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EPA Project Summary

Chemical Surface Washing Agents for Oil Spills: Update State-of-the-Art on Mechanisms of Action and Evaluation of Two Laboratory Effectiveness Tests

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Chemical surface washing agents are formulations designed to help release stranded oil from shoreline substrates. The U.S. Environmental Protection Agency (EPA), in response to the Oil Pollution Act of 1990, initiated study of these cleaning agents. The project summarized here had two primary objectives and generated two reports. The first, a state-of-the-art (SOTA) report, updated information on the cleaning agents, their mode of action, and variables affecting their cleaning performance in the field and in the laboratory. A number of laboratory tests for estimating cleaning performance were also discussed. EPA's second report presented a detailed evaluation of two laboratory testing procedures for estimating the effectiveness of the cleaning agents. These were the Inclined Trough Test and a new Swirling Coupon Test. Two substrates (stainless steel and porcelain tile) were evaluated for each procedure. The two procedures were evaluated for the precision of their results in estimating cleaning performance, costs associated with conducting a given procedure, and the ease of conducting that procedure (e.g., number of tests performed in 8 hr, skill level required of an operator, and overall complexity of the procedure). The precision of results for cleaning performance were 4% to 7% (standard deviation about the mean) for the Inclined Trough Test and 10% to 12% for the Swirling Coupon Test. Costs to perform a procedure also favored the Inclined Trough Test. The number of tests performed in 8 hr, the skill level of an operator, and the overall complexity of a procedure were similar for both tests.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is documented in two reports (see ordering information at back).

Introduction

Despite all response efforts, spilled oil often reaches shorelines and other environmentally sensitive areas. When the oil arrives at the shoreline, it is usually several days old and "weathered," so it is thick, may be emulsified, and is frequently difficult to remove from shoreline substrates.

Under the proper circumstances, surface washing agents can be used to mitigate detrimental effects of stranded oil on natural shorelines. Such agents would be used to remove oil because of biological sensitivity of indigenous fauna and flora to oil, amenity considerations of the shoreline, or concern about the oil refloating and subsequently being stranded on adjacent shorelines. Chemical cleaning agents do, however, have certain limitations: indigenous fauna and flora can have a toxic response or oil can be moved into permeable shorelines.

In past years, chemical dispersants have been applied as washing agents to clean shorelines. By breaking oil-water surface bonds and creating numerous small droplets of oil, the dispersant helps move the oil off of the surface and into the water column. On the open sea, this is frequently beneficial since it prevents shoreline washups. On the beach, however, dispersion is not always desirable: dispersed oil can worsen the contamination because oil remains in the water and cannot be removed through flotation/skimming operations, thereby increasing the amount of oil in the permeable shoreline sediment.

Surface washing agents, also called shoreline cleaning agents, are similar to dispersants in that they also promote the release of oil adhered to shoreline surfaces; but they will not prevent the coalescence or reaggregation of the oil droplets. They will allow the oil to resurface so that it may be mechanically removed by booming and skimming operations. Therefore, the oil that is washed away from the substrate can be removed and further contamination does not occur.

State-of-the-Art Report On Surface Washing Agents

The SOTA report discusses the mechanism of action of chemical surface washing agents, factors affecting performance of cleaning agents, laboratory methods for testing performance of such agents, an evaluation of these laboratory methods, and recommendations for future research. The discussion of laboratory methods for performance testing presents information on the general approach used for laboratory tests, available information for identified tests, similarities and differences among tests, the laboratory apparatus required, brief summaries of the testing procedures, differences among the methods, and considerations of how the design of a particular method might affect results. The full report also considers common cleaning strategies for oil stranded on shorelines and a brief summary of applications of chemical cleaning agents and their performance in field trials and spills-of-opportunity.

General Mechanism of Action of Chemical Cleaning Agents

Chemical agents for cleaning oiled shorelines can be included in three categories: (1) nonsurfactant-based solvents, (2) chemical dispersants, and (3) surfactant formulations especially designed to release stranded oil from shoreline substrates (i.e., surface washing agents). These agents are intended to release stranded oil from shoreline surfaces (e.g., rock faces, cobble, gravel, sand, mud flats, beached logs, etc.). Depending on the specific circumstances, chemical agents would generally be used to release oil into (offshore) surface waters where the oil can be recovered by mechanical procedures such as booming and skimming. In biologically sensitive environments, the chemical cleaning agents should neither facilitate dispersion of the treated oil into the offshore water column nor enhance penetration of the oil further into permeable shoreline substrates. Cleaning solvents and surface washing agents are designed to minimize dispersion of oil into the water column. In contrast, chemical dispersants will not only promote dispersion of oil into water (i.e., their intended purpose) but can also produce elevated concentrations of oil in permeable sediment substrates under appropriate conditions. Hence, use of chemical dispersants to clean shorelines may not be appropriate, or may be limited to beaches with low permeability or to offshore waters where the dispersed oil can be rapidly diluted.

