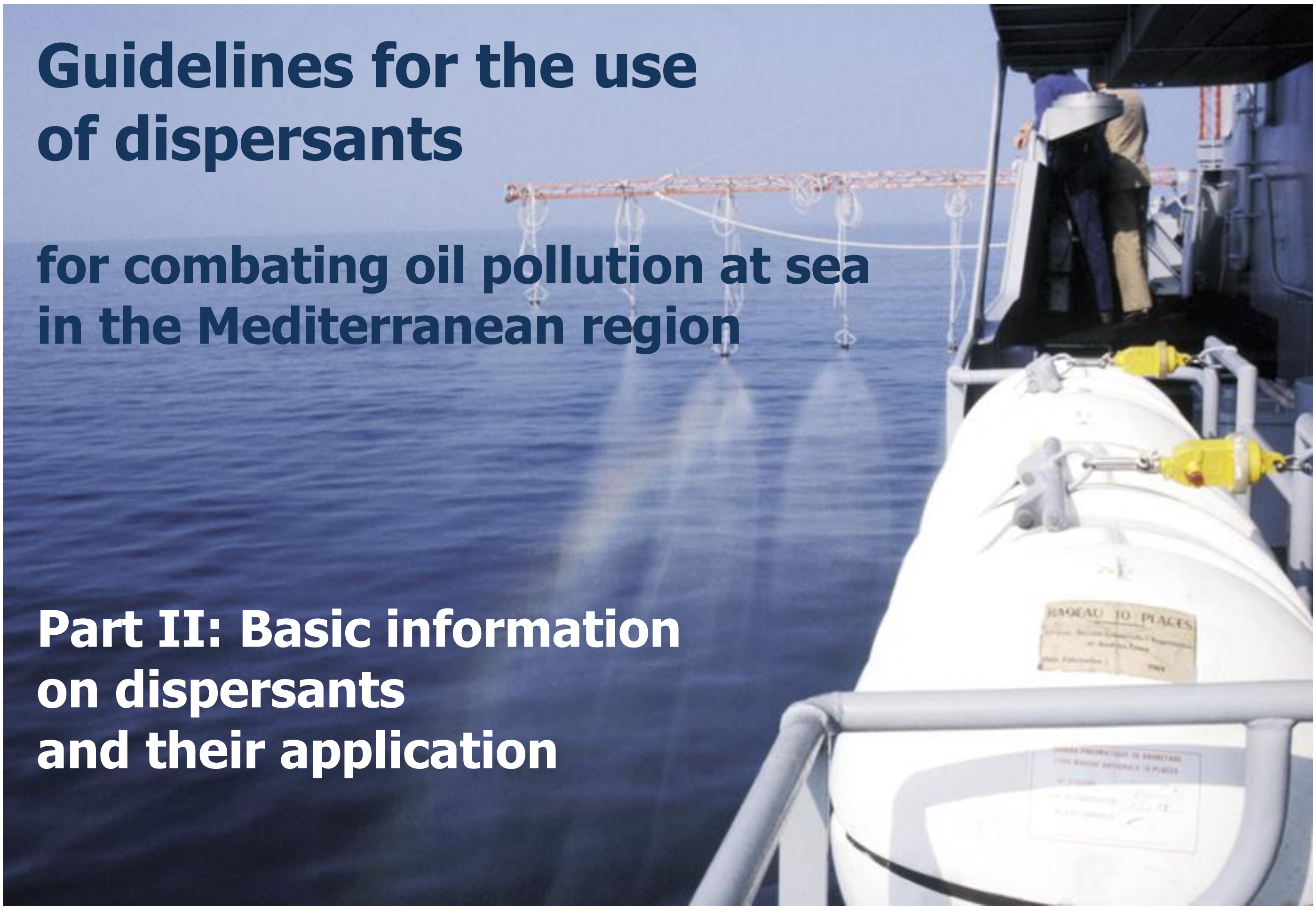

Guidelines for the use of dispersants

for combating oil pollution at sea in the Mediterranean region

Part II: Basic information on dispersants and their application

MEDITERRANEAN ACTION PLAN (MAP)
REGIONAL MARINE POLLUTION EMERGENCY RESPONSE CENTRE FOR THE MEDITERRANEAN SEA (REMPEC)

INTERNATIONAL MARITIME ORGANIZATION

UNEP-PNUE

REGIONAL MARINE POLLUTION EMERGENCY

RESPONSE CENTRE FOR THE MEDITERRANEAN SEA (REMPEC)

MEDITERRANEAN ACTION PLAN

Guidelines for the use of dispersants for combating oil pollution at sea in the Mediterranean region

Part II: Basic information on dispersants and their application

Regional Information System

www.rempec.org

May 2011 Edition

Note

This document is aimed at facilitating the implementation of the “Protocol concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and Other Harmful Substances in Cases of Emergency” of the Barcelona Convention (Emergency Protocol, 1976) and the “Protocol concerning Co-operation in Preventing Pollution from Ships and, in Cases of Emergency, Combating Pollution of the Mediterranean Sea” (Prevention and Emergency Protocol, 2002) by the Contracting Parties of the Barcelona Convention.

These "Guidelines", which are advisory, do not affect in any way already existing or planned national laws and regulations related to matters covered by it. REMPEC assumes no liability whatsoever for any potentially damaging consequences which could result from the interpretation and use of information presented in this document.

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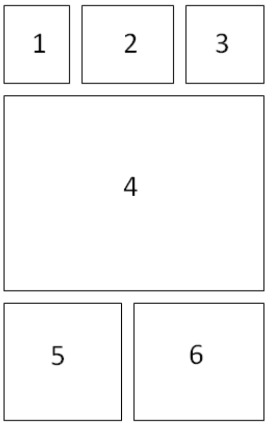

Helicopter mounted spraying system

Airborne treatment

Aerial monitoring operation

Ship mounted spraying system

Airborne treatment

Shipborne treatment

The Guidelines are downloadable from REMPEC’s website (www.rempec.org) in the section “Information resources/Regional Guidelines/Preparedness & Response”.

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Foreword

In a large part of the Mediterranean coastal States, the use of dispersants as a response method for combating accidental oil spills at sea has not as yet been covered by specific national regulations.

Controlled and appropriate use of selected dispersants on types of oil amenable to chemical dispersion, is widely recognized as one of the useful methods for combating accidental oil spills, and in particular the massive ones. Moreover, under certain sea and weather conditions the use of dispersants might be the only applicable response method for protecting sensitive natural resources, coastal installations or amenities.

However, the opportunistic attitude regarding the use of dispersants is hardly acceptable. Selection of products which might be used, definition of zones in which their use is either allowed or prohibited and their place in the general strategy of pollution response need to be adequately regulated if the use of dispersants is expected to produce desired results without creating additional risks for the environment.

Considering the developments in the field of dispersants since the October 1998 edition of the "Guidelines for the Use of Dispersants for Combating Oil Pollution at Sea in the Mediterranean Region", the Ninth Meeting of the Focal Points of the Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC), Malta, 21-24 April 2009, tasked the Mediterranean Technical Working Group (MTWG) to review their content.

This new edition of the Guidelines, endorsed by the Tenth Meeting of the Focal Points of REMPEC, Malta, 3 to 5 May 2011, has been prepared with the technical support of the 'Centre of Documentation, Research and Experimentation on Accidental Water Pollution' (CEDRE) and reviewed by the Centre in collaboration with the MTWG.

They aim at assisting the Mediterranean coastal States in developing and harmonizing national laws and regulations regarding the use of dispersants in response to oil spills at sea. It does not refer to the use of dispersants on shore.

The Guidelines are divided into four independent parts addressing different issues. Each part has been developed with a specific objective and is aimed at different end-users:

PART I REGIONAL APPROVAL

Part I which remains unchanged when compared to the version adopted by the Eighth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (UNEP (OCA)/MED IG.3/5, Appendix I, Antalya, Turkey 15 October 1993), provides regionally approved guidance for the development of national laws and regulation on the use of dispersants.

PART II BASIC INFORMATION ON DISPERSANTS AND THEIR APPLICATION

Part II provides theoretical information on dispersants and their application. It is aimed at providing background information on the matter to any person interested in the subject.

PART III OUTLINE AND TEMPLATE FOR A NATIONAL POLICY ON THE USE OF DISPERSANTS

Part III has been prepared with a view to assisting coastal States in the development of their national policy on the use of dispersants. It has been developed as a template which can be followed and adapted by the authorities in charge of the development/maintenance of the national policy on the use of dispersants and can also be used for the implementation of national or local contingency plan for dispersants.

PART IV OPERATIONAL AND TECHNICAL SHEETS

Part IV is based on the publication entitled "Using dispersant to treat oil slicks at sea. Airborne and shipborne treatment. Response manual" (CEDRE 2005). It provides a set of practical technical sheets which point out the different operational issues when using dispersants. It has been developed for operational users with a view to providing them with the required knowledge for efficient dispersant application.

In order to keep the coastal States regularly informed of the current situation regarding the use of dispersants, REMPEC shall update this document to include any new and significant developments in the research field.

