Mechanism of Dispersion and Dispersant Composition

Following an oil spill, some of the oil will disperse naturally into the water column. The extent to which this occurs depends on the type of oil spilt and the mixing energy. Oils with a lower viscosity are more amenable to natural dispersion than the ones with a higher viscosity. Natural dispersion takes place when the mixing energy provided by the waves and wind is sufficient to overcome surface tension at the oil/water interface and break the oil slick into droplets of variable sizes. Generally, larger oil droplets will rapidly resurface and then coalesce to form an oil slick, but the smaller droplets will remain suspended in the water column where they will be diluted by turbulence and subsurface currents.

The process of natural dispersion takes place in moderately rough seas with breaking waves and winds above 10 knots (5 m/s). Severe storm conditions in Shetland, UK, at the time of the grounding of the M.T. BRAER caused virtually all of the 84,000 tonne cargo of Gulfaks North Sea crude oil to be dispersed naturally and resulted in minimal shoreline impact.

Chemical dispersants are designed to enhance natural dispersion by reducing the surface tension at the oil/water interface, making it easier for waves to create small oil droplets. Modern chemical dispersants are a blend of surfactants (surface active agents) in a solvent. The solvent has two functions: it reduces the viscosity of the surfactant which enables it to be sprayed and it promotes the penetration of the surfactant into the oil slick.

The surfactant molecules are the key component of the dispersant. They are made up of two parts: an oleophilic part (oil-loving) and a hydrophilic part (water-loving). When dispersants are sprayed onto an oil slick, the solvent transports and distributes the surfactants through the oil slick to the oil/water interface where they re-arrange so that the oleophilic part of the molecule is in the oil and the hydrophilic part is in the water. This creates a sharp reduction in the surface tension of the oil/water interface and small oil droplets break away from the oil slick with the help of wave energy. Re-coalescence is minimised by the presence of the surfactant molecules on the droplet surface and the reduced probability of encountering other oil droplets as they move apart.

To achieve an efficient dispersion, oil droplet size must be in the range of 1 µm* to 70 µm with the most stable size being less than 45 µm. Smaller droplets are better as they remain suspended in

* µm = micro-metres = 10⁻⁶ metres.
the water column where they will be diluted rapidly in the top few metres of the sea to below harmful concentrations. The increased surface area provided by the small droplets also enhances the opportunity for biodegradation of the oil.

The dispersants which are available on the market today comprise a solvent and a blend of two or three surfactants. The most common surfactants used are non-ionic (fatty acid esters and ethoxylated fatty acid esters) and anionic (sodium alkyl sulphosuccinate). Generally, around the world, two main compositions are encountered:

**Hydrocarbon-based dispersants** The solvent is a hydrocarbon with a low or no aromatic content. These dispersants typically contain between 15-25% surfactant and are intended for neat application to oil. They should not be pre-diluted with sea water since this renders them ineffective. They also require a high application rate of between 1:1 to 1:3 (dispersant to oil). Hydrocarbon-based dispersants are less effective and may be more toxic than concentrate dispersants and, as a consequence, in many countries are not now commonly in use.

**Concentrate or self-mix dispersants** These dispersants contain a blend of different surfactants with both oxygenated and hydrocarbon solvents. They contain a higher concentration of surfactants (25% to 65%) and can be applied either undiluted (neat) or pre-diluted with sea water although it is more common to apply them undiluted. A typical dosage ranges between 1:5 to 1:30 (undiluted dispersant to oil).

It is important to remember that dispersants are manufactured primarily for use in the marine environment. Their efficiency will be optimum in waters with a salinity of around 30-35 parts per thousand (ppt) but will decrease rapidly in waters with a salinity below 5-10 ppt, especially when pre-diluted. Similarly, efficiency is also affected when salinity rises above 35 ppt. In freshwater, dispersant effectiveness is dramatically reduced because the surfactants tend to travel through the oil layer into the water column instead of stabilising at the oil/water interface. Nevertheless, some dispersants have been specially formulated for use in freshwater. In a confined freshwater system, other factors also need to be considered, such as whether there is sufficient water depth or exchange of water to achieve adequate dilution.

**Limitations of Chemical Dispersants**

Dispersant effectiveness is limited by certain physical and chemical parameters, the most important of which are sea state
and oil properties. An awareness of these limitations is important to identify circumstances when dispersant use is appropriate.