The purpose of cleaning agents that do not contain surfactants is to soften or lower the viscosity of the treated oil. This can help release oil when flushed with water. When released, the oil should rise to the water's surface, as long as its overall density remains less than that of the water. The oil can then be recovered by mechanical means.

Surfactant-based cleaning formulations (chemical dispersants and surface washing agents) contain solvents, additives, and surface-active agents (surfactants). The solvents primarily help surfactants dissolve in the cleaning formulations and enhance penetration and mixing of the surfactants into oil. Additives increase the biodegradability of the oil and improve the dissolution of the surfactants in the oil. Surfactants, the major ingredient, contain both oil-compatible and water-compatible groups. Because of this amphiphatic nature (i.e., opposing solubility tendencies), surfactant molecules will tend to gather at oil/water interfaces and reduce the oil/water interfacial tension. Although surfactants are present in both surface washing agents and dispersants, those present in surface washing agents are generally more hydrophilic.

The cleaning action of both surface washing agents and dispersants is basically a detergent action that reduces the adhesion of oil to a substrate. Oil initially adheres to a substrate surface as a film characterized by a relatively large contact angle between the oil and substrate. After applying a surface washing agent or dispersant to the oil film, surfactant molecules reside at the oil/water interface. The presence of the surfactants decreases the oil/water interfacial tension; this, in turn, promotes roll-up of the oil film from the substrate surface into a droplet shape (i.e., increasing oil/water interfacial surface area) and reduces the contact angle between the oil and substrate surface. The reduced adhesion helps release the oil when the substrate is flushed with water. If surfactant molecules remain at the oil/water interface (e.g., the more hydrophobic surfactants in dispersants), the oil will tend to remain dispersed in a water column and not re-adhere to shoreline substrates. In contrast, the more hydrophilic surfactants in surface washing agents have a greater tendency to dissolve into the water phase, which favors subsequent coalescence or reaggregation of the oil droplets into surface slicks after release of the oil from substrate surfaces. As long the oil can be mechanically recovered from a surface slick, it is best not to disperse the droplets.

Factors Affecting Release of Oil from Surfaces

Factors that promote release of stranded oil from substrate surfaces can include physical and chemical properties of an oil, composition of the cleaning-agent formulation, characteristics of shoreline substrates, method for applying a cleaning agent to stranded oil, characteristics of the flushing or washing method, ratio of cleaning agent-to-oil, temperature, and salinity. Crude and refined petroleum products are complex mixtures of hydrocarbon compounds that can contain compounds in five broad categories: lower-molecular-weight aliphatics and aromatics, and higher-molecular-weight asphaltenes, resins, and waxes. Interactions between these allow all of the compounds to be maintained in a liquid-oil state. The lower-molecular-weight aliphatics and aromatics act as solvents for the less soluble, higher-molecular-weight asphaltenes, resins, and waxes. In addition to inherent differences in chemical compositions among different parent oils, oil that is released onto a water's surface and is stranded on a shoreline undergoes rapid, dynamic changes in both its chemical composition and physical properties because of natural weathering processes (e.g., selective dissolution and evaporation losses of lower-molecular-weight components as well as photo-oxidation and microbial degradation of selective compounds). With loss of lower-molecular-weight components, the solvency strength of an oil may become insufficient to keep higher-molecular-weight components in solution and thus lead to their precipitation as solid particles. Accompanying changes in the physical state and chemical properties of the oil can affect the way cleaning agents interact with the oil.

Adhesion of oil to substrates depends on the physical and chemical characteristics of substrates: the size, surface properties, and chemical composition of substrate particles. Roughness and porosity of individual particles influence the degree of penetration and persistence of oil on or in the particles.

