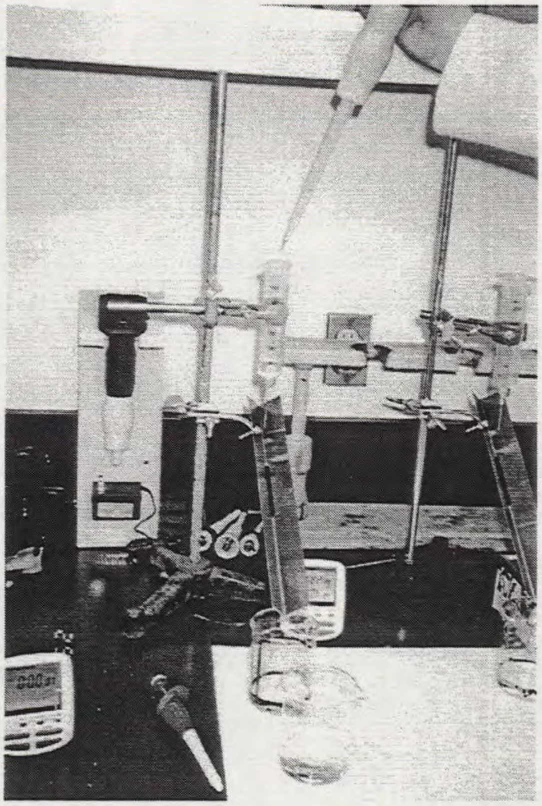
17. The test oil is aspirated using a 'pipette' and applied along the crease of a pre-weighed metal (stainless steel) trough. The weathered bitumen was heated to facilitate application.
18. Bitumen was applied to a pre-weighed trough and weighed.
19. The chemical agent was applied along the entire surface of the oil, with the trough lying horizontally. For tests at 5°C, the trough and oil were allowed to cool in the cold room for 20 minutes prior to adding the agents. Additionally, the chemical agents were stored at 5°C.
20. After a 10-minute waiting period, the trough was positioned at a 30° angle from horizontal using a laboratory stand. A syringe was positioned above the trough to dispense the rinse water. The lower end of the trough was placed over a beaker to collect the runoff.
21. After a second 10-minute waiting period, a second rinse of salt water was applied.
22. The trough was dried, re-weighed, and the amount of oil removed from the trough was calculated.

The tests were carried out at room temperature and at 5°C in a cold room. The agents were stored and applied to the bitumen or Bunker C at each test temperature. The setup is shown in Figure 2. Tests with surface washing agents were carried out in triplicate whereas tests with dispersants were carried out in duplicate. Replicate values were within 3.4% for bitumen and 6.8% for Bunker C.

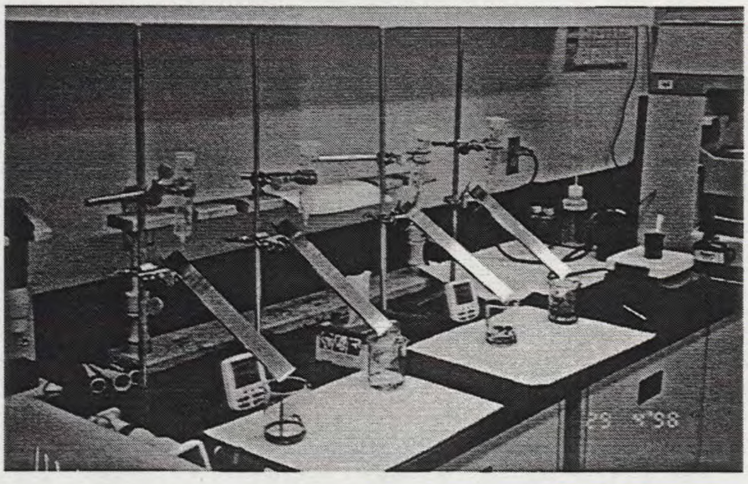
Some modifications were made to this test method, which was designed to use Bunker C as the test oil, to render it more suitable for testing with weathered bitumen as the test oil. These included the following:

- increasing the length over which the oil is applied to the trough by 50%; (In the original test method, following application of Bunker C to the trough, the trough was placed vertically for a period of 10 minutes causing the oil to flow. The length of the trough covered by oil was thereby increased by approximately 50%. As bitumen does not flow, it was applied over this length).
- omitting the standing time prior to addition of the chemical agent; and
- increasing the volume of rinse water from 5 to 10 mL.

a) Application of bitumen to trough



b) Flushing with salt water



c) Test set-up

Figure 2: Test Set-up for Surface Washing Tests

4. RESULTS

Six commercial surface washing agents and five dispersants were tested for their effectiveness in enhancing the removal of weathered bitumen from a solid surface by flushing with salt water. The results of the surface washing tests are given in Table 3. The complete data set is provided in Appendix B. It should be noted that this test is meant as a preliminary screening and ranking of potential products rather than as a test of their absolute effectiveness. The toxicity for each of these agents also is included in Table 3. These values were obtained from the Environment Canada Spilltox Database (Blenkinsopp,1999), which contains the toxicity of oils, chemicals, and spill treating agents and is maintained by the Emergencies Science Division of Environment Canada.

Table 3 Surface Washing Agent Test Results

PRODUCT	PERCENT OIL REMOVED				TOXICITY
	Orimulsion		Bunker C		Rainbow Trout 96-hour LC-50 (mg/L)
	22°C	5°C	22°C	5°C	
D-Limonene	36	20	46	32	35
PES 51	32	23	42	30	14
Corexit 9580	27	15	57	24	>10,000
Oriclean	27	14	35	19	70
BP1100X	23	10	44	12	2900
Champion JS10-232	0	-4	27	-1	1061
Simple Green	0	--	--	--	205
Palmolive	-1	--	--	--	13
Corexit 9500	-1	--	--	--	354
Corexit 9527	-1	--	--	--	33
Citrikleen 1850	-2	--	--	--	18
Blank (water)	0	--	2	--	--

The data show that surface washing agents enhanced the removal of weathered bitumen, while dispersants had no effect. Between 23 and 36% of the initial oil was removed when surface washing agents were applied to the weathered bitumen at room temperature, followed by two rinses with salt water. It was observed during these tests that most of the oil was removed on the first rinse. No bitumen was removed when flushed with salt water only. Dispersants, applied to the weathered bitumen prior to flushing, did not enhance removal. The negative percent removal observed for some of the dispersants indicates that the agent did not completely flush away with the water rinses. At 5°C, the surface washing agent effectiveness ranged from 10 to 20%. The agents were roughly 30 to 55% less effective at the lower temperature. PES 51 appeared to be the least affected by temperature, while D-Limonene was the most affected.

The agents were also tested with Bunker C for comparison, using the modified standard method. It is immediately apparent from the data that Bunker C is more readily removed than bitumen. While all agents were more effective with Bunker C than with bitumen, with the exception of Champion JS10-232, the effectiveness was within the same order of magnitude. Interestingly, the surface washing agents ranked differently in terms of effectiveness with Bunker C than with bitumen. Corexit 9580 was the most effective agent in these currents test and in earlier screening tests performed by Environment Canada (Fingas *et al.,* 1994) with Bunker C as the test oil. In addition, flushing with water alone was not effective in removing bitumen, whereas 2% of the Bunker could be removed. The effect of temperature was more pronounced with Bunker C than with bitumen.

The toxicity data presented in Table 2 is from 96-hour Rainbow Trout LC-50 test results expressed as milligrams of chemical agent per litre of water (mg/L). Environment Canada requires that chemicals used for oil spill response meet the following toxicity levels: >1000 mg/L for surface washing agents and >100 mg/L for dispersants. Of the agents tested, Corexit 9580, Corexit 9500, BP 1100X, Champion JS10-232, and Simple Green (if used as a dispersant) meet these requirements.