**Sea State** A minimum amount of wave energy is required to achieve successful chemical dispersion at sea. In the absence of sufficient wave energy to form and maintain the dispersion of oil droplets into the water column, they may re-surface and form a slick. However, the efficiency of chemical dispersion will improve with increasing sea state only to a certain level. In severe sea conditions, the oil will be submerged by breaking waves, preventing direct contact between the dispersant and the oil. Dispersant sprayed on to water rather than oil will be ineffective. Field trials indicate that a wind speed between 4 to 12 m/s (about 5 to 25 knots) is optimum.

**Oil properties** The properties of the oil and the way these properties change with time on the sea are important when assessing the likelihood of successful chemical dispersion. The viscosity and pour point of an oil provide a good indication of its dispersability. As a general rule, fresh light to medium crude oils (group 2 or 3 oils—see ITOPF Technical Information Paper No. 2 ‘Fate of Marine Oil Spills’) are considered to be readily dispersible whereas highly viscous oils are not. The upper limit of dispersability is likely to be reached with heavier oils (group 4 oils). As a general rule, dispersant effectiveness will decrease as oil viscosities increase. They are likely to be ineffective for oils with an initial viscosity above 10,000 cSt at the time they are spilled. Pour point is also an important parameter. Any oil with a pour point higher than the ambient temperature (such oils are usually transported heated) will start to become very viscous as they cool after spillage and may even become solid. As a general rule, oil with a pour point 10-15°C below sea temperature will be difficult to disperse chemically.

Group 1 oils, such as diesel, gasoline and kerosene, spread to form very thin films of oil on the water surface (often referred to as ‘sheen’ because they are iridescent) and they readily evaporate without need for the use of dispersants. It is therefore not advisable to use dispersants on oils from this group or on sheens which have formed from any crude or fuel oil. This is because the dispersant droplets tend to punch through the thin film or sheen and cause ‘herding’ of the oil. This effect creates an immediate area of clear water that should not be mistaken for dispersion.

Once an oil has been spilled, the viscosity rapidly increases from its initial value due to the loss of volatile components through evaporation and through emulsification. Some oils are particularly prone to forming water-in-oil emulsions (especially those that have a relatively high asphaltene content (>0.5%) and a combined nickel/vanadium concentration greater than 15 parts per million). Emulsification causes an increase in both viscosity and volume.

The increase in viscosity caused by evaporation and emulsion formation restricts the ability of the dispersant to reach the oil/water interface and makes it difficult to overcome the mechanical resistance to mixing. This prevents the formation of small oil droplets. However, if the emulsion is unstable, concentrate dispersants may be able to break it back to its parent oil, releasing the water and allowing the relatively fresh oil to be dispersed by a second application of dispersant. Given these changes in oil properties over time, the opportunity for the successful application of dispersants is limited. The time available usually ranges from a few hours to a few days depending on the type of oil involved and the environmental conditions.

**Dispersant Choice and Dosage** The choice of dispersant and the dosage will affect the amount of oil actually dispersed. In many circumstances it is preferable to use undiluted concentrate dispersants in open waters. Dispersants are manufactured to slightly different formulations, and their effectiveness varies to a greater or lesser degree with the type of oil treated. Some dispersants have been formulated specifically with the aim of treating viscous oils. Laboratory tests may be carried out to rank one dispersant relative to another for a particular oil and some countries require operators of oil terminals or rigs to undertake such studies to identify the most effective dispersant for the oil involved. However, the results from these tests cannot be based solely on laboratory data.
extrapolated to predict the amount of oil that will be dispersed at sea as the test conditions are not designed to mimic sea conditions. For planning purposes a dosage of 1:20 dispersant to oil is commonly used and spraying equipment is often pre-configured to achieve this. This dosage may be decreased on fresh oils and conversely increased for viscous oils or emulsified oils where more than one application may be needed.

Application Methods

Dispersants can be applied to spilled oil on open water by boats or aircraft. Large multi-engine aircraft are best suited to dealing with major off-shore spills whereas, boats, single-engine aircraft and helicopters are suitable for treating smaller spills that are closer to the shore. In the right circumstances, helicopters can also reload with dispersants from a vessel or offshore oil platform for open water response.