GUIDELINES FOR THE USE OF DISPERSANTS
FOR COMBATING OIL POLLUTION AT SEA
IN THE MEDITERRANEAN REGION

P A R T II

BASIC INFORMATION ON DISPERSANTS AND THEIR APPLICATION

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P A R T II

BASIC INFORMATION ON DISPERSANTS AND THEIR APPLICATION

1. INTRODUCTION

Since their first application on a large scale (in the aftermath of the "Torrey Canyon" oil spill in 1967), the use of dispersants as a response method for combating accidental oil spills has remained a controversial issue. Although often recognized by clean-up specialists as one of the most effective methods for dealing with oil spills, chemical dispersion of spilled oil has numerous setback. The controversy partly stems from lack of information, prejudice and misunderstanding of the action of dispersants. The opposition to using dispersants is often also inspired by the results of their insufficiently planned or improper application. The use of dispersants, especially the decision making process as well as the application process, need to be planned carefully at national level and supported by an appropriate rational stated in a policy.

A relatively small number of countries in the Mediterranean region have a clearly defined policy regarding the use of dispersants. The current status on the policy of use of dispersant in Mediterranean Coastal States can be consulted on REMPEC's Country Profile (http://www.rempec.org/country.asp) available on REMPEC's website (www.rempec.org). The lack of a clear policy regarding dispersants and their use inevitably results in heated discussions at the time of the spill.

The objective of this document is to provide relevant, up to date information on dispersants and their place in oil spill response strategy, which may help the Mediterranean coastal States in creating their policy regarding the use of these products in combating accidental oil pollution. In this respect the document proposes, in Part III, a standard policy for the use of dispersants to be used as a model and adapted by States which would set their National Policy on the Use of Dispersant.

Generally speaking a policy for the use of dispersants should be based on a full understanding of the action of dispersants and currently utilized application methods and operational practices, as well as on adopting compatible and, if possible, standardized procedures for testing and assessing efficiency, toxicity and biodegradability of dispersants and oil/dispersants mixtures.

2. THE MEDITERRANEAN SEA: BASIC CONSIDERATIONS

Despite the fact that the Mediterranean sea is an almost closed sea, with limited exchange of water with the open Atlantic ocean. Generally speaking the volume of the surface sea water concerned by the dispersion process remains quasi infinite regarding the size of a possible major oil spill, and would allow a full dilution of a dispersed oil plume and a return to the background level in such a case.

However, close to the shore and/or in shallow waters the dilution process can meet locally some limitations which should be taken into consideration in the decision to use dispersants.

Considering the use of dispersants, the Mediterranean surface water is salty water (between 37 and 39.50 g/L from the West to the East) except in the very North of the Aegean Sea due to the Black sea water supply (18g/L) and close to some large river estuaries or delta.

The surface water temperature is generally comprised between 18 and 24 °C. Close to the coast the surface water temperature can exceed 24 °C while during winter in northern parts it can drop (e.g. Adriatic Sea, 14 °C…)[1].

Table 1 : Basic considerations for the Mediterranean sea

Surface area (total) 2000 - 3000 m depth contour less than 200 m depth contour	2.5×10^6 km^2 30% 20%
Volume- less than 200 m depth contour	55.5 10^3 km^3
Salinity of surface water	36 to 39.5
Temperature of surface seawater (average)	18 to 24 °C

Tides in the Mediterranean are generally regarded as weak, i.e. tidal amplitudes are much lower than in the oceans.

Figure 1: Map of the Mediterranean Sea

3. GENERAL NOTIONS ON DISPERSANTS

3.1 Definition

Oil spill dispersants are mixtures of surface active agents in one or more organic solvents, specifically formulated to enhance the dispersion of oil into the sea-water column by reducing the interfacial tension between oil and water. Natural or induced movement of water causes a rapid distribution within the water mass of very fine oil droplets formed by the

[1] 1969-P^r P Tchernia-Cours d'Océanographie Régionale- Service Hydrographique et Océanographique de la Marine.

dispersant action, thus enhancing the biodegradation processes. At the same time, oil that is dispersed is no longer subject to the action of wind which makes it drift towards the coast or other sensitive areas. Moreover, dispersants prevent coalescence of oil droplets and reforming of the oil slick.

3.2 History of dispersants

The idea of applying the well known principle of removing a greasy substance by mixing it with a dispersing agent (soap, detergent) and washing it with water was first proposed in the early sixties.

The first extensive use of mixtures of industrial detergents and hydrocarbon aromatics solvents used as dispersants (first generation), in response to the "Torrey Canyon" oil spill in March 1967, unfortunately demonstrated that their toxicity was much too high and that devastating impact on marine life outweighed their efficiency as pollution clean-up agents.

Very soon after, new formulations environmentally acceptable made of less toxic surfactants much less toxic low-aromatic or non-aromatic hydrocarbons (e.g. low aromatic kerosene or high boiling solvents containing branched saturated hydrocarbons) appeared on the market. These new products became known as "second generation" dispersants or referred to as “conventionals” and are less and less in use nowadays.

Dispersants of "the third generation" often referred to as "concentrates" appeared by the mid seventies. These mixtures of emulsifiers, wetting agents and oxygenated solvents which have an higher content of active components (surfactants) and less solvents are more efficient than "the second generation" dispersants and therefore can be used at lower dispersant – oil dosage than the conventionals.They can be applied from boat neat or pre-diluted into seawater, or by aircrafts (always neat). Most of the products marketed today belong to this category.

Since their appearance, dispersants have been used during numerous oil spills of various sizes all over the world and they became an important tool in responding to oil spills. The development of application techniques and significant scientific research in the field of environmental effects of dispersants and dispersed oil was followed by the development of new products.

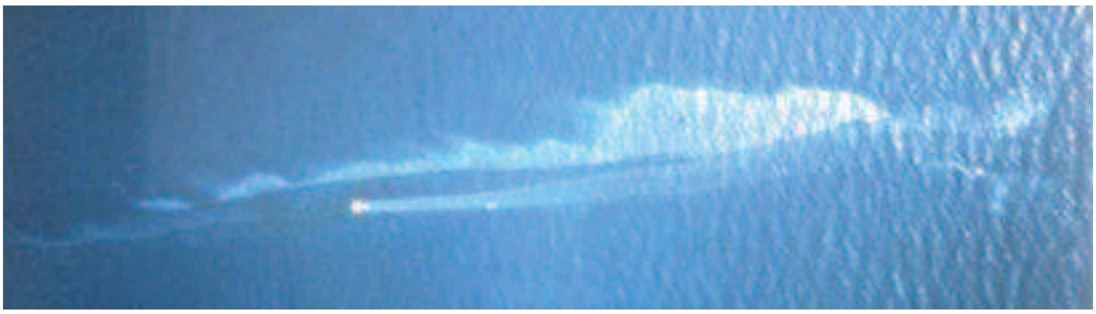

Figure 2: Slicks being dispersed by a helicopter

3.3 Nomenclature of dispersants

The following table summarizes the nomenclature of current dispersants. Dispersants are classified basically into 2 classes: second and third “generations”, commonly called conventionals and concentrates. Aside this classification, the UK authorities classified dispersants according to the generation and to the application method for which the product has been approved: type 1, conventional dispersants; type 2 concentrates approved to be applied pre-diluted into sea water (from boats); type 3, concentrates approved to be applied neat (from boats or aircrafts).

The table below gives a comparative presentation of these systems:

Table 2: Dispersants classification

GENERATION	STANDARD NAME	DISPERSANT-OIL DOSAGE	TYPE OF SOLVENT	TYPE	APPROVED TO BE APPLIED (U.K.)
2nd	Conventional dispersants	High dispersant dosage: 30 – 50% of the oil quantity	Non-aromatic hydrocarbons	1	Undiluted (neat), from vessels
3rd	Concentrate dispersants	Low dispersant dosage: 5 –10% of the oil quantity	Oxygenates (e.g. glycol ethers) and non-aromatic hydrocarbons	2	Diluted, from vessels
				3	Undiluted (neat), from vessels and/or aircraft

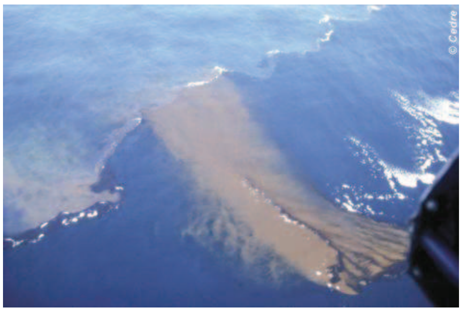

Figure 3: Plume of dispersed oil at sea

3.4 <u>Composition of dispersants</u>

Oil spill dispersants are composed of two main groups of components:

- surface active agents (surfactants),
- solvents

Surfactants (or surface active agents) are chemical compounds with molecules composed of two dissimilar parts: a “water-loving” (hydrophilic) part and an “oil-loving” (oleophilic) part. Surfactants act as a ’chemical bridge’ between oily materials and water and enable these two phases to mix with each other more easily (in other words the surfactant molecules when migrating to the oil – water interface, contribute to reduce the interfacial tension between oil and water). Therefore, the natural agitation (e.g. waves) can break the oil into myriads of tiny droplets which disseminate as a plume into the top layers of the water column.

In order to improve the performance of the dispersant, several surfactants are often combined but only nonionic and anionic surfactants are used in modern formulations:

⇨ nonionic surfactants: sorbitan esters of oleic or lauric acid, ethoxylated sorbitan esters of oleic or lauric acid, polyethylene glycol esters of oleic acid, ethoxylated and propoxylated fatty alcohols, ethoxylated octylphenol.