5. DISCUSSION

5.1 Effectiveness of Surface Washing Agents

These preliminary tests have demonstrated that some surface washing agents may have the potential to enhance hydraulic washing for the removal of bitumen stranded on shorelines. All surface washing agents tested were more effective than water alone except Champion JS10-232. All products removed Bunker C more effectively than bitumen. However, with the exception of Champion JS10-232, the results were all within the same order of magnitude.

A decrease in temperature from 22 to 5°C resulted in a significant decrease in removal effectiveness with bitumen and Bunker C. At the lower temperature, however, the difference in effectiveness between Bunker C and bitumen was smaller.

The effect of temperature on the removal of bitumen from sediment using hydraulic flushing has been noted in previous work (Harper and Kory, 1997). Preliminary column studies indicated that temperatures higher than 25°C are likely required to mobilize weathered bitumen. Larger scale testing of high pressure washing systems to remove bitumen (derived from Orimulsion) from various types of solid surfaces indicated that hot water was more effective than cold water (Clement *et al.*, 1997). One of the conclusions from these tests was that solvents (e.g., diesel) and beach cleaners (Corexit 9580) are most effective when applied to a thin layer of bitumen (i.e., <1 mm). The results described in Harper and Kory, 1997 and Clement *et al.*, 1997, combined with the findings of this current study suggest that surface washing agents could be effective for the removal of weathered bitumen coatings, which are likely to be deposited in as thin layers on beach sediment.

It should be noted that although Corexit 9580 did not perform as well as other agents with bitumen, the manufacturer recommended a 30- to 60-minute soak time prior to flushing rather than the 10 minutes used in the standard test method. Greater effectiveness would therefore be expected with a longer soak time. The toxicity of Corexit 9580 is orders of magnitude lower than that of other surface washing agents, which combined with its effectiveness, make this product a preferable choice for shoreline treatment.

5.2 Effectiveness of Dispersants

None of the dispersants tested were effective in removing bitumen from a solid surface when applied as a surface washing agent. Earlier tests with these dispersants and Bunker C have indicated a very small degree of effectiveness. A highly effective dispersant is typically a poor beach cleaner, therefore this result was not unexpected. However, these results do not necessarily preclude the use of dispersants for cleaning beach sediment.

The dispersants were tested under low energy conditions, although it is known that a minimum degree of energy is required for dispersants to be effective. Dispersant effectiveness results in the current testing were therefore only applicable to a low energy beach spill scenario and without complimentary high pressure washing. The results are, however, directly comparable to the surface washing agent performance (i.e., how well do dispersants perform when used like a chemical beach cleaner). Flushing at higher pressures may enhance the effectiveness of dispersants for the removal of bitumen from shoreline material. Further experimental work is required to assess this possibility and to determine optimal operational conditions and methods. Tests should assess the combined use of dispersants with deluge or hydraulic washing.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

These preliminary investigations have provided some useful information about the use of chemical agents in a shoreline cleanup operation of bitumen resulting from an Orimulsion spill. A number of conclusions concerning the feasibility of using surface washing agents or beach cleaners can be made.

1. There is a potential for the use of chemical agents in the removal of stranded bitumen from shorelines.
2. The effectiveness of the surface washing agents tested ranged from 23 to 36% removal of bitumen. Of the agents tested, D-Limonene was the most effective.
3. A decrease in temperature from 22°C to 5°C resulted in a decrease in effectiveness of 28 to 56%. PES-51 was least affected by temperature.
4. When applied and tested as a surface washing agent, dispersants were not effective in removing bitumen from a solid surface.
5. Only Corexit 9580 and BP 1100X were both effective and met the Environment Canada toxicity requirements.

6.2 Recommendations

The findings from these preliminary investigations demonstrated a potential for using chemical agents to remove stranded bitumen from solid surfaces. Further work is recommended to define the capabilities, limitations, and operational conditions for the use of chemical treating agent to remove stranded bitumen from shorelines. The following issues should be addressed.

1. There is a need to develop a standard method for the preparation of dispersed and weathered bitumen for experimental purposes.
2. Phase II of this project is recommended which could include the following.