The droplet size of the dispersant is important as it needs to be sufficiently large to overcome the effects of wind and evaporative loss but not so large that it will result in the droplets being able to “punch” through the oil slick. The optimum droplet size is between 600 and 800 µm. Ultimately, whichever method of application is used, the key to a successful response using chemical dispersants is the ability to target the thickest part of the oil slick within a short time and before weathering or sea state render the oil undispersable.

Vessel spraying Dispersants are usually applied from boats equipped with spray arms. In a typical spray arm system, diesel or electric pumps are used to pump dispersants from a storage tank through a set of nozzles calibrated to produce a uniform spray pattern of droplets. Spray units can be portable or permanently installed on a vessel and systems are available that deliver the dispersant either undiluted or diluted with sea water.

Spray arms are usually mounted as far forward on the vessel as possible to avoid the effect of the bow wave which can push the oil beyond the spray swath. Mounting the spray arms on the bow allows the vessel to travel faster and, because freeboard is often greater at the bow, also allows the spray arms to be made longer. However, if the arms are too long they risk damage when the vessel rolls. This combination of benefits optimises the amount of oil that can be treated (‘encounter rate’) with a limited dispersant payload.

If spray arms are not available, fire hoses or monitors are sometimes used to apply diluted concentrate dispersants. However, optimum dilution of the dispersant is difficult to achieve because of the very high flow rates and wastage of dispersant is a common problem. The high-powered jet of water also makes it difficult to apply the dispersant as a uniform spray of droplets and it is frequently forced through the oil making it ineffective. Thus fire monitors are unlikely to be an effective application tool unless specially modified for the purpose.

Vessels offer certain advantages for dispersant spraying because they are usually readily available, easy to load and deploy, have cost advantages over aircraft and can apply dispersant fairly accurately to specific areas of a slick. Nevertheless, they also have serious limitations, particularly for larger spills, because of the low treatment rate which they offer and the added difficulty of locating the heaviest concentrations of oil from the bridge of a vessel. Furthermore, when slicks become fragmented or form narrow windrows, it is inevitable that some dispersant will be sprayed onto clear sea. These problems can be partially overcome by controlling the operation from a spotter aircraft.

Aerial spraying Aerial spraying of dispersant offers the advantages of rapid response, high treatment rates and optimum dispersant use. Two categories of aircraft are used: those designed for agricultural or pest control operations which require minor modification for dispersant application and those that have been adapted specifically for the application of dispersant. Some helicopters are able to carry under-slung bucket spray systems, usually without the need for modifications.

The ideal aircraft will be determined primarily by the size and location of the spill, although in reality local availability will be the crucial factor. The aircraft should be capable of operating safely at a low altitude (typically 50 to 100 feet for larger aircraft) and at relatively slow speeds (50 to 150 knots) and in addition need to be highly manoeuvrable. Endurance, fuel consumption, turn around time, payload and the ability to operate from short or improvised landing strips are also important considerations when selecting suitable aircraft.
Dispersants are sometimes used to remove oil or 1,000 litres x 15 m x 45 m/s = 3.37 litres/s within a few hours to reach an average thickness of 0.1 mm. As a general rule, most fresh oils on the sea surface will spread depending on the type of dispersant, the type of oil and the thinning conditions. The application rate may be calculated in two steps as follows:

1. Estimation of the volume of oil (in litres/hectare)
2. Calculation of the quantity of dispersant needed to achieve the dose required (litres) and the application rate (litres/hectare)

As a general rule, most fresh oils on the sea surface will spread within a few hours to reach an average thickness of 0.1 mm (0.1 m). At this thickness, the volume of oil in one hectare (104 m²) would be:

\[10^4 \text{ m} \times 10^3 \text{ m}^2 = 1 \text{ m}^3 \text{ or 1,000 litres}\]

For a dosage of 1:20, the quantity of dispersant required would be: 1000 litres / 20 = 50 litres, and the application rate would be 50 litres/hectare (10 imp. gal/acre). The discharge rate can then be calculated by multiplying the application rate (litre/m²) by the swath width of the spraying arm (m) and the speed of the aircraft (m/s).