⇨ anionic surfactants: sodium dioctyl sulfosuccinate, sodium ditridecanoyl sulfosuccinate.

Solvents are simple or mixed added to dispersants in order to dissolve solid surfactants, to reduce the viscosity of the product thus enabling uniform application, to enhance the solubility of the surfactant in the oil and/or to depress the freezing point of the dispersant. Solvents may be divided in 3 main groups: (a) water, (b) water miscible hydroxy compounds and (c) hydrocarbons. Hydroxy compounds used in dispersant formulations include ethylene glycol monobutyl ether, diethylene glycol monomethyl ether and diethylene glycol monobutyl ether. Hydrocarbon solvents used in modern dispersants include odourless, low aromatic kerosene and high boiling solvents containing branched saturated hydrocarbons.

The two groups of modern dispersants have approximately the following composition:

Table 3: Composition of conventional and concentrate dispersants

Conventional (2nd generation) dispersants	Concentrate (3rd generation) dispersants
10 to 25% surfactant	25 to 60% surfactant
Hydrocarbon solvent	Polar organic solvent or mixed with hydrocarbon solvent

Figure 4: Dispersant stockpile in drums

Table 4: Typical compounds used in dispersant formulations

Generation	Description	UK Type	Surfactants	Solvents
Second	Hydrocarbon-base, Conventional	**Type 1**	(i) **Fatty acid esters** (ii) **Ethoxylated fatty acid esters**	**Light petroleum distillates:** Odourless or de-aromatised kerosene Low aromatics (less than 3% wt.) kerosene CAS No. 64742-47-8 EC No. 265-149-8
Third	Water-dilutable concentrate	**Type 2**	(i) **Fatty acid esters** or sorbitan esters such as Span™ series CAS No.1338-43-8 (ii) **Ethoxylated fatty acid esters** (PEG esters) or ethoxylated sorbitan esters such as Tween™ series CAS No. 103991-30-6 (iii) **Sodium di-iso-octyl sulphosuccinate** EC No. 209-406-4 CAS No. 577-11-7	**Glycol ethers such as:** Ethylene glycol Dipropylene glycol 2-butoxyethanol (Butyl Cellosolve™) CAS No. 111-76-2 Di-propylene glycol monomethyl ether CAS No. 34590-94-8 EC No. 252-104-2 **Light petroleum distillates:** Hydrotreated light distillates CAS No 64742-47-8 EC No. 265-149-8
	Concentrate	**Type 3**		

4. USE OF DISPERSANTS IN THE OIL SPILL RESPONSE STRATEGY

Chemical dispersion is one of the response options at sea, with “mechanical recovery associated with containment”, “do nothing and monitor the spill”, and (for general reference) “in situ burning”.

The use of dispersants in oil spill response has a number of advantages:

- By removing the oil from the surface it helps to stop the wind effect on the oil slick’s movement that may otherwise push the surface slick towards sensitive areas (often the shoreline).
- In contrast to containment and recovery, dispersants can be used in stronger currents and greater sea states.
- It is often the quickest response option.
- It reduces the possibility of contamination of some resources sensitive to the floating oil (surface slick) such as sea birds and mammals.
- It inhibits the formation of "chocolate mousse".
- It enhances the natural degradation of oil.
- Dispersion does not produce wastes to be disposed.

The use of dispersants has also its disadvantages:

- By dislocating the floating oil into the water column, it may adversely affect certain parts of biota which otherwise would not be reached by surface oil .
- If oil dispersion is not achieved, effectiveness of other response methods on oil treated by dispersants decreases.
- Dispersant are not efficient towards all oil pollutants, especially those which present a high viscosity.
- When initially efficient, chemical dispersion is applicable only for the first hours/days of the operation, before the oil becomes non dispersible.
- On significant pollution, chemical dispersion is not applicable in a too calm sea state (sea state 0, 1 possibly 2 according to the situation).
- If used near the shore and in shallow waters, it may increase the penetration of oil into the sediments; similarly, if suspended sediments are present, dispersants facilitate the adhesion of oil to the particles.
- It introduces an additional quantity of extraneous substances into the marine environment.

Figure 5: Aerial dispersant application with a DC3 aircraft from the UK authorities (source MPCU)

The possibility of balancing properly these advantages and disadvantages decreases in an emergency situation, and accordingly the use of dispersants and its place in a general response strategy for oil spills needs to be defined in advance. Where and under which circumstances the use of dispersants will be given priority over other available combating methods needs to be analysed and decided during the preparation of the contingency plan. By evaluating different interests for each particular zone, geographical boundaries may be defined within which dispersants may or may not be used. As a general rule, dispersants should not be used in the areas with poor water circulation, near fish spawning areas, coral reefs, shellfish beds, wetland areas, and industrial water intakes (Refer to Part III of these Guidelines).

Massive oil spills also often necessitate international co-operation. Application of dispersants may be a part of the assistance offered to a country confronted with such a spill. In order to facilitate inclusion of offered assistance in the national response activities, some countries or groups of countries (Bonn Agreement countries) have agreed to mutually accept the application of products approved for use by each country, in case of emergency. Part I ("Regional Appoval") of these Guidelines provides guidance on regional cooperation.

When such a general policy has been adopted in advance, a final decision on the use of dispersants in a spill situation will have to be taken only on the basis of given circumstances (type of oil, conditions, availability of material and personnel, etc.). The preparation of decision trees to help responsible officers greatly facilitates this process (Refer to the Annex of Part III of these Guidelines).

Taking a decision on the use of dispersants is one of the priorities in each spill situation since relatively shortly after the spillage most oils will no longer be amenable to chemical dispersion.

Once the decision to use dispersants has been taken, the strategy of their use becomes decisive for the positive outcome of the operation. From a strategic viewpoint, some basic principles in this regard can be defined:

- dispersants should be applied to the spill as early as possible;
- dispersant spraying operation should be terminated when the oil reaches the state of weathering (viscosity, mousse formation) in which it is not readily dispersed anymore;
- if the oil is approaching a sensitive area, dispersants should be applied to the part of the slick nearest to it.

In case of a massive oil pollution affecting an extensive area, it is possible and often necessary to use a combination of spill response methods. In such situations dispersants can be used on one part of the slick while oil is mechanically recovered on the other end of it.

On location dispersant should be applied according to specific operational rules such as:

- dispersants should be applied to thick and medium thick parts of the slick and not to the low thickness areas (sheen);
- treatment should be methodical, in parallel and contiguous or slightly overlapping runs;
- it is important to treat the slick against the wind;
- vessels are suitable for treatment of smaller spills near the shore, but aircrafts permit a rapid response (less than 24 hours after the spillage), in particular when large offshore spills are concerned;
- regardless of whether dispersants are sprayed from vessels or aircraft, spotter aircraft should be used for guiding them and assessing the results.

Figure 6: Spotter aircraft of the British Maritime Coastguard

Visual aerial observation, complemented with photography, video recording or using one of the available remote sensing techniques should be used for evaluating the results of the application of dispersants. Such reports and records can be also used for record keeping purposes of the different phases of the operation.

Finally, from a practical viewpoint, countries which decide to consider the use of the chemical dispersion in the response strategy need to pay particular attention to:

a) storage of sufficient quantities of selected and approved products;

b) procurement and maintenance of adequate spraying equipment;

c) training of personnel on all aspects of dispersants use, including organizing practical exercises at regular intervals.

5. FACTORS AFFECTING THE ACTION OF DISPERSANTS

Regardless of the application **technique** (Chapter 10) and **dosage** used (Chapter 9), dispersant action will primarily be determined by:

- type of oil to be treated;
- contact dispersant/oil;
- mixing;
- weather conditions.

5.1 Type of oil

Characteristics determining the **type of oil** which can be chemically dispersed are basically:

a) Viscosity:

Only oils with **viscosity <u>at seawater (ambient) temperature</u>** of not more than 5 000 cSt (most fresh crudes, medium fuel oils) are considered to be chemically dispersible by presently existing products. Chemical dispersion of oils with viscosity between 5 000 and 10 000 cSt may be uncertain (reduced); chemical dispersion above 10 000 cSt (heavy, weathered and emulsified crudes, heavy fuels) is very little or non effective.

Even oils with low initial viscosity are likely to reach quickly the limits proposed above (often 24 hours from the moment of spillage) due to the weathering process. The time during which oil remains dispersible is called “the window of opportunity for dispersion”. It would vary according to the type of oil and the meteorological and oceanographic conditions (mainly temperature, agitation/wind).

The more viscous the oil is the more agitation (waves) is required for its chemical dispersion.

b) Pour point:

Oils with a high paraffin (wax) content i.e. with a high **pour point** can cease to be dispersable if ambient temperature is significantly lower than their pour point.

c) Oil emulsification:

With the emulsification process, the oil viscosity increases, and dispersant are generally not effective on water-in-oil emulsions ("chocolate mousse"). However, when the emulsion is very fresh, (not entirely stabilized) research studies showed that dispersants may be effective. In such a case, the dispersant application can be undertaken in two stages : a first application to break the emulsion and therefore to reduce the oil viscosity, followed with a second application to carry out the dispersion itself.