- Bench-scale testing of a selected product using the Surface Washing Test method to investigate the following variables: temperature, soak time, and flushing volume.
- The recommended surface washing agent for further testing would be Corexit 9580. While it was not the most effective agent tested, it was the most effective of those agents meeting the acceptable levels of toxicity.
- Column experiments are recommended to assess the use of treatment chemicals to remove weathered bitumen and weathered bitumen coatings from shoreline sediment. Test parameters could include temperature, soak time, salinity, tidal cycles, sediment grain size, SWA application method, and number of applications. These experiments would also address the fate and behaviour of released bitumen.

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APPENDIX A
Surface Washing Test Methods

Surface Washing Test

Remove the clean trough from drying oven. Place the trough on a Kimwipe near the balance or in a suitable place for cooling. After approximately seven to ten minutes, check to see if the trough is cool or cold to the touch about halfway along its length. If not, allow it to cool longer.

While the trough is cooling, measure the oil to be used in the test with an SMI Digitron positive displacement pipette. Set the pipette to 150 μL. Aspirate the oil, heavy Bunker C, which has been previously stirred, into the pipette and make sure no air bubbles are present. Wipe the end of the pipette tip to ensure that the oil inside the tip is flush with the end.

Place the cool, dry trough on the balance and allow reading to become stable, then record the weight. Return the trough to work area. Pick up the trough and dispense the oil in the pipette tip onto the trough in a slick of even thickness along its length. The slick is positioned along the fold of the trough at approximately 160 mm from the trough's lower end and moved upward in an even flowing motion for about 45 to 50 mm. Any remaining oil on the pipette tip can be removed by wiping the tip end on the trough at a point just below the beginning of the slick. Place the oiled trough on the balance. Record the weight of the oiled trough. Aspirate the surface washing agent into the pipette. The pipette is set to 30 μL.

Apply the washing agent onto the slick. This is accomplished by depressing the plunger of the SMI Digitron pipette until a drop protrudes about halfway out of the tip. Place the drop onto the oil slick. Repeat this technique in order to get a thin and even coating over the slick. Place the trough horizontally for a ten minute SWA soaking time.

At t=9:45 minutes, set up the trough in the stand in a way that the needle (usually 18 gauge in preliminary and most "standard" runs) can be positioned to let the water run down from the trough for approximately 5 to 10 mm before the oil slick. The lower end of the trough will just clear the tip of a 250-mL Pyrex waste beaker that is set up to catch the runoff. The spout of the beaker is placed just beneath the lower end of the trough and the inclination angle from horizontal is adjusted to 30°. The point of impact of the water rinse stream is located in the centre of the trough's fold, 205 mm from the lower end of the trough.

Aspirate water into the oxford pipette. At t=10 minutes place 5 mL of salt or fresh water in the rinse dispensing syringe body. The water should then drip out of needle onto the trough thus rinsing away the oil/SWA mixture.

At t=19:45 minutes, aspirate 5 mL of water into the oxford pipette. At t=20 minutes, repeat the rinse procedure.

At t=30 minutes, visually examine the trough to determine how much water remains on or in the oil slick (the water is fairly obvious). Cut Kimwipes into 45 by 50 mm pieces and roll between finger and thumb tightly to form blotters. Start at the narrow end of the rectangular swath and roll lengthwise. Do not blot out water droplets on the oil until the Kimwipe roll has been dampened by blotting up water from an area where there is little or no oil. There is usually a droplet of water at the end of the needle and at the extreme lower end of the trough. The slightly dampened blotter roll has a lesser affinity for picking up oil, thus it will blot up the remaining water without removing the oil that is on the trough. To blot out the water on the oil, it is best to place the end of the dampened roll into a droplet that is in the middle of the slick. Once the water has been removed, the trough can be weighed and recorded.

