Surface-washing Agents: An Update, 2013

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Abstract

Surface washing agents or beach cleaners or shoreline cleaning agents, are formulations containing surfactants and are designed to remove oil from surfaces such as shorelines. The desired mechanism is that of detergency rather than dispersion. These agents generally have properties different from dispersants and are of typically lower aquatic toxicity, do not disperse oil except at higher mixing energies and are applied quite differently than dispersants. Surface washing agents are typically applied on oil stranded on beaches during low-tide phases and then the oil is removed using low-pressure water and directed toward an oil recovery area.

Testing on surface washing agents has been limited and was usually carried out in the laboratory. Application on real spilled oil has been carried out with some documentation. Older use of dispersants showed that there was increased beach penetration. Newer specifically-formulated surface washing agents, have been used without these or other adverse effects.

Tests show that several surface washing agents will disperse oil if high mixing energy is applied. These dispersions are relatively unstable and will largely revert within 24 hours.

The aquatic toxicity of surface washing agents varies widely. Some effective products have high effectiveness and low toxicity, thus toxicity concerns are not as great as with some other treating agents.

This version of the report reviews the old work and updates the topic until 2013..

1 Introduction to surface washing agents

Surface-washing agents or beach cleaners are formulations of surfactants designed to remove oil from solid surfaces such as shorelines. Since they are intended to remove oil rather than to disperse it, surface-washing agents contain surfactants with higher hydrophilic-lipophilic balance (HLB) than those in dispersants. Most surface-washing agents are formulated not to disperse oil into the water column, but to release oil from the surface where it floats. Higher water flushing energy will, typically, result in some dispersion. Agents have been classified as surface-washing agents rather than dispersants in the past 25 years, with most of the newer products promoted after the *Exxon Valdez* spill in 1989. Before that, dispersants were assessed on shorelines, with mixed results.[1,2] In the oil spill industry, the new specially-designed products may still be called dispersants by some.

As with dispersants, effectiveness and toxicity are the main issues with surface-washing agents, although the level of concern is not as great. There are several reasons for this. Firstly, surface-washing agents have not been used on a large scale anywhere in the world. Unlike dispersants, they are not a universally applicable agent, but are used in specific cases of supratidal or intertidal oiling. Secondly, no adverse incidents have been documented using surface-washing agents, such as the killing of aquatic life when dispersants were used after the *Torrey Canyon* spill.[3] Finally, many surface-washing agents can be relatively effective and much less toxic than dispersants. The ability to remove oil from a surface appears to be easier than dispersing it from the sea surface. Furthermore, some of the surfactants used in surface washing agents have far less aquatic toxicity than those used for dispersants.

There is some concern about whether surface-washing agents can result in appreciable amounts of dispersed oil. Some products currently listed as surface-washing agents do disperse the oil when exposed to moderate agitation or sea energies. Tests of products at high sea energies shows that they do disperse the oil to a degree. If this occurs, the situation can be similar to that with dispersants.[4]

At this time, the only product approved by Environment Canada as a surface-washing agent is Corexit 9580 from Nalco.[5] The U.S. Environmental Protection Agency has approved more than 70 agents as listed in Table 1.[6]

1.1 Motivations for using surface washing agents

The major motivations for using surface washing agents on shorelines is to remove as much of the oil as possible without the incumbent disruption that often occurs with physical removal techniques. The procedure for using a surface washing agent on a shoreline is to apply the agent, let it soak (typically ½ to 4 hours or as much as possible) and rinse off the surface with low pressure and cool water. The oil is then recovered, typically with skimmers. This can result in minimal disturbance to the shoreline and recovery of much of the oil.

The motivations for using surface washing agents on impermeable surfaces are similar, however there are few uses on impermeable surfaces.

The use of surface washing agents on permeable surfaces such as soil is not recommended. Potential users are advised to consult the ASTM Guides on these products.[7-9]

1.2 Surface washing agent issues

The issues with surface washing agents are the effectiveness of the products on aged oils on surfaces; the dispersion of the oil with higher energies, the toxicity of the product and resulting re-mobilized oil and possible movement of oil down into the shoreline or sub-surface. In many countries there are regulations and tests for acceptability of these agents. [10-12]

1.3 Surface washing agent chemistry

Little information is available on specific formulations for surface-washing agents because the formulations vary extensively and many are not patented. Several basic types of formulations are:

1. Non-ionic or anionic surfactants with HLBs of more than 11 in a low-aromatic hydrocarbon solvent;
2. d-Limonene in various solvents;
3. Surfactants mixed with various solvents;
4. Surfactants in glycol-type solvents similar to dispersants;
5. Detergents with little or no solvent; and
6. Solvent mixtures.

Several papers have been written on the development of surface-washing agents.[13-17] Many of the agents were developed after the *Exxon Valdez* spill in 1989. The following three products were tested on oiled shorelines resulting from the *Exxon Valdez* spill: Corexit 7664, Corexit 9580, and PES-51. Most products functioned as expected and Corexit 9580 appeared to be most successful.

2 Review of Major Surface washing agent Issues

2.1 Effectiveness

Field Trials Several tests of the effectiveness of surface-washing agents have been conducted at actual spills. The results of some of these tests are listed in Table 2.[1,15,18-28] Effectiveness was not quantified in any of these field tests, however, in every case, except where dispersants were used in earlier years, the tests were declared to be successful. The earlier dispersant trials showed variable effectiveness and, where penetration was measured, showed that dispersants promoted penetration of the oil into the sub-sediments.[28]

Little and Baker reported on field and laboratory studies of the use of dispersants in nearshore areas or on shorelines.[28] Tests showed that some dispersant treatments can increase the penetration of oil into sediment and that the oil may be retained in the sub-surface. The nature of the shoreline or sediment was the main factor determining whether the penetration was enhanced by dispersant. On some shorelines it was shown that natural removal can be enhanced by dispersant usage. It was also found that dispersant-enhanced toxicity of oil could pose a problem and suggested that work be done on defining an effective minimum dispersant-to-oil ratio.

