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DRAFT

CODE OF PRACTICE FOR THE USE OF DISPERSANTS

FOR COMBATING OIL POLLUTION AT SE

IN THE MEDITERRANEAN REGION

Proposal by the Secretariat

DRAFT CODE OF PRACTICE FOR THE USE OF DISPERSANTS FOR COMBATING OIL POLLUTION AT SEA IN THE MEDITERRANEAN REGION

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INTRODUCTION

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 regarded 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.

Following the requests put forward by the representatives of the Contracting Parties, and in accordance with its Objectives and Functions, the Regional Centre has prepared the present document to serve as a guideline to 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 the shore.

The "Code of Practice" itself, which forms the first and the main part of the document, sets up certain basic principles on which specific national policies should be built up, proposes subjects which need to be addressed in national regulations and suggests a framework for regional co-operation in that field.

The document, which is advisory, does not affect in any way already existing or planned national laws and regulations related to matters covered by it.

The "Code of Practice" is complemented by six Annexes, including a review of basic facts on dispersants' characteristics and use, as well as a summary presentation of the current situation recording the use of dispersants in the Mediterranean. These presentations include a summary of national policies concerning the use of dispersants, a list of products approved by the Mediterranean coastal States, geographic boundaries for use of dispersants established by the Mediterranean countries, descriptions of testing procedures currently applied by national authorities and a list of laboratories competent for testing dispersants in those countries which already require it by their national regulations.

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

With a view to implementing the Protocol concerning cooperation in Combating Pollution of the Mediterranean Sea by Oil and Other Harmful Substances in Cases of Emargency (Barcelona, 16 February 1976)

the Contracting Parties to the Barcelona Convention,

Have approved the following Code of Practice as a guideline to the Mediterranean coastal States for developing and harmonizing their national laws and regulations regarding the use of dispersants in combating accidental marine oil pollution.

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

The Contracting Parties to the Barcelona Convention,

- 1 Aware of the limited number of methods for combating oil spills at sea,
- Noting that chemical dispersion of spilled oil is applicable to combating pollution even of large size.
- Emphasizing that this method must be properly used and that a minimum consensus should be reached concerning its use,
- 4. **Recognizing** the need for each coastal State, to define its respective policy regarding the use of dispersants through adoption of relevant rules and regulation,
- 5. **Being of the opinion** that it is essential for the protection of the marine environment that the coastal States of the same region adopt a harmonized policy regarding the use of dispersants in combating oil spills,
- 6. **Being further of the opinion** that such policy should be based on the thorough understanding of advantages, disadvantages and limitations of using dispersants in oil spill response,
- Recalling the Protocol Concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and Other Harmful Substances in Case of Emergency,
- 8. **Emphasizing** the importance of regional co-operation in increasing the level of preparedness to respond to major oil spills at both the level of individual States and at the level of the Region as a whole, through harmonizing accepted practices and corresponding technical standards, and
- 9. **Recognizing** the importance of the role of the Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC) in that connection,

Have agreed that the following Code of Practice should serve as a guideline to the Mediterranean coastal States for developing and harmonizing their national laws and regulations regarding the use of dispersants in combating accidental marine oil pollution.

I. SCOPE

1.1 This Code of Practice applies to the conditions and limits of use of dispersants in combating accidental marine oil pollution.

It relies on the state-of-the-art in the field of dispersants' use, as presented in Annex 1 prepared by REMPEC on the basis of currently available technical literature.

1.2 This Code of Practice, which is advisory, does not affect in any way existing and future national laws and regulations related to matters covered by it and compatible with its objectives.

II. DEFINITIONS

For the purpose of this Code of Practice:

"Dispersant" means a mixture 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.

"Regional Information System" (hereinafter referred to as "RIS") means a set of written documents and computerized databanks, models and a decision-support system which REMPEC compiles, prepares, keeps up-to-date, publishes and regularly disseminates to the Mediterranean coastal States, comprising necessary information on various aspects of preparedness and response to accidental marine pollution by oil and other harmful substances.

III. GENERAL PRINCIPLES

- 3.1 Each Mediterranean coastal State shall endeavour to take the necessary measures to ensure that when dispersants are used for combating accidental marine oil pollution within its territorial waters or during combating operations conducted under its authority outside its territorial waters according to international law, these are used in an appropriate way with a view to reducing the negative effects of such pollution and, in particular, with a view to minimizing its overall effect on the marine environment.
- 3.2 Each Mediterranean coastal State shall endeavour to take the appropriate steps necessary to define its policy regarding the use of dispersants in combating accidental oil pollution, applying the principle of prior authorization for the use of dispersants.
- 3.3 Each Mediterranean coastal State shall endeavour to take the necessary measures to ensure that national regulations regarding the use of dispersants, including any limitations for their use, are clearly reflected in the national contingency plan for accidental oil pollution combating, as well as in any bilateral or multilateral operational agreement concerning co-operation and mutual assistance in response to accidental oil spills.
- 3.4 With a view to facilitating international co-operation in combating massive oil spills which may threaten the interests of one or more coastal States, each Mediterranean coastal State should make available to the other Mediterranean coastal States, information concerning its policy regarding the use of dispersants. Such information should be made available through RIS.