Calculation:

Amount of oil deposited = (trough weight + oil) - trough weight (1)

Amount of oil removed = (trough weight + oil) - rinsed, blotted trough weight (2)

Percentage of oil removed (POR) = (2) / (1) x 100

Blanks should be run using the same procedure. The surface washing agent would not be applied at t=10 minutes for the blanks; however, rinses would still be run at t=20 and t=30 minutes.

Elevated temperature rinsing is assessed using the same procedure except rinsing water is warmed up to elevate the temperature, for example, 71^0 C in our "hot water" rinsing runs.

Different gauge needles, with a smaller internal diameter, may be used to give lengthened rinse times due to smaller flow rates. For example, it takes about 10 minutes to drop 5 mL of water with a 22-gauge needle, but only takes 42 seconds with an 18-gauge needle.

After the final weighing is completed, the trough is cleaned by using 3M polypropylene oil-sorb mat. The mat pieces are approximately 20 by 20 mm and held with needlenose pliers. The excess oil is wiped off. Methylene chloride (DCM) is used to rinse the trough in order to dissolve and carry away the remaining oil film. The trough is then rinsed with plenty of fresh water followed by acetone and a wipe with a Kimtowel. The trough is placed in a drying oven for two to three minutes to remove any moisture, then removed from the oven and allowed to cool.

APPENDIX B
Test Data Set

Oil	Product	Temp (C)	Trough#	Position	Clean	Oiled	Washed	Weight of Oil	Final Weight	% Effect.	Average Effect.	Standard Deviation
Orimulsion	C9580	21.5	10	3	116.7787	116.9284	116.8857	0.1497	0.0427	28.5		
	27.35%	21.5	15	1	115.0139	115.1628	115.1254	0.1489	0.0374	25.1		
		21.5	6	1	117.2058	117.3540	117.3119	0.1482	0.0421	28.4	27.3	1.9
	PES51	21.5	15	2	115.0138	115.1649	115.1162	0.1511	0.0487	32.2		
	32.30%	22.0	9	1	117.2046	117.3564	117.3049	0.1518	0.0515	33.9		
		21.5	12	3	117.8811	118.0324	117.9859	0.1513	0.0465	30.7	32.3	1.6
	Oriclean	21.5	6	2	117.2060	117.3570	117.3158	0.151	0.0412	27.3		
	26.57%	22.0	12	4	117.8818	118.0307	117.9862	0.1489	0.0445	29.9		
		21.5	8	2	116.4391	116.5917	116.5573	0.1526	0.0344	22.5	26.6	3.7
	D-Limonene	22.5	11	1	116.7354	116.8870	116.8337	0.1516	0.0533	35.2		
	35.65%	22.5	14	2	117.3941	117.5418	117.4891	0.1477	0.0527	35.7		
		22.5	9	3	117.2048	117.3541	117.3002	0.1493	0.0539	36.1	35.6	0.5
	BP1100X	22.5	10	4	116.7774	116.9212	116.8867	0.1438	0.0345	24.0		
	22.87%	22.5	1	3	116.3585	116.5115	116.4757	0.153	0.0358	23.4		
		23.0	2	2	116.7250	116.8805	116.8475	0.1555	0.033	21.2	22.9	1.5
	JS10-232	22.5	5	2	117.4257	117.5802	117.5781	0.1545	0.0021	1.4		
	-0.07%	22.5	15	1	115.0142	115.1672	115.1696	0.153	-0.0024	-1.6		
		23.0	4	1	117.5764	117.7267	117.7267	0.1503	0	0.0	-0.1	1.5
	C9500	21.5	7	1	117.0283	117.1798	117.1811	0.1515	-0.0013	-0.9		
	-1.23%	21.5	3	4	117.4684	117.6178	117.6202	0.1494	-0.0024	-1.6	-1.2	0.5
	C9527	21.5	14	2	117.3933	117.5384	117.5384	0.1451	0	0.0		
	-1.43%	22.0	11	2	116.7388	116.8860	116.8902	0.1472	-0.0042	-2.9	-1.4	2.0
	Citrikleen 1850	21.5	13	3	117.2720	117.4278	117.4307	0.1558	-0.0029	-1.9		
	-2.14%	22.5	1	4	116.3579	116.5070	116.5106	0.1491	-0.0036	-2.4	-2.1	0.4
	Simple Green	21.5	2	4	116.7244	116.8766	116.8768	0.1522	-0.0002	-0.1		
	-0.50%	23.0	10	2	116.7770	116.9268	116.9281	0.1498	-0.0013	-0.9	-0.5	0.5
	Palmolive	21.5	1	1	116.3575	116.5068	116.5083	0.1493	-0.0015	-1.0		
	-0.97%	23.0	5	1	117.4247	117.5741	117.5755	0.1494	-0.0014	-0.9	-1.0	0.0
Blanks		23.5	2	3	116.7255	116.8776	116.8786	0.1521	-0.001	-0.7		
	-0.43%	23.5	12	4	117.8821	118.0362	118.0352	0.1541	0.001	0.6	0.0	0.9