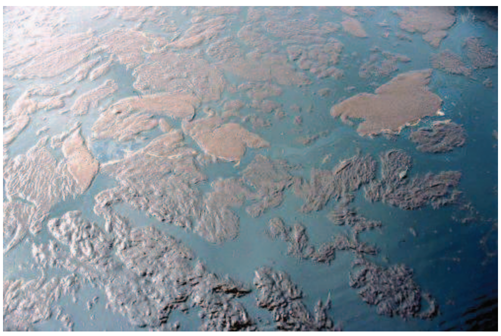

Figure 7: Weathered oil emulsion which dispersion remains uncertain

5.2 Dispersant/oil contact

In order to achieve a good dispersant/oil contact, a dispersant needs to be sprayed onto the floating oil in such a way as **to reach the surface** of oil and **not to penetrate** through the oil layer. These goals are achieved by combining appropriate spraying technique (Chapter 10) and appropriate droplet size. Optimal droplet size is considered to be in the range of 350 and 1000 µm, or approximately 700 µm. Smaller droplets will be carried away by wind and may never reach the oil, while the bigger ones penetrate through the oil layer and enter directly in contact with the water without having sufficient time to bind themselves to the oil. Application spraying system should be chosen to reach such requirements.

5.3 Mixing

Once the dispersant has come in contact with oil and the oleophilic end of its molecule has been attached to oil, the dispersant/oil mixture needs to be agitated in order to be broken down in droplets and dispersed in the sea-water mass.

Natural agitation of the sea surface (waves) is required for completing this process (e.g. sea state 2, Beaufort 3).

In some cases, if the wave energy is insufficient (very calm sea), on limited pollution, the mixing of dispersant/oil system and water can be supplied locally:

- by sailing through the oil slick and stirring it with bow wave and propeller action;
- by mixing oil and water with fire hoses.

Figure 8: Ship applying dispersant
(a part of mixing energy is generated by the bow wave)

5.4 Weather conditions

Chemical dispersion of oil is less affected by adverse **weather conditions** than other spill response methods (e.g. containment and recovery). In addition, weather conditions do not directly affect the physicochemical process of dispersion, but rather the application of dispersants.

Winds may blow the sprayed dispersants away from the target area and consequently cause significant loss of product. In case of the aerial spraying of dispersants, high winds may also affect the safety of spraying aircraft.

Waves: Whilst waves provide the required mixing energy to enable the dispersion process (the more energy is provided, the better is the dispersion); large waves or breaking waves can also be an obstacle and render spraying operation difficult for boats. Interaction between dispersant and oil slicks broken by the wave effect can also be reduced since part of the dispersant would be sprayed directly on the water surface rather than on the oil.

Poor **visibility** affects dispersants' action only indirectly through impeding spraying operations.

6. PHYSICAL CHARACTERISTICS OF DISPERSANTS

Some physical properties of dispersants may have practical consequences on the use of these products (application, fire hazard, conservation). For this reason some countries include in their approval procedure some requirements concerning the viscosity and/or pour point, flash point, and stability/shelf life.

6.1 Viscosity

The viscosity of a liquid is defined as its resistance to flow. The units most commonly used in the Mediterranean region for quantifying viscosity are the dynamic viscosity in "centipoise" (cP) and the kinematic viscosity in "centistoke" (cSt).

Note: in this context, as dispersant density is not far from 1, especially for the concentrates, the units centipoise and centistoke are roughly equivalent.

The viscosity of dispersants depends of the temperature. Typical viscosity range are indicated in the table below:

Table 5: Dipersant typical viscosity range

Dispersant typical viscosity ranges cP/ temperature °C	0 °C	20 °C
Conventionals	10–50	5–25
Concentrates	60–250	30–100

Viscosity has an effect on the dispersant droplets size. In this respect, some countries may require some limitations in the dispersant viscosity (e.g. France dispersant viscosity must be below 80 cP at 20 °C).

6.2 Specific gravity

The ratio of the weight of a solid or a liquid to the weight of an equal volume of water, at some specified temperature.

Conventional dispersants have generally lower specific gravities (0.80–0.90) than concentrates (0.90 - 1.05).

6.3 Pour point

The temperature below which this liquid will not flow.

Pour point of most dispersants is well below 0 °C (-40 to -10 °C) and in the conditions prevailing in the Mediterranean these should never solidify.

6.4 Flash point

The lowest temperature at which vapours above the volatile substance will ignite in air when exposed to a flame.
Most dispersants have flash point above 60 °C and should be considered as non-flammable. For practical safety reasons some countries may limit the flash point (e.g. in France dispersant flash point must be higher than 60 °C).

6.5 Stability / Shelf-life

During the period declared by the manufacturer as the shelf-life of the product, its properties should not change. Most manufacturers claim a shelf-life of 5 years or more for their product.

6.6 Others

Some dispersants' components may cause the corrosion of the packages (drums or containers) in which the product is stored over the prolonged periods. Accordingly, regulations concerning dispersants in some countries require that the product does not contain such components.

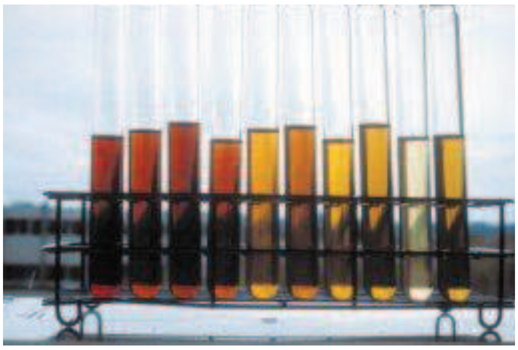

Figure 9: Samples of dispersant during quality control in the laboratory

7. ENVIRONMENTAL EFFECTS

Environmental effects of dispersants' use are mainly related to: (a) the toxicity of dispersants or oil/dispersant mixtures; (b) their influence on microbial degradation of spilled oil; and (c) their effects on seabirds and marine mammals populations.

7.1 Toxicity

Toxicity can be defined as the negative effects on organisms caused by exposure to a chemical or substance.

These negative effects may be lethal (causing death) or sub-lethal (causing negative effects that damage the organism in some way, but do not cause death). Exposure depends on the concentration of the substance and the period of time for which the organism is exposed to.

Toxicity is usually expressed as an effect concentration at a specific time, or as an effect time at a specific concentration. Most often, effect concentrations are expressed by ratios, as parts per million (ppm) or parts per billion (ppb), sometimes replaced by the mg/L and µg/L.

Toxicity of dispersants should be ideally tested on organisms *in situ*. However, the impracticability of such field tests has led to the development of numerous laboratory testing procedures. Results of such tests should be interpreted very cautiously since the tests are not intended to be ecologically realistic or to predict effects of using dispersants in the field. Most tests use concentrations and exposure duration which substantially exceed expected field exposures. In addition, organisms are exposed to fixed concentrations for several days, while in the sea initial concentrations of dispersant and/or dispersed oil would be diluted progressively and generally rapidly. Moreover, major errors in interpreting laboratory test results may also originate from the fact that thresholds are most often reported as nominal concentrations (total amount of dispersant or oil divided by the total volume of water in the experimental chamber) rather than measured concentrations of materials to which organisms are actually exposed. Last but not the least, testing conditions may lead to overestimate the oil toxicity. Indeed oil toxicity tests are often performed on fresh oil while, at sea, the oil would have been partly weathered, for few hours, losing its more toxic compounds (see paragraph below “Toxicity of oil”).

Figure 10: Toxicity tests with shrimps conducted on dispersed oil in UK

<u>Intrinsic toxicity of dispersant</u>

Lethal concentrations of dispersants have been the main concern and most toxicity tests aim at determining these. However, certain sub-lethal effects including changes in reproduction, behaviour, growth, metabolism and respiration may also occur when organisms are exposed to levels well below lethal thresholds.

It is to be emphasized that these responses have been noted in laboratory experiments where the duration of exposure is 1 to 4 days, much longer than those expected in most dispersant use situations in open water. Besides exposure concentrations of reported sub-lethal effects normally are 1 or 2 orders of magnitude above highest anticipated concentrations in field use.

Few reports of measurements of concentrations following the use of dispersants in the field exist, however, these suggest that even initial concentrations in the water column are typically below estimated lethal and sub lethal concentrations derived from experiments.

In conclusion, results of studies investigating the effects of dispersants suggest that major effects should not occur in the near-surface waters due to a dispersant alone, provided properly screened dispersants are used at recommended application rates.

<u>Toxicity of oil</u>

Oils of different types contain a small proportion of chemical compounds that are toxic to many marine organisms. Some of the more acutely toxic lower molecular weight compounds (benzene, toluene, ethyl benzene and xylenes, often referred to as BTEX compounds) are also volatile and water-soluble to some degree. Freshly spilled crude oils are much more acutely toxic than modern oil spill dispersants.

Higher molecular weight compounds that are present in low concentrations in many oils that often cause concern over toxicity are the PAHs (Polycyclic Aromatic Hydrocarbons). PAHs are known to be carcinogenic and can cause other effects by chronic exposure.

Toxicity of oil affected by the use of dispersants

Dispersing spilled oil converts the oil from a surface slick to a plume or ‘cloud’ of very small oil droplets dispersed in the water column. These oil droplets might be ingested by filter feeding organisms, such as copepods, oysters, scallops and clams.