In our example, if dispersants were applied by an aircraft travelling at a speed of 90 knots (45 m/s) with a swath width of 15 m and an application rate of 50 litres/hectare (0.005 litre/m²), the discharge rate would be:

Discharge rate = 0.005 litres/m² x 15 m x 45 m/s = 3.37 litres/s (or about 200 litres/minute).

Thus, to disperse a slick of 0.1 mm thickness at a dose rate of 1:20, the discharge rate of the pump of the spraying system would need to be adjusted to a rate of about 200 litres per minute. The same calculation is made to determine the discharge rate for vessel application.

In practice, it is impossible to evaluate precisely the amount of oil in a slick and determine the optimum dosage since the thickness varies significantly within the slick. Provided that the thickest part of a slick is targeted, it is unlikely that over-application of dispersants will be an issue. Application rates of the order of 50 litres/hectare have been found to be appropriate in many situations, but adjustment is required to compensate for possible variation in slick thickness caused by different types of oil and environmental conditions. The application rate may be controlled by varying the discharge rate of the pumps or the speed of the vessel or aircraft.

Shoreline application

Dispersants are sometimes used to remove oil from hard surfaces such as rocks, sea walls and other man-made structures. They are generally applied to the surface and scrubbed into the oil before flushing with sea water. The dispersed oil cannot be collected and for this reason dispersant use on the shoreline is restricted to areas of low environmental concern. Shoreline cleaners may also be used but it is important to note that their mechanism of action is different to that of dispersants. Degreasers are often carried on board ships to deal with small spillages of oil on deck but most are more toxic than dispersant and should not be used as a dispersant at sea or as a shoreline cleaner.

**Application rate**

One of the main challenges for the application of dispersants lies in the estimation of the volume of oil to be treated and, hence, the calculation of the appropriate application rate. To achieve this, assumptions must be made concerning the average thickness and volume of an oil slick. The ratio of dispersant to oil required for effective dispersion varies between 1:3 and 1:50 depending on the type of dispersant, the type of oil and the prevailing conditions. For planning purposes, the application rate can be calculated in two steps as follows:

1. Estimation of the volume of oil (in litres/hectare)
2. Calculation of the quantity of dispersant needed to achieve the dose required (litres) and the application rate (litres/hectare)

*Shoreline cleanup using chemicals during the SEA EMPRESS incident, UK, 1996.*

**Monitoring Dispersant Effectiveness**

The effectiveness of chemical dispersion should be monitored continually and the response terminated as soon as the dispersant is no longer working. In clear weather conditions, successful dispersion will often produce a coffee-coloured plume seen to spread under the water surface. However, visual observation of effectiveness may be impaired in poor weather conditions, in waters with a high sediment content, when dispersing pale-coloured oils, and in poor light. Clearly, it is impractical to spray effectively at night.

Experience has shown that for the application of dispersants to be worthwhile, the oil will need to disperse sufficiently rapidly to effect a change in appearance of the slick and a subsequent reduction in oiled area, which should be visible from the air shortly after spraying. Conversely, if there is no change in oil appearance or coverage, and the dispersant runs off the oil to create a milky white plume in the water, these are signs that the dispersant is not working. Equally, if the oil has become fragmented and widely scattered, it is unlikely that sufficient oil...
will be removed from the water surface by the dispersant to achieve a significant reduction in pollution damage.

Ultra-violet fluorimetry (UVF) is sometimes used to provide ‘real-time’ data on the concentration of dispersed oil in the water column during the application of dispersants. Typically, the variation in the concentration of fluorescent components is measured at least 1 metre under the slick using a fluorimeter that is towed behind a sampling boat. In open water, dispersion is demonstrated by a significant increase in the concentration of oil detected by the sensor compared with that measured prior to dispersant application. However, when used operationally, UVF does not provide a quantitative measurement of the amount of oil that is actually being removed from the sea surface and it should be used in combination with visual observations to decide whether a worthwhile response can be achieved.

**Logistics and Control**

Dispersant application is a specialised operation that requires preparation and trained operators. In the interests of safety and effectiveness it is desirable to use spotter aircraft to guide and coordinate spraying vessels and aircraft. The crew of the spotter aircraft should be able to identify the heavier concentrations of oil or the slicks posing the greatest threat and they need to have good communication with the spraying aircraft or vessel crews in order to guide them to the target. During the spraying operation itself, spotter aircraft can be used to judge the accuracy of the application and the effectiveness of the treatment. These functions are particularly important when large multi-engine aircraft are used for spraying because at low altitude the crew have great difficulty in distinguishing between oil and sheen, especially if the slick is broken up.