Ori-5C

Oil	Product	Temp (C)	Trough#	Position	Clean	Oiled	Washed	Weight of Oil	Final Weight	% Effect.	Average Effect.	Standard Deviation
Orimulsion	C9580	5C	7	2	117.0285	117.1764	117.1501	0.1479	0.0263	17.8		
	14.9		6	1	117.2058	117.3614	117.3386	0.1556	0.0228	14.7		
			2	4	116.7257	116.8791	116.8603	0.1534	0.0188	12.3	14.9	2.8
	PES51		2	4	116.7287	116.8770	116.8425	0.1483	0.0345	23.3		
	23.1		13	1	117.2721	117.4278	117.3898	0.1557	0.038	24.4		
			11	2	116.7338	116.8876	116.8545	0.1538	0.0331	21.5	23.1	1.5
	Oriclean		4	1	117.5804	117.7289	117.7066	0.1485	0.0223	15.0		
	14.3		15	1	115.0131	115.1645	115.1426	0.1514	0.0219	14.5		
			9	3	117.2040	117.3554	117.3349	0.1514	0.0205	13.5	14.3	0.7
	D-Limonene		7	2	117.0259	117.1794	117.1480	0.1535	0.0314	20.5		
	20.1		3	2	117.4690	117.6216	117.5894	0.1526	0.0322	21.1		
			4	3	117.5778	117.7324	117.7034	0.1546	0.029	18.8	20.1	1.2
	BP1100X		4	3	117.5759	117.7289	117.7085	0.153	0.0204	13.3		
	10.3		12	3	117.8806	118.0352	118.0186	0.1546	0.0166	10.7		
			14	4	117.3938	117.5430	117.5330	0.1492	0.01	6.7	10.3	3.3
	JS10-232		2	4	116.7266	116.8762	116.8781	0.1496	-0.0019	-1.3		
	-3.7		8	4	116.4371	116.5941	116.6037	0.157	-0.0096	-6.1	-3.7	3.4