3.5 If the case requires, each State shall make all necessary arrangements, in liaison with other States, in order to eliminate dispersants which have reached their expiry date.

IV. USE OF DISPERSANTS IN COMBATING ACCIDENTAL OIL POLLUTION

- 4.1 It is the sovereign right of each Mediterranean coastal State to prohibit within its territorial sea the use of dispersants for combating accidental oil pollution.
- 4.2 Each Mediterranean coastal State which considers the use of dispersants as one of the possible methods for combating accidental oil pollution and which incorporates this method in its oil pollution response strategy shall adopt rules and regulations regarding:
 - Requirements for use of dispersants;
 - Restrictions on use of dispersants;
 - Conditions for use of dispersants.

4.3 Requirements for use of dispersants:

- a) Within the powers given to the On-Scene Commander by the competent national authorities, he shall take the decision to use dispersants taking into account the applicable national rules and specific circumstances of the accident and shall rely on the advice given by specialized organizations.
- b) Only dispersants which have been approved for use in the territorial waters of a respective coastal State shall be eligible for such an authorization taking into account the reservations mentioned in (ii) below.
 - i) Approval for use may be granted by the competent national authorities to products satisfying certain established and defined criteria, concerning at least the product efficiency, toxicity and biodegradability.
 - ii) Coastal States which have no defined testing and approval procedures or do not possess the necessary means to carry out the tests, may approve for use in its territorial waters products approved for use by another State, taking into consideration the compatibility of standards adopted by each State concerned.
 - When granting approvals for use of particular products in its territorial waters, competent national authorities shall take into consideration the changes in original properties of dispersants which may occur with aging and the lack of sufficient scientific knowledge of these processes. Accordingly, they may grant such approvals for only a limited period of time or stipulate periodical checking of original properties of approved products.
 - iv) Competent national authorities shall prohibit the use of products whose properties have changed beyond acceptable standards due to aging. According to circumstances, all such products shall be either recuperated or destroyed, disposed of and/or used for other purposes.

4.4 Restrictions on the use of dispersants:

- a) Each coastal State shall endeavour to designate zones, precisely defining their geographical boundaries, where the use of dispersants is either allowed (subject to prior authorization), limited or prohibited.
- b) Such zones shall be designated with a view to protecting particularly sensitive marine ecosystems and/or preventing negative effects of dispersed oil on industrial or other installations in zones not considered as environmentally sensitive
- In designating such zones, competent national authorities shall take into consideration, at least:
 - the environmental sensitivity of the area (specific habitats, fish spawning areas, shellfish breeding areas, seasonal changes in the environment, etc.);
 - the oceanographic features of the area (sea depths, currents, wave energy, etc.);
 - the distance from the shore and the type of adjacent coastal formations.
- d) Once such zones have been designated, the competent national authorities responsible for the preparation of national contingency plans, shall endeavour to prepare maps showing the geographical limits of these zones and to include these maps in their respective contingency plans.
- e) When updating contingency plans and in particular as regards the zones where dispersants can be used, the competent national authorities may take into consideration assessment studies on the impact of the use of dispersants during previous pollution events.

4.5 Conditions for the use of dispersants:

With a view to achieving the maximum effectiveness of dispersants' treatment and to minimizing any possible deleterious effects of such treatment, each Mediterranean coastal State shall include in the operational part of its contingency plan, precise technical conditions for the use of dispersants, regarding inter alia:

- types and characteristic of oil which might be chemically dispersable;
- recommended application techniques;
- recommended dosages of dispersants;
- . **limits of weather/sea state conditions in which the use of dispersants could be envisaged.**
- 4.6 All such requirements, restrictions and conditions for use of dispersants, established by each Mediterranean coastal State individually, should be reflected in their respective national contingency plans and taken into consideration in any bilateral or multilateral operational agreements concerning response to accidental marine oil pollution which the coastal States may wish to enter into.