The widening of the oil surface area increases the rate at which partially water-soluble chemical compounds in the oil are transferred into the sea. The localised concentration of these potentially toxic Water Accommodated Fraction (WAF) compounds will rise before they are diluted. This is the justification for the argument that dispersants can never be a valid oil spill response because its use, if they are effective, will inevitably cause an increase in the dispersed oil concentration in the water column, leading to toxic effects on marine life. However, it is important to distinguish between:

(i) the increased potential for toxic effects to occur; and,
(ii) the possibility of toxic effects actually occurring.

Dispersed oil concentrations will certainly be higher if dispersants are used, than if they are not. This does not mean that the dispersed oil concentrations will be high enough, or persist for long enough, to cause actual toxic effects. Most spilled oils will naturally disperse to some degree in the initial stages of an oil spill, before the oil becomes emulsified. The successful use of dispersants will obviously increase the concentration of dispersed oil in the sea. However, this is a matter of degree rather than an absolute difference; some spilled oil is likely to naturally dissolve and/or disperse even if dispersants are not used.

By dispersing the oil in the water column the exposure of the organisms living in the upper layer of the water column increases. If the dilution of the plume of dispersed oil in the water column is rapid the exposure will be low: experience from both experimental field trials and dispersant offshore operations at real spills have shown that dispersed oil will quickly be diluted into the sea. The concentration of oil in water rapidly drops from a maximum of 30-50 ppm just below the spill short time after treatment, to concentrations under 1-10 ppm of oil in the top 10-20 meters after a few hours.

Because oil will disseminate in the environment by natural dispersion which is a process that proceeds quite rapidly in rough seas with low viscosity oils, exposure of some marine organisms to dispersed oil at some concentration will occur even when dispersants are not used.

Table 6: Data from the Sea Empress incident

During the “Sea Empress” incident, (Wales 1996), which led to the largest dispersant treatment operation (440 tons of dispersant where applied on fresh crude at sea), oil concentrations were monitored in the upper water column as follows:

Time after dispersant application	Oil concentration in the upper water column (ppm)
Just after treatment	10
2 days	1
1 week	0.5
1 month	0.2
3 months	Background level

Figure 11: The Sea Empress incident (UK)

Various studies have been carried out to devise toxicity test methods which expose test organisms in conditions closer to their real environment. Toxicity tests performed with more realistic "spike-exposure" regimes show that the use of dispersants does not cause significant effects at dispersed oil concentrations of lower than 5-10 ppm with embryos and larvae. A level of 10-40 ppm-hours (concentration in ppm multiplied by exposure in hours) was found to produce no significant effects on higher marine life, such as older larvae, fish and shellfish.

However, recent studies (e.g. Discobiol), show that:

- lethal concentration on adults and juveniles are much higher than the concentration observed in real incidents;
- sub-lethal effects can be observed after the exposure time (bio-accumulation, metabolites in leaver, stress indicators…); however most of these observed effects are reversible in a relatively short delay: after 2 weeks of recovery the observed effects disappeared or reduced close to the background level.

Figure 12: Assessment of the impact of dispersed oil on fish – (Discobiol program)

Provided that dispersants are used to disperse oil in water where there is adequate depth and water exchange to cause adequate dilution, there is little risk of dispersed oil concentrations reaching levels for prolonged periods that could cause significant effects to most marine creatures.

Generally speaking, after incidents where large quantities of oil were dispersed at sea (e.g. "Sea Empress"), the environmental impact, when observed, has been much lower than expected, and the overall advantages resulting from the use of dispersants confirmed.

7.2 Microbial Degradation

Dispersion of oil, either mechanically or chemically, renders oil more available to microorganisms present in the sea water. The influence of dispersants on microbial degradation of oil is hence of prime importance.

Microorganisms capable to grow on petroleum hydrocarbons are present in all sea waters, and the rate of microbial degradation is directly related to the degree of oil dispersion. Paraffinic and high and medium aromatic fractions of oil are biodegradable, while for polyaromatic hydrocarbons (4, 5 cycles) and asphaltenes it has not been proven beyond doubt. There is no evidence of biodegradation of polar fractions, nitrogen-, sulphur- and oxygen-containing compounds.

Dispersants increase the rate of oil biodegradation through:

- increasing surface to volume ratio of oil;
- increasing oil bioavailability, (reduce the tendency of oil to form tar balls or mousse; stabilization of oil droplets in the water column instead of beaching or sedimenting).

However, dispersants may also reduce the rate of biodegradation by adding new bacterial substrate (the dispersant) that may be more attractive to microorganisms than oil or possibly increasing dispersed oil concentrations in the water column, which may have temporary toxic or inhibitory effects on the natural microbial populations.

As for toxicity, most of the knowledge of dispersed oil degradation is limited to results of laboratory or other small scale studies. Some laboratory studies and all mesocosm studies have shown an increase in rates of oil biodegradation when dispersants are used. Temporary inhibition of biodegradation with dispersed oil was also recorded in laboratory tests. However, it appears to occur at higher dispersed oil concentrations than expected in the field. Data from pond and mesocosm studies strongly indicate that effective use of dispersants would increase the biodegradation rate of spilled oil. The question whether dispersants enhance the extent of biodegradation needs to be further studied, although available information suggests that refractory compounds would not be degraded despite the addition of dispersants.

7.3 Effects on Seabirds and Marine Mammals

Oil affects seabirds and marine mammals due to:

- toxic effects of either direct ingestion of oil from the sea surface or indirect ingestion through grooming or preening;
- effects on the water-repellency of feathers or fur needed for thermal insulation.

Reduction of these effects by use of dispersant has not been studied extensively.

Review of available studies did not indicate differences of the toxicity to seabirds of oil components in chemically and mechanically dispersed oil. However, there is an obvious need to reduce surface oiling for bird protection. Exposure to dispersants and dispersed oil seems to be a greater problem than enhanced toxicity of oil.

It is known that marine mammals are affected by exposure to oil. The effects reported include the dysfunction of physiological processes such as thermoregulation, balancing and swimming ability as well as impairment of biochemical processes such as enzyme activity. Other overt effects such as eye irritation and lesions have also been reported. Exposure of marine mammals to oil can lead to changes in the ability of animals to deal with the uptake, storage and depuration of hydrocarbons whilst acute exposures can result in mortality in particular with young mammals which are more susceptible to the toxicological effects of oil.

Oiling causes reduction in fur insulating capacity and dispersants have been experimentally used for the removal of crude oil attached to fur. These experiments resulted in the removal of natural skin oils together with crude thus destroying the fur's water-repellency. Surfactants can increase the wettability of fur or feathers, allowing cold water penetration and subsequent increase of the thermal conductance. This is particularly dangerous to animals that are buoyed or insulated by their fur or feathers. Records of animal deaths due to direct ingestion of oil during grooming also exist. Extremely limited information on the influence of dispersants or dispersed oil on marine mammals exists, nevertheless the use of dispersants may not reduce the physical threat of spilled oil to some fur-insulated sea mammals.

7.4 The use of dispersant on underwater oil releases (e.g. blow out)

Dispersant can be used to disperse under water releases such as blow out coming from sub sea well head.

This technique has been used recently during the “Deep Water Horizon” incident, in the Gulf of Mexico in 2010, where large quantities of oil were released at sea (high pressure / high shear rate). Large quantities of dispersants have been injected directly at the source of the spillage at the sea bottom (1300 m depth) into the damaged riser to disperse the oil just released (fresh), in order to:

- reduce the quantity of oil resurfacing from the damaged well;
- reduce the amount of volatile in the atmosphere close to the damaged well (for security reason);
- reduce the amount of oil liable to be drifted to the sensitive Louisiana shoreline (environmental issue).

The formation of a large plume of dispersed oil between 1100 and 1300 m, with low oil concentrations has been observed. At the time this text has written there was still debate on the effects (efficiency and impact) of this peculiar dispersant application.

In terms of efficiency, uncertainties remain on the real effect of dispersants (e.g. what was really dispersed by the dispersant and what would have been naturally dispersed).

Waiting for further investigations, the preliminary feeling of the scientists community is “that the use of dispersants and the effects of dispersing oil into the water column has generally been less environmentally harmful than allowing the oil to migrate on the surface into the sensitive wetlands and near shore coastal habitats” (“Deep Water Horizon” Dispersant Use Meeting Report – May 26-27, 2010 CRRC).

It should be highlighted that the usual recommendations for regular dispersant application on surface slicks may not be suitable to the sub-sea application of dispersant on a sub-sea blowout plume. In sub-sea application the oil is fresh with its light ends, (the most toxic fractions) while surface slicks are usually partly weathered. However, considering ultra-deep environment the environmental conditions are so different (temperature, ecological sensitivity and diversity, temperature… etc.) in comparison with surface water (photic zone) that the usual way to assess the possible impact of chemical dispersion (as described in Part II and Part III of these Guidelines) is not applicable as they are (e.g. regular NEBA process as described in the next chapter 8).

If required, this chapter on sub-sea dispersant application could be further expended in a future edition of the Guidelines when the results of the ongoing studies on the Deep Water Horizon incident and its consequences will be made available.