While field evaluation methods have not been fully developed for surface-washing agents, field screening kits for evaluating both effectiveness and toxicity have been developed and tested. Clayton and co-workers reported on the development of test kits for evaluating the effectiveness and aquatic toxicity of surface-washing agents. [29-32] The test was evaluated using natural substrates including gravel, rock fragments, and eelgrass. It was concluded from laboratory tests that the field test would be an appropriate indicator of effectiveness in the field. Four field- applicable methodologies for testing the aquatic toxicity of surface-washing agents were tested, including the Microtox unit, echinoderm fertilization, byssal thread attachment in mussels, and righting and water-escaping ability in periwinkle snails. While all methodologies were able to detect differences in toxicity, the Microtox and echinoderm fertilization showed greater sensitivity and/or precision.

Laboratory Testing. Laboratory tests for surface-washing agents were first developed by Environment Canada .[33] After evaluating about 25 testing methods including troughs, surfaces and coupons in flasks, the trough was found to be the most repeatable and a close simulator of field processes. A coupon is a small wafer of material such as brick or stone. A close-up of the sloped-trough test is shown in Figure 1. A heavy oil such as Bunker C was placed on a small metal trough, agent applied, and then the oil was flushed away with water. Quantitation is by weight. The U.S. EPA subsequently evaluated a number of test methods and then evaluated several products with a trough test similar to that used by Environment Canada.[34,35] In recent times, the U.S. EPA has worked on a revised gravel-washing test.[36,37] This new test is summarized in the Appendix. The French government laboratory developed a small coupon test to screen products for acceptability.[38] Initial findings were that the surface washing agent dosage, applied as a dilution, was a factor in the removal, however effectiveness did not increase once the ratio of agent to oil was 1:1.

A variety of agents, including dispersants, have been extensively tested by Environment Canada using the trough test.[4,39,40] The results of some of these tests are shown in Table 3. Included in this table are effectiveness results from the trough test for both freshwater and salt water and effectiveness as a dispersant using the swirling flask test and Alberta Sweet Mixed Blend crude oil. These test results show that products which are effective as a dispersant are not effective as a surface-washing agent and vice versa. This effect, which was noted in previous studies, is thought to be due to the difference in HLB needed for a dispersant (HLB ~ 10) and for a surface-washing agent (HLB > 10).[41] The table also includes household products and other products that are not intended for use on oil spills for comparison.

Guenette et al. tested a number of agents for effectiveness using the Environment Canada test as described in the Appendix.[42] The standard oil, Bunker C and Orimulsion bitumen, were used. The latter was the primary target of testing. Results are summarized in Table 4. It was found that the removal of both oils was greatly enhanced by the use of the treating agents. D-Limonene was the best agent, but several agents yield similar results. The product effectiveness was highly influenced by temperature and some removed little at 5ºC. It was also noted that household cleaning products and dispersants were not effective in removing oils and were frequently toxic to fish.

Use

The main point on any treating agent is that it should be effective in the field. Table 2 lists a number of uses of surface washing agents.

Thumm et al. reported on the successful 2001 use of PES 51 to remove weathered crude oil from the side of a ship.[43]

2.2 Toxicity

The acute lethal toxicity of many surface-washing agents is shown in Table 3.[41,44] Unlike dispersants, the aquatic toxicity of surface-washing agents varies from nontoxic (>1000 mg/L) to highly toxic (<50 mg/L). Toxicity does not correlate with effectiveness. In fact, the most effective product noted in Table 3, Corexit 9580, is also the least toxic as measured on the Rainbow Trout.

Shigenaka *et al.* found no adverse biological effects of Corexit 9580 during an application to a salt water marsh.[45] Pezeshki and coworkers studied the effects of Corexit 9580 on seagrasses and also found no adverse effects.[24,26] Similarly, Teas *et al.* studied the use of Corexit 9580 on mangroves and found benefits and no toxicity.[46] Hoff *et al.* reviewed PES-51, which consists primarily of d-Limonene and found its aquatic toxicity relatively high.[15] Michel et al. reviewed the toxicity of various surface washing agents.[47] A summary of these data are given in Table 5.

Buday et al. Tested water from a application of Corexit 9580 before and after application to a spill of synthetic crude oil in Burrard Inlet, Vancouver.[48] Water samples from the foreshore were collected after the oil spill, before and after the shoreline treatments. The seawater samples were not acutely toxic to Microtox bacteria (*Vibrio fischeri*), Coho salmon (*Oncorhynchus kisutch)* and echinoid fertilization (*Dendraster excentricus*). Elevated hydrocarbon concentrations were detected in the water samples taken after the shoreline treatments compared to the water samples taken before the shoreline treatments.

3 Other issues

3.1 Application

Surface-washing agents are applied directly on the stranded oils and left to penetrate for at least 15 to 30 minutes.[7,17] The oil is then flushed with water to remove the oil and direct it to a cleanup area. From there, the oil is generally removed with a conventional skimmer system. Since the surface-washing agents are typically applied to a small expanse of oil at the upper or intertidal zone, they are applied manually using hand-held or backpack sprayers or using large vehicle or vessel-mounted sprayers. Such an application is illustrated in Figure 2. It would be difficult to apply the agent using airborne spray systems and much product would be lost. On shorelines, the product must be applied during low tide and the oil removed before the tide rises and the oil is no longer accessible. No extensive research or testing of application methods for surface-washing agents have yet been done.