V. REGIONAL CO-OPERATION

- 5.1 Mediterranean coastal States shall exchange the information concerning their respective national policies regarding the use of dispersants, including inter alia information on products approved for use, criteria for approval of products, laboratories authorized to perform testing of products, restrictions and conditions for use of dispersants. Such information will be disseminated through RIS
- 5.2 Mediterranean coastal States agree to mutually accept, in joint response operations in case of emergency, the policy regarding the use of dispersants of the coastal State in whose territorial waters the response operations are carried out.
- 5.3 In all such cases, the competent national authorities of the affected coastal State, agree to consider authorization for use in their territorial waters of dispersants approved by the assisting coastal State, providing that such approval was granted in conformity with the principles on which this Code of Practice is based.
- 5.4 Mediterranean coastal States shall endeavour to co-operate in developing compatible testing procedures for approval for use of products commercially available with a view to eventually harmonizing such testing procedures.
- 5.5 Mediterranean coastal States shall endeavour to facilitate the transfer of technology among themselves with regard to the use of dispersants, in particular through REMPEC.
- 5.6 If a State, affected by pollution, does not possess the pre-established national regulations for the use of dispersants, it shall seek the most qualified advice and endeavour to take into account the regulations of the neighbouring States.

VI. ROLE OF REMPEC

- 6.1 REMPEC shall continue to collect and disseminate, through RIS, information concerning:
 - a) the state-of-the-art in the field of using dispersants in oil pollution response;
 - b) new products and application techniques;
 - c) research on the process of aging of stored dispersants and related developments;
 - d) policy, including rules and regulations regarding the use of dispersants, of the Mediterranean coastal States;
 - e) products approved for use in the Mediterranean coastal States;
 - delineation of zones for the use of dispersants established by the coastal States;
 - g) testing procedures adopted by the Mediterranean coastal States;
 - h) laboratories authorized to test dispersants on behalf of the competent national authorities in their respective countries.

- 6.2 On the request of the competent national authorities of the Mediterranean coastal States, REMPEC shall provide advice and technical assistance concerning all aspects of developing national policies regarding the use of dispersants.
- 6.3 REMPEC shall organize training activities on the use of dispersants aimed at personnel involved in planning and response, either by including these activities in general training courses or by organizing specialized courses.
- 6.4 REMPEC shall maintain updated versions to the Annexes of the Code of Practice taking into consideration acquired experience and technology developments on the one hand and information provided by the member States on the other hand. It shall submit to the Contracting Parties for approval the modifications to be introduced in the Code of Practice itself.

ANNEX 1

BASIC FACTS ON DISPERSANTS, THEIR CHARACTERISTICS, USE AND APPLICATION

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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 the most controversial issue in the entire palette of available oil pollution response techniques. 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 opponents. 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 improper or completely erroneous application.

A relatively small number of countries has a clearly defined policy regarding the use of dispersants. The lack of a clear policy regarding dispersants and their use inevitably results in heated discussions, when applying these products is contemplated as a possible pollution response measure, in case of emergency.

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. Such a policy 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 FACTS

Certain characteristics of the Mediterranean Sea distinguish it from other sea areas and in particular from the open oceans. Since these characteristics may have a significant influence on defining policy concerning the use of dispersants, it is necessary to briefly outline them.

Surface area (total) 2000 - 3000 m depth contour less than 200 m depth contour	2.5 x 10 ⁶ km ² 30% 20%
Volume 2000 - 3000 m depth contour less than 200 m depth contour	3.7 x 10 ⁶ km ³ 50% 1.5%
Average depth	1500 m
Maximum length (Gibraltar - Syria)	3800 km
Maximum width (France - Algeria)	900 km
Distance from the nearest coast of any point maximum more than 50% of the Med. basin	370 km less than 100 km
Salinity surface deep seawater	36 38.4 - 39
Temperature of deep seawater western Mediterranean eastern Mediterranean	12.5 - 13.5 °C 13.5 - 15.0 °C

The **surface currents** system of the Mediterranean is characterized by the migration of Atlantic water eastward, with numerous spin-off eddies along the way. The westward surface currents return system does not exist. Strong vertical convections, caused by temperature differences, are also present.

Tides in the Mediterranean are generally regarded as weak, i.e. tidal amplitudes are much lower than in the oceans. However, regardless of low tidal elevations, the energy of the tides is considerable.

It should be noted that as a result of high evaporation rates, the Mediterranean Sea has a very high salinity. Only the Red Sea and Dead Sea are known to have higher salinity than the Mediterranean.

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 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. Moreoever, dispersants prevent coalescence of oil droplets and reforming of the oil slick.