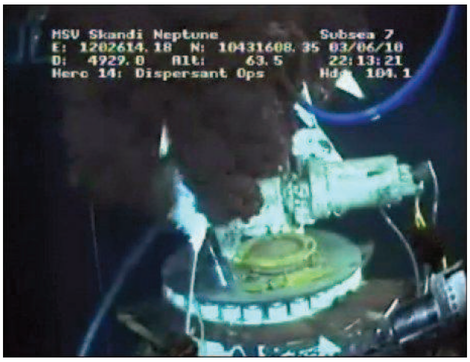

Figure 13: Under water blowout in ultradeep environment during Deep Water Horizon incident (source SINTEF)

8. NET ENVIRONMENTAL BENEFIT ANALYSIS (NEBA)

As the aim of the spill response is to minimise the overall environmental impacts on natural and economic resources, the decision on the use of dispersants should be based on the following comparison: "***What would be the impact of the pollution when treated with dispersant and when non treated with dispersant?***".

This comparison is named: the NEBA[2] (the Net Environmental Benefit Analysis).

The NEBA should:

- consider the behaviour (drift and ageing) of the treated oil (drift according to the stream, speed of dilution of the plume) and of the non treated oil (drift according to the stream and the wind);
- assess consequently the different resources which will be concerned either by the treated oil or by the surface oil;
- assess the sensibility of the different resources at concern towards the dispersed oil and toward the surface oil (non dispersed);
- consider also the time frame of the restoration of the items which may be impacted.

These analyses assist decision makers when considering whether or not the use of dispersants is appropriate, to minimize the environmental/economic damage.

Often, the NEBA can lead to compare the damage of the oil dispersed at sea with the damage of the slick drifted on the shoreline.

In most cases, the damages at sea caused by the dispersed oil are less than those generated by the oil weathered (often persistent) and stranded on the shoreline. However, the closer it affects the shoreline, the more difficult is the NEBA, as depending on the response strategy,

[2] The concept of NEBA can be found in the literature under different names : NEEBA (Net Environmental & Economic Benefit Analysis, or NEDRA (Net Environmental Damage Risk Assessment), etc.…

the dispersed oil and the non-dispersed oil may affect different sensitive areas and therefore may require prioritisation of resources to be preserved.

Habitats/resources should be considered as a whole and not independently, as the decision of applying dispersant may benefit to particular habitat/resource and at the same time affect adjacent ecosystems. For example, if an oil spill occurs in shallow water above submerged coral reef with current and wind conditions leading the slick toward mangrove swamp, it is advisable to disperse the oil above the reef (even though it may increase oil exposure of the corals) in order to avoid oil from becoming incorporated into the mangrove sediments from where it will seep out over the years thereby forming a chronic pollution source for both the mangrove and coral reef ecosystems.

Figure 14: Field experiment conducted on mangrove with dispersed oil in order to assess the impact of the dispersion in TROPIC experiment (source: Clean Caribbean)

The NEBA process takes time and should be planned in advance. In order to conduct a NEBA it is essential to list resources present in an area by order of the protection priority. Such list should take into account factors such as possible seasonal variations which may affect priorities. When drawing up such a list, both natural and economic resources should be considered. In general it can be said that endangered species, highly productive areas, sheltered habitats with poor flushing rates, habitats which take a long time to recover should receive top protection priority.

In Part III of these Guidelines, the reader will find elements of practical guidance for conducting a NEBA process.

9. TESTING, ASSESSMENT AND SELECTION OF DISPERSANTS

Indiscriminate use of dispersants in combating oil spills may have deleterious effects on the marine environment and therefore most of the countries, which consider the use of dispersants as part of their oil spill response strategy, have developed certain criteria or specifications with which dispersants should comply.

These specifications may be used for the selection of the most adequate products on an informal basis, while some countries have established formal approval criteria.

For the moment, there are no real agreements at international level on these criteria, despite the efforts made by intergovernmental bodies such as European Maritime Safety Agency (EMSA) or Bonn Agreement while trying to harmonise the use of dispersant in their respective region. However, on a case by case basis, instead of setting their own approval procedure, some countries would simply follow other countries approvals for dispersants. For instance, Croatia accepts certain products approved in other countries such as Cyprus, France, and United Kingdom. Another example is Israel, which accepts products approved by CEDRE.

Most often the specifications are based only on the effectiveness and toxicity testing of products. In addition, some countries have set standards on the biodegradability of the product and/or dispersed oil. There are also countries which specify required physical characteristics of dispersants which may be used.

On the basis of screening tests for any of these characteristics, individual competent national authorities develop their lists of approved products, which might be used in conformity with the approved response strategy.

There is also no agreement on testing procedures between different national administrations. However, regardless of the tests chosen, these should allow for ranking of products with regard to their relative effectiveness, toxicity or biodegradability.

All known testing procedures are based on laboratory tests. Such tests are not aimed at simulating real field situations and are accordingly designed to give relative values of tested properties. Field experience shows that there are no significant discrepancies between relative values obtained in laboratory tests and behaviour of tested products in the field, although differences sometimes appear. The same applies to the comparison between results of different tests: although absolute values can largely differ for a specific characteristic of a tested dispersant, depending on the testing procedure used, products which show better results according to a certain procedure, normally also appear superior when tested in accordance with another procedure.

The main concern in the early years of the use of dispersants was their toxicity. With the development of new, much less toxic formulations, more and more attention has been paid to the efficiency of dispersants. **At present, the effectiveness of dispersants is the most important selection criteria**. It is considered that toxicity, as well as biodegradability, of an ineffective product are irrelevant. The objective is to select a product with the best possible combination of relatively high effectiveness and relatively low toxicity.

Regardless of specific test procedures, a generally accepted testing pattern follows several common steps. The effectiveness of the product is tested first. Products which pass this criterion are then tested on toxicity and biodegradability. Results of toxicity and biodegradability tests are compared, and the products which pass defined criteria are approved for possible use.

9.1 Effectiveness tests

Most of these tests measure the degree and/or the stability of dispersion (droplet size distribution) either by visual observation or by some kind of analytical technique, after mixing oil and dispersants under standard conditions.

The measurement of the lowering of interfacial tension between oil and water following the addition of a dispersant or the speed of resurfacing of dispersed oil after mixing can also be used for the assessment of the dispersant's efficiency.

The differences in results and rankings often originate from differences in the parameters of the tests (type of oil, temperature, oil and water volumes, dose rates, contact between the dispersant and the oil – application or premixed level and type of mixing energy, close test tank of continuous dilution, test duration, etc. Refer to table in the next page).

Table 7: Effectiveness tests parameters

Test ID	Energy source	Energy level	Water volume	Oil/water ratio	Dispersant application method	Dispersant/oil ratio	Settling time
IFP	Oscillating hoop	1-2	4-5	1:1000	Dropwise	variable	1
Labofina rotating flask	Rotating vessel	3	0.25	1:50	Dropwise	1:25	1
Swirling flask	Shaker table	1-2	0.12	1:1200	Premix/dropwise	1:10 to 1:25	10

Among the main effectiveness laboratory test procedures:

- The LABOFINA test (or WSL test) procedure used in UK which is ran in a separating funnel in rotation to provide strong energy to promote the dispersion process (ref to WSL Report LR448. appendix A).
- The IFP test (flow through test) procedure used in France which is ran in a test tank in which the water is renewed in order to reproduce the dilution which would occur at sea; in this test the mixing energy brought by a wave generator remains gentle (ref: French standard AFNOR NFT 90-345).
- The Swirling test, used in North America, carried out on oil samples premixed which dispersant in a very small funnel which rotate gently to promote the dispersion process (ref . ASTM F2059 - 06 Standard Test Method).
- The MNS is a very high energy test used in Norway .

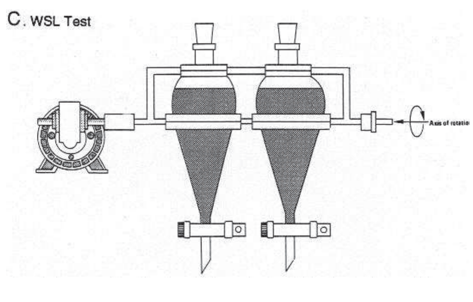

Figure 15: the Labofina / WSL test apparatus

Figure 16: The IFP / flow through test apparatus (source SINTEF)

Figure 17: The swirling flask test method (source: www.marinemanagement.org.uk/protecting/pollution/documents/approval_lr448.pdf)

Figure 18: The MNS test apparatus

At last, when a vessel is on site, it is possible to assess the oil dispersibility by collecting a sample in a glass jar directly from the slick and by testing it in the field. The field test procedure consist in comparing the dispersion of a sample containing dispersant and oil and one containing only oil following manual agitation (hand checking). (e.g. National Plan Oil Spill Dispersant Effectiveness Field Test Kit - Nat-DET). Such tests can be useful to oil spill responders to decide on the opportunity of applying dispersant on oil which degree of weathering is unknown.

9.2 Toxicity tests

Test materials are usually dispersants, dispersed oil (oil/dispersant mixture) and sometimes oil alone. Test species could be fish, arthropods (usually decapod crustaceans), molluscs (pelecypods), annalids (polychaetes) and algae. Ideally, test species should be selected among locally significant populations. Tests may be acute (short term) single species, lethal or sublethal.

The main goals of these tests are to determine the relative toxicity of a certain dispersant versus other previously tested products.

Due to the increase of toxicity with the increase of temperature, toxicity tests should take into consideration expected changes in seawater temperature.

Measure of the Lethal Concentration 50 (LC_{50}) in a determined period (usually 24 or 48 hours) is a common criteria used in toxicity tests.