3.2 Dispersion with higher applied energy

It has been known that surface washing agents will disperse oil, if high energy is applied.[2] Fieldhouse performed tests on dispersion using a modified method that applied higher energy.[4] Test results are shown in Table 6 and illustrated in Figure 3. The findings of this study are:

a) at the high mixing energies noted, all three products tested, Corexit 9580, PES-51 and Cytosol, dispersed the oil to a large degree,

b) only Corexit 9580 dispersed the oil significantly at 5°C and 15 and 25°C, PES-51 and Cytosol dispersed the oil as well,

c) the salinity of the water had only a minor effect on the dispersion,

d) the untreated oils dispersed to the extent of about 40% in saline water and up to about 30 % in fresh water, and

e) all dispersion were unstable over a 24-hour period, but were stable in the first few minutes.

The implications of this study are that to avoid dispersion, low energy flushing must be used. Similar findings are noted by Jezuquel. [49]

3.3 Assessment of the use of surface washing agents

Several parties have assessed the use of surface washing agents for use on both fresh and saltwater shorelines.[49,50] In summary, surface washing agents are recommended for use where: weathered or heavy oil is stranded on beach or similar surface, where adequate soaking time can be achieved and where the oil can be flushed to a recovery system using low-pressure water. In some countries surface washing agents are used to clean oil from surfaces such as roads.

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Appendix

5.1 Environment Canada's Test Method [33,39]

Summary:

The method uses a stainless-steel 'trough' which is placed at a specified angle. Heavy oil, or the target oil, is placed on an area on the trough. The treating agent is applied in droplets to the surface of the oil and after 10 minutes at 5 minute intervals, rises of water are applied to the trough. After drying the trough is weighed and the removal calculated by weight loss. Repeatability is within 5%.

Method:

Measure the oil to be used in test using a positive-displacement pipette. Set the pipette to 150 microlitres (μL). Aspirate the oil, (the target or Environment Canada set aside an aliquot of 1987 Bunker C as a standard) which has been previously stirred, into the pipette making sure no air bubbles are present. Wipe the end of the pipette tip off to ensure that the oil inside the tip is flush with the end.

Place the clean trough on the balance and allow reading to become steady. Record the weight. Return to work area with trough. Dispense the oil onto the trough in a slick of even thickness along its length. The slick is positioned along the fold of the trough commencing approximately 160 millimetres from the trough's lower end and moving upward in an even flowing motion for about 45 to 50 millimetres. Any remaining oil on the tip of the pipette can be removed by wiping the tip on the trough (at a point just below the beginning of the slick). Start the time. Place the oiled trough on the balance. While waiting for a steady reading, start the clock/stopwatch/timer. Record the weight of the oiled trough and stand vertically after weighing.

At t = 9:30 minutes, aspirate the dispersant or surface washing agent into the pipette. The pipette is set to 30 microlitres (μL).

At t = 10:00 minutes, place the trough horizontal and apply washing agent onto the now lengthened slick. This is accomplished by depressing the plunger of the pipette until a drop protrudes about halfway out of the tip. This drop is then touched to the oil slick. Repeat this technique in order to get a thin and even coating over the slick. Record the weight and place the trough horizontally for a 10-minute surface-washing agent soaking.

At t = 19:45 minutes, set up the trough in the stand at a 45^{o} angle at a height such that a collection beaker can be placed under the lower end. A 30 mL syringe with an 18 gauge needle is positioned over the centre of the trough so that the water will run down the trough approximately 5-10 millimetres before encountering the oil slick. The lower end of the trough will just clear the tip of the 240 millilitre pyrex waste beaker that is set up to catch the runoff. The point of impact of the water rinse stream is in the centre of the trough's fold and 205 millimetres from the lower end of the trough.

Aspirate the water into the 'Oxford' pipette. At t = 20 minutes, place 5 millilitres of fresh or salt water in the rinse dispensing syringe body. The water should then drip out of the needle onto the trough, thereby rinsing away the oil/dispersant/surface-washing agent mixture.

At t = 29:45 minutes, aspirate 5 millilitres of water, again using the pipette. At t = 30 minutes, repeat the rinse procedure.

At t = 40 minutes, visually examine the trough to determine how much water remains on or in the oil slick (the water is fairly obvious). Non-linting laboratory issue is used to absorb excess water, blot up the remaining water without removing any of the oil that is on the trough. To blot up the water that is 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. This usually results in absorbtion of the water droplet without absobing much of the oil at the same time. Once all the water has been removed, the trough can be weighed and the weight recorded.
Calculations:
Equation 1: Amount of Oil Deposited = Trough Weight (freshly oiled) - Weight of Clean, Dry Trough
Equation 2: Amount of Oil Removed = Trough Weight (freshly oiled) - Weight of Rinsed, Blotted Trough
Equation 3: Percentage of Oil Removed = (Equation 2 / Equation 1) x 100%
Notes:
Blanks should be run using the same procedure with minimal changes. The surface washing agent would not be applied at t = 10 minutes; however, rinses would still be run at t = 20 and t = 30 minutes. All the weighings should be identical with the exception that the amount of surface washing agent applied would not be weighed.
Elevated temperature rinsing runs are the same except the rinse water is warmed to elevated temperatures, for example 50 ºC.
Different gauge needles, with smaller internal diameters, may be used to give lengthened rinse times due to smaller flow rates.
After the final weighing is completed, the trough is cleaned using small pieces of a polypropylene oil-sorbent mat. These pieces are approximately 20 by 20 millimetres and are held using needle-nose pliers. The excess oil is then wiped off. The trough is then rinsed with Dichloromethane to dissolve and carry away the remaining oil film. A final rinse with Acetone followed by a wipe with a towel finishes the cleaning procedure.