To ensure safety during the spraying operation, aircraft exclusion zones need to be in force during spraying. Relief crews may be called for as flying over the sea at low altitude is extremely arduous. Periodic checks of the aircraft are also recommended to ensure that the dispersant does not contaminate lubricants, particularly in the tail rotor of helicopters, or attack exposed rubber components of aircraft flight control systems. It is advisable to wash down the aircraft frequently with fresh water to remove both dispersant and salt water spray.

Good organisation on the ground is also needed to enable spraying operations to continue for the maximum available time during daylight hours. This may require routine maintenance and transport of additional supplies of fuel and dispersant to be carried out at night. Consequently, stockpiles of dispersant should be sufficiently well stocked and conveniently located in order to supply vessels or aircraft with the minimum delay. Thought should also be given to the equipment required for reloading vessels or aircraft, such as high capacity pumps and road tankers. Dispersants can either be stored in 200 litre drums or in intermediate bulk containers (IBCs). While dispersants in drums will be adequate to support a small-scale operation, a large aircraft would have to be supplied from bulk containers or road tankers.

For long-term storage of dispersants, plastic drums are preferable provided that they are kept out of direct sunlight. Dispersants that are stored unopened should last for many years. However, once opened, the dispersant should be tested periodically for its effectiveness. Recommendations from manufacturers include an annual visual inspection together with a control of the main physical characteristics such as density, viscosity and flash point. If these physical parameters have significantly changed or the expiry date has been reached, a dispersant effectiveness test should be conducted. Dispersants of different types, ages or brands should not be mixed in the same tank or storage container as this may alter the viscosity of the dispersant or cause some components to precipitate or coagulate. Dispersants should not be stored after they have been diluted with sea water. The optimum storage temperature for most dispersants is between -15°C and 30°C and manufacturers recommend that temperature fluctuations are kept minimal during storage. In very cold temperatures, some dispersants may become too viscous to pass through the spray nozzles.

**Environmental Considerations**

Dispersant use has always been controversial. It may be viewed as a way of minimising potential impacts on sensitive resources by preventing or reducing shoreline contamination, but it is also sometimes seen as adding another pollutant to the environment. Despite improvements in dispersant formulations, toxicity of the dispersant/oil mixture to marine fauna and flora is often the major environmental concern. Approval processes for dispersant use are normally in place which are designed to take both effectiveness and toxicity into account. For example, some countries require the dispersant/oil mixture to be no more toxic than the oil alone.

In open water, elevated oil concentrations are normally only observed in the upper layers of the water column (≤10 m) and are rapidly diluted by water movement. Studies have shown that oil concentrations in the range of 30 to 50 ppm can be expected in the surface 10 metres or so of the water column immediately after dispersant application, diminishing to 1 to 10 ppm after a few hours. The exposure for marine organisms is thus acute rather than...
chronic and the limited exposure time reduces the likelihood of long-term adverse effects on fauna and flora. However, spraying dispersants in shallow water is inadvisable if dilution of the dispersed oil plume may be restricted or if the dispersed oil may interact with suspended sediment in the water column and sink.

An estimation of the dilution potential is a useful basis for making the decision whether dispersants should be used to protect certain resources without risking undue damage to others. Relevant factors to take into account are water depth, oil quantity per unit area, the distance between the application site and sensitive areas as well as the direction of currents and the mixing depth of the surface waters.

By removing oil from the water surface, dispersants minimise impacts on sea birds and sensitive shorelines such as salt marshes, mangroves and tourist beaches. In addition, the ability of many free swimming fish species to detect and avoid oil in the water column will help to reduce their potential exposure. However, corals, sea grass and fish spawning areas may be highly sensitive to dispersed oil and dispersants are not normally used if these resources could be affected. The use of dispersants would not normally be recommended in the vicinity of fish cages, shellfish beds or other shallow water fisheries due to the increased risk of tainting. Similarly, the use of dispersants close to industrial water intakes is not advisable.