Toxicity testing issue can be considered from two different approaches:

(i) either, checking the intrinsic toxicity of the dispersant in order to reject the most toxic ones, in that case only the dispersant is tested;

(ii) or, checking that the dispersant does not increase the oil toxicity; in that case the tests are performed on the oil alone and on the oil and dispersant mixture.

Due to the fact that dispersing the oil in the water column lead to increase the oil toxicity of oil towards the animals living in the water column, the toxicity of the mixture oil and dispersant should be higher than the one of the oil alone. The more efficient the dispersant, the more toxic the mixture of oil and dispersant may appear as the oil will be better dispersed. Therefore, such approach can be more restrictive and eventually reject the most efficient dispersant. This is in contradiction with the goal of an approval procedure which should be designed to select the more efficient and less toxic ones.

Considering the objectives of the approval procedure (selection of the best products, i.e. the less toxic ones), the control of the intrinsic toxicity of the dispersant is sufficient. However the issue of the toxicity of the dispersed oil remains a concern when considering the policy for the use of dispersants. The toxicity of the dispersed oil (toxicity of the “oil and dispersant” mixture) is required when defining scenarios (environmental conditions) for which the use of dispersant will remain environmentally acceptable (e.g. part of the NEBA process).

Among the main toxicity tests procedure:

- The test procedures in force in United Kingdom :
  - the sea test -comparison on brown shrimp of the toxicity of the oil with and without dispersant-
  - the rocky shore test –effect of the dispersant on the common limpet- ref: MAFF Fisheries Research Technical Report Number 102.

- The test procedure used in France: comparison of the LC_{50}(6h) of the dispersant alone with the one of a reference toxicant on white shrimp. (ref French standard NF T90-349).

- The standard toxicity test used in United States involves exposing silversides mysid shrimp to concentrations of the test product and No. 2 fuel oil alone and in a 1:10 mixture of product to oil (ref: http://www.epa.gov/osweroe1/docs/oil/cfr/appendix c.pdf)

Figure 19: The British testing equipment for assessing the toxicity

9.3 Biodegradability tests

Dispersants and dispersant/oil mixtures are often tested for biodegradability. There is no consensus on a standard method for testing biodegradability of dispersants and various adapted standard tests on organic material are in use (e.g. the method used in France – Standard NF 90 346).

9.4 Other tests

Standard analytical methods are used for testing other properties (density, viscosity, etc.) if so required by the competent authorities.

10. DOSAGES OF DISPERSANTS AND APPLICATION RATES

The amount of dispersants which needs to be applied to a certain quantity of oil, in order to achieve a desired level of dispersion, depends on the oil type, its weathering degree, its thickness, the environmental conditions (e.g. waves), and the dispersant itself.

In certain cases as during the “Sea Empress” incident in 1995, the oil is easily dispersible and therefore a low dosage (oil/dispersant ratio) may be sufficient, whilst in other incident less favorable (low dispersibility of the oil), it may be suitable to increase the dosage.

Practically, it is advisable to refer to the dose recommended by the manufacturer (often 5% for “concentrates”), dosage which can be adjusted during the operations on the basis of certain average figures.

In general terms **conventional dispersants or 2nd generation** (hydrocarbon based dispersant) are usually applied in doses of approximately 30 - 50 % of estimated oil quantity for low viscosity oil (up to 1000 cSt) and 100% for oils in the viscosity range of 1000 - 2000 cSt.

Figures for **concentrate dispersants or 3rd generation,** are in the range of 5 % for oils of up to 5 000 cSt, and 5 - 10% for treatment of oil between 5 000 and 10 000 cSt. Treatment of oils with viscosities of more than 10 000 cSt is considered ineffective. For fresh light oils easily dispersible viscosity less than 500 cSt a dosage lower than 5% may be sufficient.

Considering the application rate versus the oil thickness required **application rates** can be calculated on the basis of generally accepted rules for the assessment of oil thickness (dark patches of oil are assumed to be approximately 0.1 mm thick and areas covered by a thin oil sheen are estimated to be between 0.001 and 0.01 mm).

Regardless of the spraying device used, application rate is determined by the discharge rate of dispersant pump, speed of the vessel or aircraft and the width of the area covered by the spray (swath). The relation between these variables is the following:

Application rate = Discharge rate / Speed x Swath

Consequently, given the constant swath of the available spraying equipment, the required application rate for each particular slick area can be achieved by:

a) either selecting the appropriate discharge rate of the dispersant pump;

b) or selecting the appropriate speed of the vessel or aircraft.

Very often, an average treatment rate of 100 litres of concentrate dispersant per hectare, corresponding to oil thickness of 0.1 mm and a dose of 1:10 is used in approximate calculations for the use of dispersants.

Figure 20: Ship mounted modern application spraying equipment (source SINTEF)

11 SYSTEMS FOR THE APPLICATION OF DISPERSANTS

Selection of the dispersants' application technique basically depends on:

- the type of dispersant available;
- the type of spraying device available;

although the size and location of the spill must also be taken into consideration.

Several dispersant spraying systems exist and they can be grouped in accordance with the carrier for which they were designed:

- aircraft mounted spraying systems;
- boat mounted spraying systems;
- portable units for individual use.

11.1 Aircraft mounted spraying systems

As a result of advantages offered by the aerial spraying of dispersants (good control and assessment of results, rapid response, high treatment rates, optimum use of the product, regardless of the sea state), a number of spraying systems have been developed for use with both fixed and rotating wing aircraft (helicopters). Existing units are either of a type which can be used by the aircraft of convenience or of the permanently installed type. Standard built-in spraying systems of crop spraying aircraft, widely used in agriculture, can be adapted for the spraying of dispersants.

Only neat concentrate dispersants are suitable for use with airborne spraying systems.

11.1.1 Airplanes

Crop spraying airplanes are readily available. However, it is advisable to modify the spraying nozzles because the application rate of dispersants is much higher than that of agrochemical products. They could not be used far from the shore due to limited tank capacity and insufficient safety offered by a single engine.

Figure 21: Crop spraying aircraft

Fixed systems for converted **multi-engine aircraft** comprise storage for dispersants, a pump including powerpack spray arms with nozzles and a remote control system.

As an alternative, some independent system (with tank, pump and spray booms), have being developed which can be clamped under the fuselage as a detachable pod (i.e. instead the luggage chest); these systems allow to convert quickly regular planes into spraying aircrafts.

Figure 22: Spraying multi-engine aircraft during Deep Water Incident (source US Coast Guard)

POD spraying systems for small aircraft; self container spraying system which can be rigged under a small plane as a POD (luggage trunk). It is quick and easy to convert regular plane usually devoted to good or passenger transportation into a spraying aircraft. The capacity of these systems is around 1.5 t of dispersant.

Figure 23: POD spraying aircraft (source French Customs)

Self-contained airborne spraying systems are built to suit large transport airplanes which have rear cargo doors able to remain open during the flight. Containerized units comprise tank, power pack, pump and retractable spray arms and can be easily loaded into the cargo hold.

Figure 24: Large Self Contained spraying system (20t capacity) on C130 Hercules

11.1.2 Helicopters

Fixed spraying systems for helicopters are mounted under the fuselage and are made up of the same parts as the units built-in fixed wing aircraft.

Figure 25: Fixed spraying systems for helicopter

Helicopter **spray buckets** can be used with any helicopter having a cargo hook for under slung loads. Units are self contained (tank, pump, power pack, spraying arms) and can be remotely controlled from the cockpit.

Figure 26: Helicopter equipped with independent spraying bucket (source SINTEF)

Aerial application of dispersants depends on the visibility over the slick area and relies on wave energy for mixing dispersant with spilled oil.

Aircraft permanently equipped for dispersant spraying are rare due to high costs involved and the use of under slung helicopter buckets seems to be the most readily available solution. In addition, the use of helicopters has the advantage of extremely good manoeuvrability but their carrying capacity decreases very quickly when the distance to be covered increases. The selection of fixed wing aircraft is limited by the lowest speed at which the aircraft can operate and which should not exceed 150 knots.

11.2 Boat mounted spraying systems:

Several types of this equipment exist including units fixed on the vessel as well as removable ones.

11.2.1 Systems for spraying conventional dispersants

Systems for spraying **conventional / 2nd generation** (hydrocarbon based dispersants) are rarely used nowadays since these dispersants are sprayed undiluted and due to the 1:1 or maximum 1:3 dispersant/oil rate, a large amount of dispersant needs to be carried on board. They comprise a fixed flow rate pump and 2 spraying arms usually with 3 nozzles each; these units were often stern mounted.

Figure 27: Conventional dispersant spraying system for boat

11.2.2 Systems for spraying concentrate pre-diluted into sea water

The application of dispersant pre-diluted into sea water was invented to apply the concentrate dispersant (low dispersant/oil dosage) using the equipment originally developed for applying conventional dispersants (high dispersant/oil dosage). Indeed, the dilution enables an increase of the flow rate to be sprayed and therefore allow spraying with the same equipment (large nozzles). These systems are designed to pre-dilute the dispersant generally around 10% dispersant into sea water.

This goal can be achieved by:

Eductor systems are designed to work with the ship's built-in fire-fighting system. The eductor connected to the discharge side of the pump, causes a negative pressure at the point of dispersant intake, thus sucking it in into a discharge line. The diluted dispersant is applied by a fire monitor or through nozzles mounted on spraying arms attached to the vessel's side.