EPA Draft Protocol [36,37, 54]

Summary:

Oil is applied to sand or gravel in a mesh basket. Diluted surface washing agent is applied to the oil. This is allowed to soak for 15 minutes and then the basket is immersed in a beaker with water. This is shaken for 5 minutes and then removed and drained. The oil in the rinse water is extracted and analyzed. A standard analytical method was not yet described.
Method: Wire mesh baskets are loaded with 15 mL of either gravel or sand. For wet test the substrate is placed in water. The applied oil is weathered for 18 hours. The diluted treating agent (either 100 or 50% diluted) is applied. The system is allowed to weather for 15 minutes. The baskets are then placed into a 600 mL flask and 100 mL water added. This is placed on a shaker and shaken for 5 minutes at 150 rpm. The baskets are allowed to drain for 5 minutes. The wash is extracted with three 5 mL aliquots of dichloromethane. The remaining oil on the substrate is extratied with two 20 mL aliquots of dichlormethane. These should be analyzed by a standard method and the amount of oil calculated in each to determine the oil washed off and remaining.

Fiedlhouse High Energy Protocol [4]

The apparatus selected for generating dispersions was the end-over-end rotational mixer with 2.2 L fluorinated HDPE bottles.[51,53] The oil and surface washing agent was to the closure of a wide-mouthed bottle containing wash water. The test apparatus and energy profile have been detailed elsewhere.[54] For this test, the total force on the cap end each rotation is 9.8 newtons, the work per revolution is 0.735 J, and the total work over the mixing time is 162 J. The surface washing agent (SWA) product was pre-mixed with the target oil to limit variation between tests, as well as to accommodate the short soak time of one product compared to the other two products. This also offers greater homogeneity of the test matrix during the washing process, limiting effects of SWA application at the oil surface. The volume of water added to the bottle was 1 L, a compromise between turbulent energy considerations during mixing (greater water volume produces lower energy input as the head of water falls a shorter average distance on the down cycle) and the need to provide sufficient water volume for sampling at several time points. The volume of product/oil premix was set at a ratio of 1:1000. The primary test oil selected for evaluation was the Environment Canada SWA standard oil (see first method above). The ratio of surface washing agent to oil was set at 2:5 for Corexit 9580, which is the manufacturer's recommended dosage, and required approximately 2 minutes at a 55 RPM mixing rate to fully remove the oil, the highest setting for the mixer. At the same dosage of PES-51, a time of 4 minutes was required. Full cleaning was not achieved by the Cytosol product at this dosage for times up to 10 minutes, however four minutes mixing later proved sufficient in the higher temperature test at 25ºC. The test condition of 4 minutes at 55 RPM was adopted to enable direct comparison of Corexit 9580 with PES-51. Quantification by gas chromatograph with flame ionization detector (GC-FID) was used rather than the alternative gravimetric analysis to provide greater precision for the anticipated low oil volumes.

All reagents and equipment are left overnight in a temperature controlled room to thermally equilibrate at the test temperature, ± 0.5ºC. A 1 L volume of water of specified salinity is transferred to a 2.2 L wide-mouthed bottle and inserted upright into a rotary Agitator with variable speed motor, by Associated Design (www.AssociatedDesign.com). The test oil and SWA are premixed in a glass vial at the designated volumetric ratio for the specific test, weighing before and after each addition for verification. The premix is thoroughly stirred until homogeneous. A 1 mL volume of the mixture is distributed across the inner surface of a polypropylene bottle closure using a positive displacement pipette. The oil is allowed to spread for 2 minutes. The closure is then inverted and secured onto a bottle containing the wash water. The mixer is rotated for 4 minutes at a rate of 55 RPM, with the cap end leading the rotation. The bottles are then removed and the contents transferred in their entirety to a 1 litre separatory funnel. Samples of 150 mL volume are collected at 1, 5 and 30 minutes and 3 and 24 hours post transfer. The collected samples are extracted with 3 volumes of 25 mL dichloromethane in 250 mL separatory funnels. It is helpful to add clean, concentrated brine to the fresh water samples to assist phase resolution of the water and solvent. The extracts are collected in a 100 mL mixing cylinder and corrected to 75 mL. Quantitation is by GC-FID using 5-α-androstane as the internal standard. Blanks are run before and after sample sets to quantify the baseline for blank subtraction. The relative response factor (RRF) of 15 alkanes in the C_9 to C_{36} range is determined by averaging the response from triplicate injections bracketing the sample analysis. The total oil volume of the samples is calculated from the GC response in the C_{16} to C_{36} range corrected by proportionality to the response of prepared oil standards of the test oil for the same range. The oil standards are prepared in triplicate by adding 150 μL of target oil to a volume of water and extracted by the same method as the samples, then analyzed. The GC response for 100% oil in the appropriate range is determined, then adjusted to correspond to the change in oil volume due to SWA dosing. The variables in test parameters were varied as indicated for SWA product, water salinity, temperature and oil type.