Dispersant use is not appropriate in environmentally sensitive areas like coral reefs and seagrass beds except in special circumstances and after careful consideration of the potential environmental consequences of using them. A balanced assessment of the net environmental and economic benefits is necessary.

The factors influencing the decision to use dispersants are seldom clear-cut and the choice is necessarily a compromise between other options, cost-effectiveness and conflicting priorities for protecting different resources from pollution damage. Because the opportunity to use dispersants may be limited, the circumstances when dispersants may or may not be used should be agreed upon before a spill occurs to avoid delays. The advantages and disadvantages of their use need to be evaluated and compared with other response methods, a process often referred to as Net Environmental and Economic Benefit Analysis (NEEBA). This process enables responders to balance the positive and negative aspects of different response options (including leaving to natural processes) according to the priorities for protection, the type of oil and the environmental conditions.

Contingency Planning

Factors to be considered during the contingency planning phase are: types of oil likely to be involved in a spill, dispersant effectiveness on these oils, sensitive resources in the area and logistics. Logistics relate mainly to the location and availability of dispersants, spraying equipment, vessels, aircraft, airstrips and refuelling capability, as well as to customs clearance for any international support required. Thought also needs to be given to the cost of maintaining an effective dispersant response capability, including consideration of sources of additional supplies of dispersant. The outcome of these discussions should be documented clearly in a contingency plan. Sensitivity maps are particularly useful to indicate when and where dispersants may or may not be used.

Dispersant use can help protect vulnerable sea birds by rapidly removing oil from the sea surface.
The International Tanker Owners Pollution Federation Limited (ITOPF) is a non-profit making organisation involved in all aspects of combating oil spills in the marine environment. Its highly experienced technical staff have responded to more than 500 ship-source spills in over 90 countries to give advice on clean-up measures, environmental and economic effects, and compensation. They also regularly undertake contingency planning and training assignments. ITOPF is a source of comprehensive information on marine oil pollution through its library, wide range of technical publications, videos and website.

Maps are often used in contingency plans to zone dispersant use. In the example, dispersant use is prohibited in the red area because of year-round commercial fishing, but is pre-approved seasonally for treating oil around a bird colony at Pelican Island (blue) and to treat floating oil to protect over-wintering duck using coastal marshes (green).

In many countries, national regulations require dispersant use to be approved by the competent national authority. For responders, an awareness of dispersant use policy is important as conflicts may arise and fines may be imposed when a facility or ship spills oil and dispersants are used without prior consent or regard for the policy of the country involved. Some countries maintain a list of dispersants that have been approved for use on the basis of efficacy and toxicity testing. In certain situations, the competent authority may also grant pre-approvals to oil handling facilities or ports allowing them to use dispersants without further consultation, provided that certain criteria have been met.

Training and exercises are an essential part of planning for dispersant use, as indeed they are for all aspects of spill response. Operational crews should receive comprehensive training on all aspects of dispersant application and safety, and practical exercises to mobilise resources and deploy and run spraying equipment should be held regularly.

### Summary

- Chemical dispersants enhance the natural break-up of the oil and remove it from the water surface to the water column, where it is rapidly diluted and ultimately biodegraded. They can be a rapid and effective way of minimising pollution damage to sensitive coastal resources.

- Two main types of dispersants exist. Of these, concentrate dispersants are the most effective and have the lowest toxicity. Concentrations of dispersed oil in the water column generally decrease within a few hours to below harmful levels, therefore minimising the risk of long-term adverse effects to marine organisms.

- The limitations of dispersants must be understood and carefully evaluated before any application. In particular, their inability to treat very viscous oils, stable emulsions and the inappropriateness of treating oil sheen should be appreciated.

- For most crude oils spilled at sea, the opportunity to apply dispersant is generally of brief duration and a fast response is essential.

- Whilst vessels are suitable for dealing with small oil spills close to port, large multi-engined aircraft offer a potentially more effective response for major spills offshore.

- The dilution potential in the area where dispersants are to be used is an important consideration. Dispersant application should be avoided in situations where the dispersed oil plume may cause secondary damage to sensitive resources like shellfish beds or industrial water intakes.

- The use of dispersants should be discussed and agreed by all parties involved in the response before an oil spill occurs. A well prepared and practised contingency plan, and a clear policy for dispersant use, significantly increases the likelihood of an effective dispersant operation.