How a cleaning agent is applied can affect its performance: access to stranded oil with the necessary application equipment, actual method and uniform extent of the application, ratio of cleaning agent to oil, method of penetration of the agent into the oil (including soak time), and subsequent mobilization or release of treated oil from substrate surfaces by flushing with water. In the field, the agent is generally sprayed from hand-held spray packs or motorized/wheeled spray carts that can access the shoreline, nearshore boats, or aircraft. Cleaning agent-to-oil ratios of 1:2.5 to 1:5 are preferred. Following application, soak times of 10 min to 3 hr before washing generally appear to be sufficient to diffuse cleaning agents into stranded oil. Treated oil is washed with water jets at various pressures and temperatures, and additional chemicals may be used in the wash water to assist the cleaning action. Increasing temperature in the wash water assists the cleaning process, although the absolute temperature and volume of the water can be reduced by pretreating the oil with an effective cleaning agent.

Laboratory Tests to Evaluate the Cleaning Performance of Chemical Agents

A limited number of laboratory tests exist for evaluating the performance of chemical cleaning agents under relatively well-controlled conditions in a laboratory. Testing procedures discussed in the SOTA report include the Inclined Trough Test (Environment Canada), the Swirling Coupon Test (developed in this program), the Glass Slide Test (CEDRE), and the Exxon* Beach Washing Test (Table 1). Strengths and limitations associated with each testing method are presented in the full SOTA report.

The Inclined Trough, Swirling Coupon, and Glass Slide Tests use artificial substrates such as stainless steel, porcelain tile, and/or glass; the Exxon Beach Washing Test uses aquarium gravel. All of the procedures involve applying oil to a test substrate and then applying a cleaning agent that is allowed to soak into the oil for a 10- to 60-min period before washing. Ideally, substrates for laboratory tests should mimic real-world materials to provide environmental relevance to results. Because substrates on natural shorelines encompass a broad variety of types and characteristics, no single substrate would apply to all environmental surfaces and situations. The gravel used in the Exxon Beach Washing Test comes the closest. For routine laboratory testing, however, a substrate should be well defined in terms of its morphological and chemical properties (chemical composition, surface roughness, porosity, etc.), relatively uniform over the entire surface (i.e., an absence of heterogeneity), and readily available from commercial sources. These criteria can be satisfied for materials such as stainless steel, porcelain, glass, and quartz.

Laboratory Studies

Two laboratory tests that measure cleaning performance were evaluated. Primary objectives were to obtain estimates of the repeatability of measurements for cleaning performance with different testing methods, evaluate comparability of results obtained with the procedures for selected cleaning agents and oils, and summarize the qualitative ease of conducting each testing procedure (i.e., how many individual test runs can be performed in a given period of time, the complexity of a testing procedure in relation to the required training time and skill level of an operator, and associated costs for both equipment and conduct of tests). All of these objectives have relevance to the suitability of a testing procedure for routine use.

Common elements throughout all of the testing procedures included the following: oil type (Prudhoe Bay crude and Bunker C), cleaning agent (Corexit 9580, Citrikleen XPC, Corexit 7664, and "no agent" controls), test type (Inclined Trough and Swirling Coupon), substrate type (stainless steel and porcelain tile), analytical wavelength (340, 370, and 400 meter absorbance), and duplicate measurements for particular groups.

Test results relative to the primary objectives of the study are summarized in Table 2. Separate values for cleaning performance were obtained by measuring oil that was not only released into the wash water but also remained on the test substrate after washing. Estimates of precision (or repeatability) for values of cleaning performance (i.e., standard deviations about means) were approximately 4% to 7% for the Inclined Trough Test and 9% to 12% for the Swirling Coupon. These values should be viewed as preliminary estimates, however, because they are generated with only a limited number of oils and cleaning agents. Furthermore, final estimates for precision associated with a given testing procedure should incorporate measurements from multiple laboratories. The number of tests that can be performed in 8 hr, the cost per run, and qualitative items such as necessary skill level of an operator and overall complexity of a testing procedure are approximately equivalent for the two test procedures (Table 2); however, costs required to obtain necessary equipment to perform the tests favor the Inclined Trough procedure.

General trends in cleaning performance of the chemical agents for the different testing procedures and substrates are illustrated in Figure 1 for the two test oils and test methods, four testing protocols, and three cleaning agents. Data for the figure are overall means for combinations of the particular test, substrate, oil, and cleaning agent. As illustrated, cleaning performance is consistently higher with Corexit 9580 and Citrikleen XPC for both test oils and all testing procedures. Relative rankings of cleaning performance for the three chemical agents are generally similar among the testing procedures for the two test oils. For example, general trends in performance values are Corexit 9580 ~ Citrikleen XPC > Corexit 7664 for both Prudhoe Bay crude and Bunker C. In contrast, differences occur in absolute values of cleaning performance among the procedures.