Oil	Product	Temp (C)	Trough#	Position	Clean	Oiled	Washed	Weight of Oil	Final Weight	% Effect.	Average Effect.	Standard Deviation
Bunker C	C9580	23.0	7	2	117.0264	117.1736	117.0863	0.1472	0.0873	59.3		
(1987)	56.6	23.0	14	2	117.3967	117.5494	117.4629	0.1527	0.0865	56.6		
		23.5	2	2	116.7250	116.8723	116.7911	0.1473	0.0812	55.1		
		23.5	6	3	117.2072	117.3540	117.2725	0.1468	0.0815	55.5	56.6	1.9
	PES51	23.5	11	4	116.7357	116.8873	116.8238	0.1516	0.0635	41.9		
	41.9	23.5	1	1	116.3572	116.5003	116.4399	0.1431	0.0604	42.2		
		23.5	3	2	117.4686	117.6190	117.5564	0.1504	0.0626	41.6	41.9	0.3
	Oriclean	23.0	11	4	116.7358	116.8808	116.8339	0.145	0.0469	32.3		
	35.0	23.5	7	4	117.0267	117.1764	117.1207	0.1497	0.0557	37.2		
		23.5	5	3	117.4241	117.5752	117.5217	0.1511	0.0535	35.4	35.0	2.5
	D-Limonene	22.5	8	1	116.4386	116.5821	116.5242	0.1435	0.0579	40.3		
	46.4	23.0	3	3	117.4686	117.6143	117.5518	0.1457	0.0625	42.9		
		23.0	9	1	117.2077	117.3560	117.2770	0.1483	0.079	53.3		
		23.5	10	1	116.7772	116.9246	116.8521	0.1474	0.0725	49.2	46.4	5.9
	BP1100X	23.0	9	4	117.2048	117.3466	117.2943	0.1418	0.0523	36.9		
	0.0	23.0	8	1	116.4380	116.5797	116.5045	0.1417	0.0752	53.1		
		23.0	9	3	117.2048	117.3507	117.2985	0.1459	0.0522	35.8		
		23.5	9	2	117.2040	117.3451	117.2764	0.1411	0.0687	48.7		
		23.5	14	1	117.3938	117.5441	117.4806	0.1503	0.0635	42.2		
		23.5	3	1	117.4697	117.6149	117.5467	0.1452	0.0682	47.0	43.9	6.8
	JS10-232	23.0	12	3	117.8812	118.0250	117.9785	0.1438	0.0465	32.3		
	27.4	23.5	13	4	117.2723	117.4200	117.3847	0.1477	0.0353	23.9		
		23.5	13	4	117.2724	117.4206	117.3858	0.1482	0.0348	23.5		
		23.5	8	2	116.4396	116.5855	116.5417	0.1459	0.0438	30.0	27.4	4.4
	Blanks	23.5	14	1	117.3952	117.5402	117.5391	0.1450	0.0011	0.8		
		23.5	4	2	117.5769	117.7257	117.7213	0.1488	0.0044	3.0	1.9	1.6

Bunker-5C

Oil	Product	Temp (C)	Trough#	Position	Clean	Oiled	Washed	Weight of Oil	Final Weight	% Effect.	Average Effect.	Standard Deviation
Bunker C	C9580	5C	9	3	117.2047	117.3496	117.3167	0.1449	0.0329	22.7		
(1987)	23.7		15	4	115.0132	115.1619	115.1280	0.1487	0.0339	22.8		
			14	2	117.4080	117.5538	117.5165	0.1458	0.0373	25.6	23.7	1.6
	PES51		15	4	115.0133	115.1598	115.1180	0.1465	0.0418	28.5		
	29.5		2	1	116.7248	116.8715	116.8261	0.1467	0.0454	30.9		
			5	2	117.4252	117.5658	117.5252	0.1406	0.0406	28.9	29.5	1.3
	Oriclean		12	3	117.8816	118.0254	117.9959	0.1438	0.0295	20.5		
	19.4		8	2	116.4382	116.5835	116.5546	0.1453	0.0289	19.9		
			7	1	117.0266	117.1728	117.1468	0.1462	0.026	17.8	19.4	1.4
	D-Limonene		10	1	116.7772	116.9176	116.8685	0.1404	0.0491	35.0		
	31.9		6	2	117.2065	117.3517	117.3030	0.1452	0.0487	33.5		
			12	1	117.9088	118.0575	118.0171	0.1487	0.0404	27.2	31.9	4.2
	BP1100X		14	2	117.3942	117.5381	117.5185	0.1439	0.0196	13.6		
	11.8		13	3	117.2720	117.4184	117.4085	0.1464	0.0099	6.8		
			3	4	117.4680	117.6141	117.5920	0.1461	0.0221	15.1	11.8	4.5
	JS10-232		4	1	117.5773	117.7285	117.7290	0.1512	-0.0005	-0.3		
	-1.4		11	4	116.7345	116.8803	116.8835	0.1458	-0.0032	-2.2		
			1	3	116.3572	116.4995	116.5017	0.1423	-0.0022	-1.5	-1.4	0.9