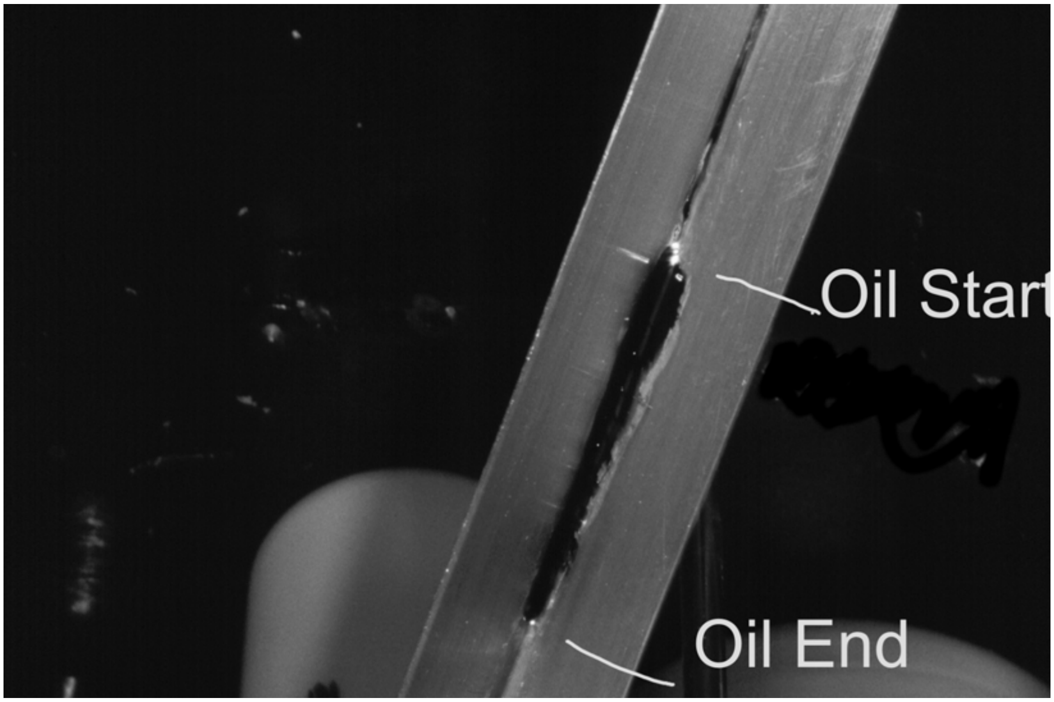

Figure 1 A close-up of the Environment Canada test trough - showing the oil deposition

Figure 2 Application of surface washing agents after the Sea Empress spill in the United Kingdom using a backpack sprayer. The two hoses were used to flush the oil to a recovery area.

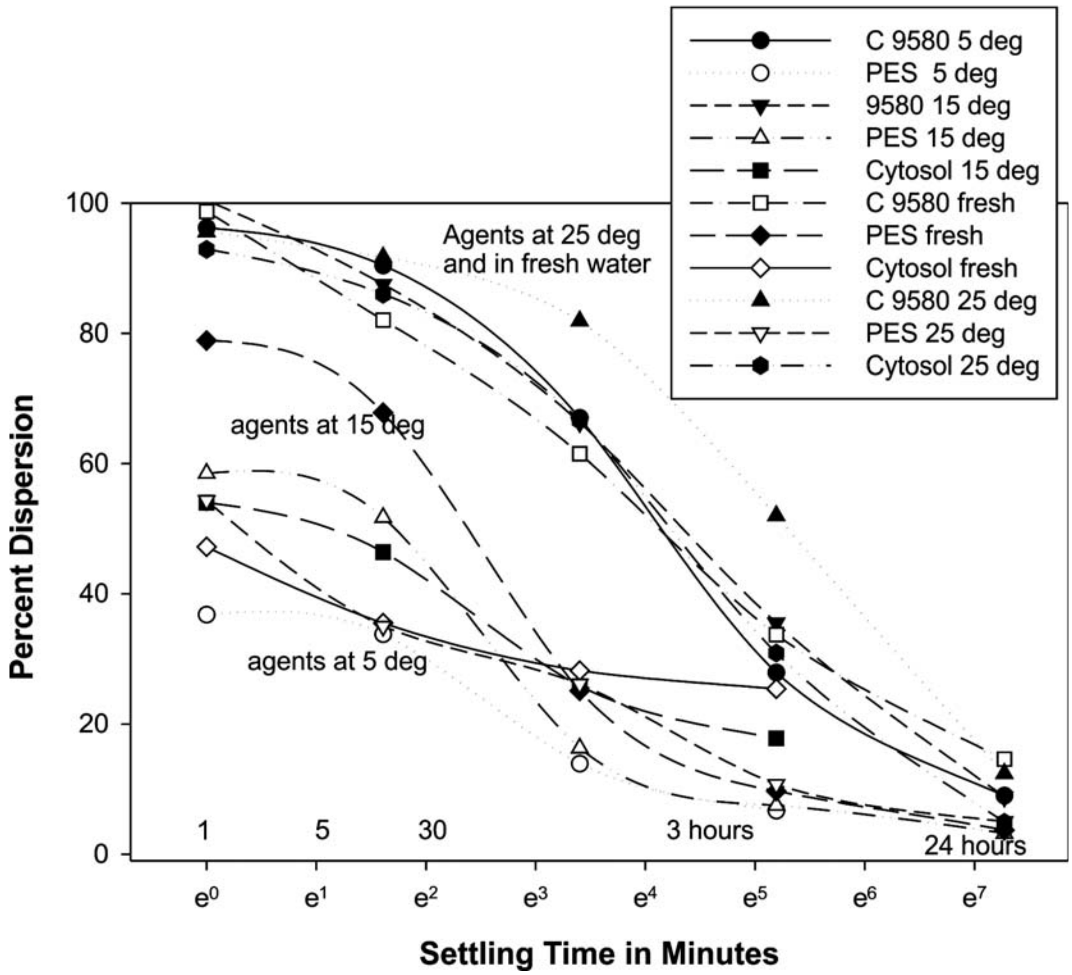

Figure 3 The dispersant percent of various surface washing agents with amounts of settling time. Higher temperatures increase the amount of dispersion but over time (eg. 24 hours) most dispersions are destabilized (Fieldhouse, 2008)

Table 1 EPA List of Surface Washing Agents
(from National Contingency Plan Product list - as of May, 2012
http://www.epa.gov/osweroe1/content/ncp/product_schedule.htm