Recommendations for Future Research

Overall, there is concern as to whether any of the four existing tests are appropriate measures of surface washing agent effectiveness. There are two problems: none of the tests measure the amount of oil remaining on the surface after washing, and none of the tests account for how easily oil is removed from the water after being washed off the surface. Therefore, more research is needed before a surface

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 1. Summary of Features of Laboratory Methods for Testing Performance of Oil-Cleaning Agents

Test ID	Reference	Substrate	Oil-to-Substrate Contact Time	Cleaning Agent Appl. Method	SOR*	Agent Soak-Time	Wash Water Add Method	Wash Water Volume (mL)	OWR †	Complexity Rating ‡
Inclined Trough	Fingas et al., 1989	Stainless steel	10 min	Dropwise	1:5	10 min	Gravity flow	20	1:67	2
Swirling Coupon	SAIC (this project)	Stainless steel/porcelain	18 hr	Dropwise	1:3	10 min	Swirling flow	250	1:5200	2
Glass Slide	CEDRE (unpublished)	Glass/quartz	20 min	Spray	1:2	10 min	Spray	560	1:1000	1
Beach Washing	Fiocco et al., 1991	Aquarium gravel	(not defined)	Spray	1:2.5	1 hr	Gravity flow	100	1:36	3

* SOR = shoreline cleaning agent-to-oil ratio (v:v; assume oil density of 0.9 g/mL).
† OWR = oil-to-water ratio (v:v; assume oil density of 0.9 g/mL).
‡ Complexity Rating: 1 = lowest; 3 = highest.

Table 2. Results of Test Procedures Used to Evaluate Performance of Shoreline Cleaning Agents

Test Procedure	Standard Deviation for Oil Recovery in Fraction: Water	Standard Deviation for Oil Recovery in Fraction: Substrate	No. Tests/8 hr	Equip. cost	Cost/Run	Complexity of Procedure	Operator Skill Level
Inclined Trough-stainless	**4.4%**	3.8%	24	$305	$32	low	low
Inclined Trough-tile	7.2%	4.8%	24	305	32	low	low
Swirling Coupon-stainless	**12.0%**	**10.4%**	24	1,570	32	low	low
Swirling Coupon-tile	10.3%	8.9%	24	1,570	32	low	low

* Bold values for standard deviations are estimates because variances among groups are heterogeneous by Bartlett's test for homogeneity.

washing agent effectiveness test can be adopted as a regulatory tool.

The major conclusion of this study is that the overall performance of the two surface washing agent effectiveness tests evaluated is similar, but that the costs for the Inclined Trough Test are lower. However, more research is needed to determine if an improved test can be developed which may be used to better measure the cleanliness of a surface or evaluate how well oil may be removed from water after it is washed from a surface.

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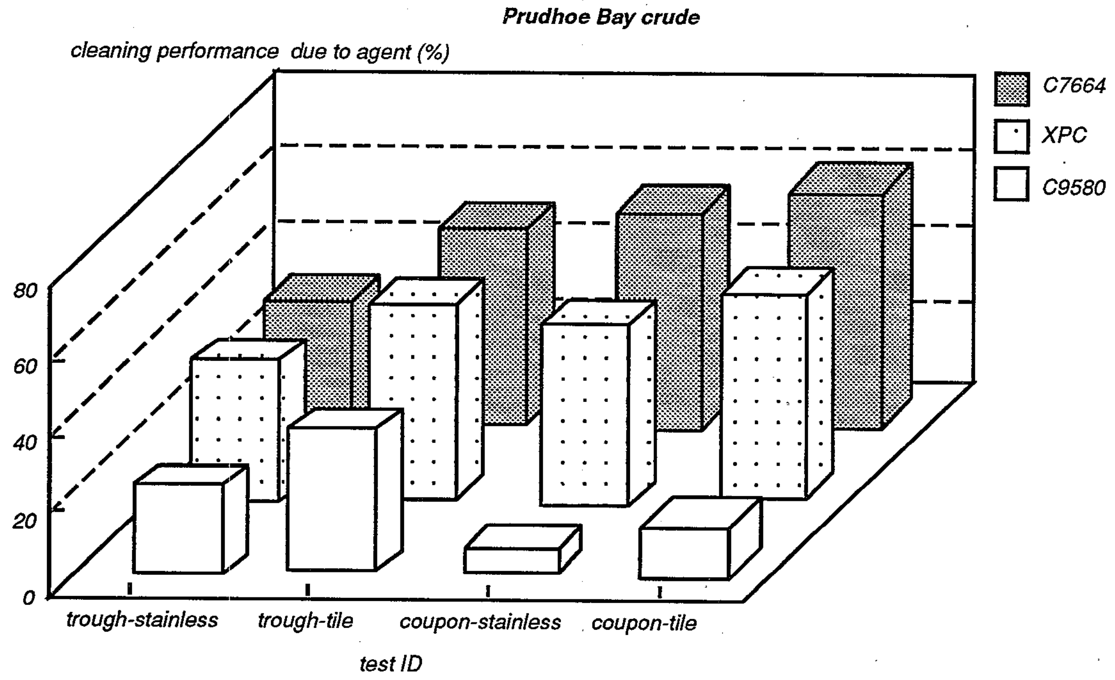