These systems tend to waste the dispersant and has limited encounter rate, although it is found on most vessels, it should be used only if no other equipment is available.

Injection systems consist of two pumps: one for water and the other, similar to chemical feeder pumps with variable flow rate, for the dispersant. The dispersant is applied through nozzles mounted on spraying arms attached to the vessel's side. Fixed and portable designs exist, and are preferably installed on the vessel's bow in order to benefit from the mixing energy provided by the bow wave.

It should be emphasized that pre-dilution into sea water can reduce the efficiency of dispersant especially when the oil is a bit viscous, i. e. weathered (>700 cSt). For this reason, the neat dispersant application (developed below) is strongly recommended.

Figure 28: Application of dispersant pre-diluted into sea water

11.2.3 Systems for spraying neat dispersants

Systems for spraying **neat concentrates** are specifically designed for the application of undiluted concentrate dispersants.

These units are usually bow mounted, have a pump with a variable flow rate and the dispersant is discharged also through nozzles mounted on spraying arms. These are usually longer as compared to stern mounted arms, having a greater oil encounter rate. Mixing energy is provided by bow wave.

In order to increase the dispersant flow rate range some units are equipped with multiple spraying assembly. By operating one or several spraying assembly, the flow rate can be adjusted to cope with different situations encountered (ship speed, oil thickness and type…).

Different types of vessels may be used for spraying dispersants and, in addition to specially built anti-pollution vessels; these include tug boats, supply vessels, trawlers or small fishing vessels. The necessity to operate at low speeds at the same time retaining the necessary manoeuvrability may be a limiting factor in the selection of vessels. Suitable vessels should also have sufficient storage space for dispersant.

Figure 29: Neat Concentrate dispersant spraying system for boat

11.3 Portable units for individual use

Light weight, cheap and easily available **back pack units**, normally used in agriculture, and mainly designed for shoreline rock cleaning, may also be used for application of dispersants to small spills near the shore. The application rates are limited.

There are designs where the tank and the pump are **trailer mounted** and connected to the portable spraying gun by a flexible hose.

Both hydrocarbon based and concentrate dispersants can be used with this group of devices.

12. LOGISTIC REQUIREMENTS FOR THE EFFICIENT USE OF DISPERSANTS

Regardless of the scale on which dispersants are applied, their use calls for well organized logistic support. As oil is liable to chemical dispersion only during the first hours or days after being spill at sea (window of opportunity for dispersion), at the time of the spill, the responder should be able to implement the dispersion application without loss of time. Therefore, all the logistics should be pre-planned. This aspect may appear particularly important when dispersants are used for the treatment of massive spills relatively far offshore. Since mechanical recovery of oil also requires significant logistic support, logistical constraints may be a decisive factor in deciding whether to use one method or the other. The availability of the necessary equipment, products and personnel will play a key role in taking decisions. However, other factors such as the size of the spill and its location, time required for mobilizing equipment and personnel and prevailing sea and weather conditions, will also strongly influence the decision on which method to choose.

To ensure maximum efficiency of the dispersant treatment operation, particular attention needs to be given to its logistic aspects:

- Treatment of oil with dispersants requires the use of significant quantities of the product. The dispersant quantity can be estimated at approximately 5 % of the volume of oil which is planned to be treated when concentrate dispersants are used. If conventional hydrocarbon-based products are used it can be up to almost the same volume of oil (100%) to be dispersed. This explains why nowadays conventional products are almost no longer used for the treatment.

- Stockpiles of dispersants existing in most of the countries are usually planned to be sufficient only for initial response. Pre-arrangements with manufacturers and/or distributors are therefore recommended to provide additional quantities of the product at an extremely short notice. International, regional, sub-regional and bilateral agreements with neighbouring countries should be considered in advance in view of mutualising national stockpiles available in the region or in remote countries. Particular attention should be given to custom pre-arrangement to ensure smooth transboundary movement. Countries affected by a spill requesting additional stockpiles and equipment can, in the framework of the Protocol Concerning Cooperation in Preventing Pollution from Ships and, in Cases of Emergency, Combating Pollution of the Mediterranean Sea, request the assistance of REMPEC to facilitate the coordination of the regional assistance.

- Transportation of dispersant from the sites of storage, production or from the airport of arrival (only airlifting the supplies from one country to another is fast enough to bring dispersants to affected country in time) to the spill site or base of operations, needs to be properly planned and precisely executed.

- If large quantities of dispersants are utilised, their transportation from the stores to the operations' base in road tankers or liquid containers is more efficient as compared to transportation in drums. High capacity pumps should be used for reloading of spraying units.

- Maintenance of spraying equipment as well as vessels or aircraft included in the operation should be planned. Supplies of the most important spare parts need to be available at the base.

- Fuel for vessels and aircraft needs to be available at the base and refueling operations executed promptly in order not to delay spraying operations. Problems are often encountered when aerial spraying is used, since in most places the fuel for piston-engined aircraft is in short supply. If local aircrafts are used, necessary arrangements for fuel supply are made in advance through the contingency planning process.

Figure 30: Dropping zone, arranged on the coast to operate a helicopter equipped with a spraying bucket

- Generally speaking, helicopters can land or change the spraying systems, even without landing, almost anywhere. Landing sites for small aircraft can be improvised if proper airfields are not available. However, larger aircrafts need long runways and only appropriate airports can be considered as bases for the refueling and reloading of dispersants.

- Accommodation for crews needs to be provided near the base. When larger vessels are used for spraying, this problem is eliminated since the crews are accommodated on board.

- Appropriate communication links, in particular those between spotter aircraft and spraying units, are essential. VHF appears to have advantages over other systems.
- Permanent contact needs to be established with national aviation authorities to obtain clearance for planned operations without delay.

- If requesting aircraft through international assistance is considered, flight authorizations, compatibility of the infrastructure (e.g. runway specification), availability of specified fuel needs to be checked in advance, preferably when preparing the contingency plan

13. STORAGE OF DISPERSANTS

13.1 Storage

Quantity of dispersants to be stored for emergency response needs to be assessed during the preparation of contingency plans. **It will be calculated on the basis of the quantity needed to respond to the most likely size of spill during the period necessary to bring in replacement stocks.** The time needed for stock replenishment (either by the manufacturers or from other sources) has also to be negotiated and determined in advance (cf. Chapter 12). Except for continuous release, arrival of new quantities of dispersants more than 48 hours after the start of spillage will be useless in most cases.

Dispersants are most often stored in 200-litre steel drums, usually in open space or preferably in sheds. Although the possibility that the drums will corrode from the inside should not be neglected, it is more likely that the corrosion will start from the outside.

Accordingly, regular control of stored drums is strongly recommended. Alternatively, dispersants may be sold and stored in plastic drums, which are corrosion resistant, however these should be protected from direct sunlight in order to avoid their deterioration.

Delivery and storage of dispersants in bulk containers is also possible. From the operational point of view, taking into account the need for quick response and hence the need for transporting large quantities of the product, this option is preferred to storage in drums. Storage in road tank trailers is even more practical.

Countries that make use of specialized anti-pollution vessels may opt for storage in vessels' integral tanks. For spraying from other vessels, when the need arises, dispersants can be transferred from storage containers to flexible pillow tanks, which can be placed on board practically any vessel.

Relatively high capacity portable pumps, made out of materials resistant to the components of dispersants, need to be available for the transfer of products from storage containers to spraying units.

13.2 Ageing

Dispersants are a complex mixture of various components, and with ageing their properties may be subject to changes, i.e. their stability is not necessarily good. During the prolonged storage, certain components may separate from the solution in layers or even crystallize. Usually dispersant deterioration results from bad storage conditions, dispersant quality may be altered (e.g. dispersant stock polluted by an external product or dispersant tank overheated under the sun for long periods…). Most often, deteriorations are reflected as a loss of effectiveness of the product. Therefore, it is advisable to check periodically the quality of the products (e.g. laboratory controls every 2 years).

Countries which have established approval or acceptance procedures regularly require the information on shelf-life from the manufacturer of the product (cf. Chapter 6, paragraph 6.5). Regardless of the manufacturer's declaration, the most reliable method for discovering changes in the original quality of the stored dispersant is to periodically test its effectiveness and to compare the results with the results obtained, using the same method and the same product when it was fresh. Such tests can be easily carried out and do not necessitate expensive laboratory equipment.

13.3 Disposal of aged stockpiles

Stockpiles of dispersant should be periodically checked for their quality and good conservation. Ideally, stockpiles should be controlled for their efficiency periodically (e.g. every 2 or 3 years), using laboratory test procedure.

In order detect corrupted dispersant stockpiles, a first assessment could consist in a simple control of physical characteristics of the product (e.g. visual appearance, density, viscosity, homogeneity, absence of decantation or separation phase). Any change in these characteristics may show an alteration of the stockpile and lead to further consideration for its replacement.

Aged dispersant stockpiles should be disposed when their characteristics, in particular the efficiency does not meet the technical requirements of the approval procedure (refer to chapter 9).

Aged dispersant stockpiles disposal should be carried out as any industrial waste, through specialised service companies. Alternatively the dispersant supplier may be required to take care of the aged dispersant disposal when replacing it by new stockpile. In such a case additional clause in the contract with the dispersant supplier may be required to ensure this service.

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