Product Name
ACCELL® CLEAN SWA
ALL PURPOSE CLEANER & REMEDIATOR (see GREEN BEAST™ OIL SPILL & ODOR REMEDIATOR)
AQUACLEAN
AWAN PRA OIL FIELD SOLUTION™ (see EPA OIL FIELD SOLUTION™)
BG-CLEAN™ 401
BIOGRASS® EXTRA
BIOSOLVE® HYDROCARBON MITIGATION™ AGENT
CLEAN GREEN
CLEANGREEN® PLANET WASH (see CLEAN GREEN)
CLEAN SPLIT (see SPLIT DECISION SC)
CLUTTER CLEANER (see GREEN BEAST™ OIL SPILL & ODOR REMEDIATOR)
CN-110
COREXIT® EC9580A (formerly COREXIT 9580 SHORELINE CLEANER)
CORIBA 700 ER (see CORIBA 700 SR)
CORIBA 700 OS (see CORIBA 700 SR)
CORIBA 700 SR
CORIBA 713 ER (see CORIBA 713 SR)
CORIBA 713 OS (see CORIBA 713 SR)
CORIBA 713 SR
CYTOSOL
DE-SOLV-IT CLEAN AWAY APC SUPER CONCENTRATE
DE-SOLV-IT INDUSTRIAL FORMULA
DO-ALL #18
DUO-SPLIT (see SPLIT DECISION SC)
DYNAMIC GREEN™
ECOVOOM-MARINE (see JEP-MARINE CLEAN)
ENVIROCLEAN (formerly ENVIRO CLEAN 165)
ENVIRONMENTAL 1 CRUDE OIL CLEANER
ENVIRONMENTAL 1 WASHING AGENT (see ENVIRONMENTAL 1 CRUDE OIL CLEANER)
EO ALL PURPOSE SOAP-LAVENDER
EPA OIL FIELD SOLUTION™
E-SAFE©
ETHOS CLEAN
F-500
FIREMAN'S BRAND SPILLCLEAN (see SPILLCLEAN)
G-CLEAN OSC-1809
GLOBAL ENVIRONMENTAL CLEANER™ (see EPA OIL FIELD SOLUTION™)
GOLD CREW SW
GREEN BEAST OIL SPILL & ODOR REMEDIATOR
GREEN BEAST WASHING AGENT (see GREEN BEAST OIL SPILL & ODOR REMEDIATOR
GREEN TECHNOLOGIES SOLUTIONS-OIL RECOVERY (GTS-OR)
HYDRO-CLEAN™ (see EPA OIL FIELD SOLUTION™)

Table 1 continued
(from National Contingency Plan Product list - as of May, 2012
http://www.epa.gov/osweroe1/content/ncp/product_schedule.htm

Product Name
JEP-MARINE CLEAN
MARINE GREEN CLEAN™
MARINE GREEN CLEAN PLUS™
MICRO CLEAN (see NATURE'S WAY HS)
NALE-IT
NATURAMA G3 A-5
NATURE'S WAY HS
NATURE'S WAY PC (see NATURE'S WAY HS)
NOKOMIS 5-W
OIL SPILL CLEANUP (see G-CLEAN OSC-1809)
OSR-10
PETRO-CLEAN
PETRO-GREEN ADP-7
PETROMAX PSC 3
PETROMAX SOIL CLEANING AND WASHING AGENT (see PETROMAX PSC 3)
PETROTECH 25
POWERCLEAN (see NATURE'S WAY HS)
PREMIER 99
PROCLEANS
SAFE KLEEN
SANDKLENE 950
SC-1000™
SHEEN-MAGIC©
SIMPLE GREEN®
SOC 10
SPILLCLEAN or SPILLCLEAN ["Concentrate"]
SPLIT DECISION SC (formerly SPLIT DECISION)
SUPERALL #38 (see TOPSALL #30)
TOPSALL #30
TULXA
TXCHEM HE-1000™
VERU-SOLVE™ MARINE 200 HP

Table 2 Use of Surface-washing Agents and Major Field Tests

Country	Date	Location	Name	Volume of 0il	Oil Type	Agent Used	Effectiveness	References Cited
Canada	1999	Quebec	Havre St. Pierre	~ 10 tons	Bunker C	Corexit 9580	successful	2
Canada	1999	Nova Scotia	Canso	~1 ton	Bunker C	Corexit 9580	successful	2
United States	1998	Alaska	*Exxon Valdez*	test only	North Slope	PES 51	not known	18
United States	1997	Maine	*Julie N.*	test only	Bunker C	Corexit 9580	50% removed	19
Uruguay	Mar-97	shoreline	*San Jorge*	test only		Corexit 9580	successful	[20] OSIR 6 mar 97
Uruguay	Mar-97	shoreline	*San Jorge*	test only		Enviroclean	successful	[20] OSIR 6 mar 97
United States	06-Oct-96	Maine	*Julie N.*	test only	Bunker C	Corexit 9580	varied	[20] OSIR, 3 Oct 96, 17 Oct
New Zealand	late 96	Wellington	*Sydney Express/Maria Luisa*	8 tonnes	Diesel	OSD 9	successful	[20] OSIR, 5 Jun 97
United States	1994	Puerto Rico	*Morris J. Berman*	test only	Bunker C	Corexit 9580	successful	21, 22
United States	1994	Puerto Rico	*Morris J. Berman*	test only	Bunker C	PES 51	successful	21, 22
United States	1994	Texas	San Jacinto River	small amount	Crude	Corexit 9580	successful	23
United States	1994	Louisiana	oil marsh	small amount	Crude	Corexit 9580	successful	23-25
United States	1993	Alaska	*Exxon Valdez*	test only	North Slope	PES 51	successful	15,27
Great Britain	1987	Fokestone	test	test only	Fuel Oils and emulsion	dispersants	variable	1
Great Britain	1985-88	Wales	test	test only	Fuel Oils and crude	dispersants	variable	28
United States	1970	Florida	*Delian Appollan*	test only	Bunker C	Corexit 8666	variable	21