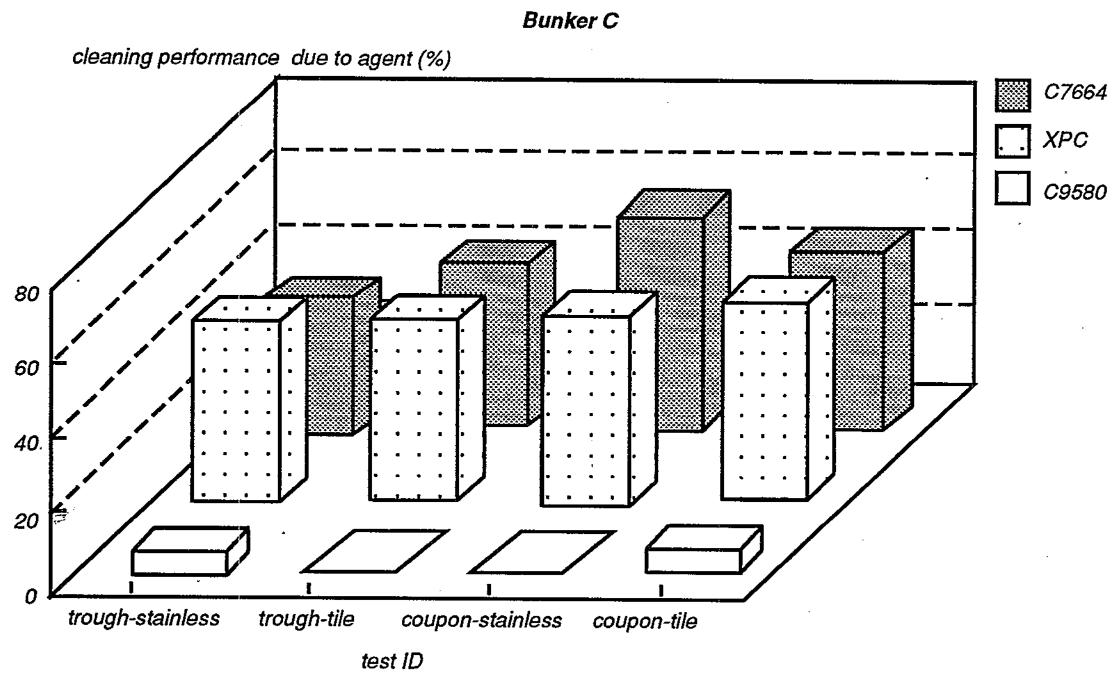

Figure 1. *Cleaning performance for four testing protocols with two oils and three cleaning agents. Values are means from replicate measurements.*

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***Choudry Sarwar** is the EPA Technical Project Monitor (see below).*
Completed reports produced in the project are the following:
(1) "Clayton, J.R., Jr. 1992. Chemical Shoreline Cleaning Agents for Oil Spills: Update State-of-the-Art on Mechanisms of Action and Factors Influencing Performance. Final Report." (Order No. PB93-203693; Cost: $27.00, subject to change)
(2) "Clayton, J., S.-F. Tsang, V. Frank, P. Marsden, N. Chau, and J. Harrington. 1992. Chemical Shoreline Cleaning Agents: Evaluation of Two Laboratory Procedures for Estimating Performance. Final Report." (Order No. PB93-203701; Cost: $19.50, subject to change)
The reports will be available only from:
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