Table 3 Surface Washing Agent Test Results

(Effectiveness results from a test using a sloped trough; Toxicity values are 96-hour Rainbow Trout LC-50 results;

Dispersant effectiveness values are from the Swirling Flask test, using the readily-dispersable ASMB)

Surface Washing Agent Test Results

PRODUCT	PERCENT OIL REMOVED		TOXICITY	EFFECTIVENESS AS
Name	FRESHWATER	SALTWATER		A DISPERSANT (%)
Corexit 9580	69	53	>10,000	0
D-Limonene	51	52	35	0
Penmul R-740	49	44	24	9
Limonene '0'	38	43	35	0
TRL-900	50	40	7	0
Formula 2067	41	39	11	0
Ecologic 5M10MB10	24	38	62	0
Citrikleen XPC	37	36	34	2
ECP 99 Oil Eater	34	36	16	7
Oriclean	-	32	70	0
Ultrasperse II	41	32	57	14
Formula 861	32	32	24	0
Core Tech 2000x	31	27		22
Corexit 7664	25	27	850	2
ECP Responder SW	20	26	57	6
Neutro Gold	18	26	50	7
Core Tech 2000	26	25	325	21
Pronatur Extra	19	25	9	0
Superall	22	24		
Bioorganic	-	23	18	0
BP 1100 X AB	28	23	2900	0
AutoScrub Gold	15	22	57	7
BP 1100WD	30	21	120	6
Tesoro Pes 51	23	21	14	0
Ecologic BF-104	35	20	62	0
Champion JS10-232	27	20	1060	0
COR 7664/Isopar	17	20	1500	1
Biosurf	15	20	42	0
Champion JS10-242	27	19	380	<5
Tesoro Pes 41	22	19	9	0
ERA 369	21	19	10	10
Oil Gon	20	19	134	0
Tierra Q-100	34	17	177	0
Pronatur	23	17	75	0
Re-Entry	17	17	8	0
Biocat 145	14	17	104	0
Sea Spray	26	16	420	0
Palmolive	14	16	13	9
Per 4m	14	16	566	0
ESP Pro	6	16	80	0
ERA 369X	15	15		15
Topsall	-	14	354	0
Aquaquick 2000	12	14	870	0
Breaker-4	17	13	340	0
M.X. #1	13	13	90	6
Nokomis 3	13	13	110	-
Oil Lift	13	13	not done	6
Ecologic 5M5B4	11	13	46	0
Ortec	0	13	123	0

Table 3 ctd Surface Washing Agent Test Results

(Effectiveness results from a test using a sloped trough; Toxicity values are 96-hour Rainbow Trout LC-50 results;

Dispersant effectiveness values are from the Swirling Flask test, using the readily-dispersable ASMB)

Surface Washing Agent Test Results

PRODUCT Name	PERCENT OIL REMOVED FRESHWATER	PERCENT OIL REMOVED SALTWATER	TOXICITY	EFFECTIVENESS AS A DISPERSANT (%)
Simple Green	24	12	205	-
Sunlight	16	12	13	9
Citrikleen 1855	14	12	55	0
Inprove	14	12	78	0
Citrikleen FC1160	10	12	75	0
Con-Lei	8	12	70	0
Alcopol 60	-	11	62	18
Ecologic 10M10B10	19	11	23	0
Pyprr	12	11	650	0
Bioversal	8	11	120	0
Oil Spill Eater	5	11	135	0
Icoshine	12	10	40	0
Oil Lift (repeat test)	12	10	not done	6
Ecologic BF-102	25	9	46	0
F-500	15	9	0.6	9
Envirosperse OSD	0	9	108	<5
Green Unikleen	13	8	165	11
ZI-808	7	8	179	59
Siallon Emulsifier	6	8	375	0
PC-100 (petro controller)	8	7	12000	0
Ecologic BF-103	7	7	71	0
IDX 20	6	7	140	0
Mr Clean	13	6	30	0
Gran Control	5	6	75	0
Envirowash 1000	20	5	1650	0
Corexit CRX8	14	5	20	45
SX-100 oil dispersant	10	5	5	0
Formula 730	3	5	33	0
ZI-800	16	4	221	55
Cytosol	8	4	1770	0
Corexit 9527	13	3	108	33
Balchip 215	8	3	157	0
Tornado	8	3	1350	0
Firezyme	4	3	521	0
BG Clean 401	3	3	88	0
Equisolve	0	3	60	0
Jansolve	25	2	57	0
Citrickleen 1850	24	2	18	11
Super Dispersant	6	2	337	18
Value 100	4	2	4250	0
Biosolve	2	2	9	0
Lestoil	9	1	51	0
Enersperse 700	1	1	50	32
Corexit 9500	26	0	354	36.3
Brady non-butyl degreaser	5	0	433	0
Oil Dissolver	5	0	40	0
Inipol EAP-22	0	0	17	9
Petrotech	0	0	1460	0
Microat S	-	-	2795	0
PPL L1094	-	-	467	0
Slickgone NS	-	-	100	30
Green Unikleen (diluted)	10		not done	
Dispersit SPC 1000			2	32

Table 4 Test of Surface Washing Agents

after Guenette et al., 1999 [42]

Product	Percent Oil Removed: Orimulsion 22°C	Orimulsion 5°C	Bunker C 22°C	Bunker C 5°C	Product Description	Aquatic Toxicity Rainbow Trout 96 hr LC50 (mg/L)
D-Limonene	36	20	56	32	natural product in citrus peels	35
PES-51	32	23	42	30	SWA	14
Corexit 9580	27	15	57	24	SWA	>10,000
Oriclean	27	14	35	19	SWA	70
BP1100X	23	10	44	12	dispersant	2900
Champion JS19-232	0	-4	27	-1	SWA	1060
Simple Green	0				household cleaner	205
Palmolive	-1				dish detergent	13
Corexit 9500	-1				dispersant	354
Corexit 9527	-1				dispersant	33
Citrikleen 1850	-2				SWA	18
Blank (water)	0				blank	

SWA = surface washing agent

Table 5 Summary Toxicity Data on Surface-Washing Agents

after Michel et al. 2001 [46]

Parameter	Agent: Aquaclean	Biosolve	CN-110	Corexit 7664
Toxicity	Mummichug 71 mg/L, 96 h brine shrimp 12 mg/L, 48 hr	Rainbow Trout 9 mg/L, 96h Fathead minnow >750 96 h	Rainbow Trout 1460 mg/L, 96h Mummichug 4,830 mg/L, 96 h	Rainbow Trout 850 mg/L, 96h Mummichug >1000 mg/L, 96 h
Toxicity Atlantic Silversides mg/L 96 h	71	6.4	52,200	87
Myside shrimp	33	3.6	12,300	584
water solubility	100%	100%		100%

	Corexit 9580	Cytosol	Nature's Way	PES-51
Toxicity	Rainbow Trout >10,000 mg/L, 96h Mummichug >10,000 mg/L, 96 h			Rainbow Trout 14 mg/L, 96h Mummichug 1425 mg/L, 96 h
Toxicity Atlantic Silversides mg/L 96 h	87	736		
Myside shrimp	32	124		
water solubility	insoluble	14 ppm, fresh, 7 ppm sea		

Table 6 Summary of High Energy Tests of Surface Washing Agents

after Fieldhouse, 2008 [4]

Bunker C tests

Dose Ratio (SWA:Oil)	Temp (ºC)	Salinity (NaCl)	Settling Time	Vol. % Oil Dispersed Corexit 9580	PES	Cytosol
0.4	5	3.30%	1min	96.2	36.8	
0.4	5	3.30%	5min	90.4	33.8	
0.4	5	3.30%	30min	67	13.9	
0.4	5	3.30%	3hr	27.9	6.7	
0.4	5	3.30%	24hr	9		
0.4	15	3.30%	1min	100.4	58.5	54
0.4	15	3.30%	5min	87.5	51.7	46.4
0.4	15	3.30%	30min	66.3	16.3	25.8
0.4	15	3.30%	3hr	35.5	7.5	17.8
0.4	15	3.30%	24hr	8.8	3.2	
0.4	15	Fresh	1min	98.7	78.9	47.2
0.4	15	Fresh	5min	82	67.8	35.5
0.4	15	Fresh	30min	61.5	25.1	28.2
0.4	15	Fresh	3hr	33.7	9.7	25.4
0.4	15	Fresh	24hr	14.6	3.7	
0.4	25	3.30%	1min	95.6	54.3	92.9
0.4	25	3.30%	5min	91.7	35	86
0.4	25	3.30%	30min	81.9	26.1	66.6
0.4	25	3.30%	3hr	52	10.7	30.9
0.4	25	3.30%	24hr	12.4	5	4.9
0.2	15	3.30%	1min	84.6		
0.2	15	3.30%	5min	78.2		
0.2	15	3.30%	30min	42.3		
0.2	15	3.30%	3hr	28.4		
0.2	15	3.30%	24hr	2.2		
0.2	15	Fresh	1min	81.6		
0.2	15	Fresh	5min	75.7		
0.2	15	Fresh	30min	43.6		
0.2	15	Fresh	3hr	35		
0.2	15	Fresh	24hr	8.2		

Oils: ASMB = a light crude, AHC = Arabian Heavy Crude

HSC = heavy synthetic crude

Other Oil Tests

Oil Type	Dose Ratio (SWA:Oil)	Salinity (NaCl)	Settling Time	Vol. % Oil Dispersed Corexit 9580
ASMB	1:10	3.30%	1min	93.2
ASMB	1:10	3.30%	5min	73.7
ASMB	1:10	3.30%	30min	27.1
ASMB	1:10	3.30%	3hr	11.4
ASMB	1:10	Fresh	1min	91.1
ASMB	1:10	Fresh	5min	68.1
ASMB	1:10	Fresh	30min	23.9
ASMB	1:10	Fresh	3hr	12
ASMB	Untreated	Fresh	1min	30.3
ASMB	Untreated	3.30%	1min	36.6
ASMB	Untreated	Fresh	5min	16.8
ASMB	Untreated	3.30%	5min	20.1
ASMB	Untreated	Fresh	30min	4.4
ASMB	Untreated	3.30%	30min	6.2
ASMB	Untreated	Fresh	3hr	1.4
ASMB	Untreated	3.30%	3hr	0.5
AHC	0.14	3.30%	1min	81.1
AHC	0.14	3.30%	5min	63.2
AHC	0.14	3.30%	30min	35.7
AHC	0.14	3.30%	3hr	25.5
AHC	0.14	3.30%	24hr	1.4
AHC	Untreated	3.30%	1min	9.6
AHC	Untreated	3.30%	30min	4.3
AHC	Untreated	3.30%	24hr	0.5
HSC	0.14	3.30%	1min	81
HSC	0.14	3.30%	5min	77.1
HSC	0.14	3.30%	30min	40.2
HSC	0.14	3.30%	3hr	24.9
HSC	0.14	3.30%	24hr	2
HSC	Untreated	3.30%	1min	1.6
HSC	Untreated	3.30%	30min	1.3
HSC	Untreated	3.30%	24hr	0.1