3.2 <u>History of dispersants</u>

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 for dealing with oil on beaches in U.K. in the early sixties. Mixtures of detergents and hydrocarbon solvents (already used by the industry as industrial cleaners or degreasing agents for engines or tank cleaning) proved their efficiency in emulsifying stranded or floating oil. It was known that these products were highly toxic due to the use of aromatic solvents, however, it was thought that the high dilution capacity of the open sea waters would suffice to bring the concentrations down, below the levels lethal to marine life.

The first extensive use of these early dispersants, in response to the "Torrey Canyon" oil spill off the English coast 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 the "Torrey Canyon" accident, new formulations appeared on the market. The use was made of less toxic surfactants and toxic aromatic solvents were replaced by much less toxic (1000 times) low-aromatic or non-aromatic hydrocarbons (e.g. low aromatic kerosene or high boiling solvents containing branched saturated hydrocarbons). Although their efficiency was lower than that of the first "detergents", very low toxicity rendered their use, even on a large scale, environmentally acceptable. These new products became known as "second generation" dispersants and are still 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 have a much lower toxicity than "the second generation" dispersants and can be used either pre-diluted with sea-water or neat. Introduction of "concentrates" with higher concentrations of active components and less solvents, made possible the use of aircraft in spill response operations. Most of the products marketed today belong to this category.

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

3.3 Nomenclature of dispersants

The nomenclature of dispersants is based on three dispersant classification systems, currently used in the world. The table in the following page gives a comparative presentation of these systems:

STANDARD NAME	NAME BY GENERATION	NAME BY TYPE	MODE OF APPLICATION	TYPE OF SOLVENT
Detergents Degreasing agents Industrial cleaners	1 st	-	undiluted (neat), from vessels	light aromatic hydrocarbons
Conventional dispersants	2 nd	1	undiluted (neat), from vessels	non-aromatic hydrocarbons
Concentrate dispersants	3 rd	2 ·	diluted, from vessels	oxygenates (e.g. glycol
		3	undiluted (neat), from vessels and/or aircraft	ethers) and non aromatic hydrocarbons

It should be noted that nowadays the first above-quoted category of products ("detergents") are not used as oil spill dispersants and hence are only mentioned for historical reasons and for reference purposes.

3.4 Composition of dispersants

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

- surface active agents (surfactants)
- solvents

Surfactants are chemical compounds whose molecules contain both hydrophilic and oleophilic groups. Those with a predominantly oleophilic character tend to stabilize water-in-oil emulsion, while those with mainly hydrophilic character stabilize oil-in-water emulsions and these are usually used in formulating dispersants. Surfactants are divided in 4 (four) groups (anionic, cationic, nonionic and amphoteric). However only nonionic and anionic surfactants are used in modern dispersant 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.

Two or more surfactants are often combined in order to improve the performance of the final product.

Solvents are liquid chemicals or their mixtures 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.

A number of dispersants in use today, are marketed as biodegrading dispersants. These are formulated with the addition of nutrients (nitrogen, phosphorus) which promote the natural biodegradation processes by micro-organisms present in the sea water.

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

Conventional (2nd generation) dispersants:

- 10 to 25% surfactant
- hydrocarbon solvent

Concentrate (3rd generation) dispersants:

- 25 to 60% surfactant
- polar organic solvent or mixed with hydrocarbon solvent

4. DISPERSANTS USE IN OIL SPILL RESPONSE STRATEGY

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

- dispersants can be used under a wider range of weather and sea conditions than other commonly used combating techniques;
- it is often the quickest response method;
- by removing the oil from the surface it helps to stop the wind drift of the oil slick, thus restricting the movement of oil;
- it reduces the risk of shore contamination:
- it reduces the possibility of contamination of sea birds and mammals;
- it inhibits the formation of "chocolate mousse";
- it enhances the natural degradation of oil.

The use of dispersants also has its disadvantages:

- by dislocating the floating oil into the water column, it may adversely affect certain parts of biota which would not be reached by oil otherwise;
- if dispersion of oil is not achieved, effectiveness of other response methods on oil treated by dispersants decreases;
- it has no effect on oils with viscosity higher than approximately 2000 cSt at ambient temperature;
- if used near the shore and in shallow waters, it may increase the penetration of oil into the sediments; similarly if there is the presence of suspended sediments, dispersants facilitate the adhesion of oil to the particles;
- it introduces an additional quantity of extraneous substances into the marine environment.

Possibility of properly balancing 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 guideline, 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.

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.). Preparing decision trees to help responsible officers greatly facilitates this process.

Taking the decision on the use of dispersants is one of the priorities in each spill situation since relatively shortly after the spillage most oils will not 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. Some basic principals in this regard can be defined:

- dispersants should be applied to the spill as early as possible,
- 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;
- if the oil is approaching a sensitive area, dispersants should be applied to the part of the slick nearest to it:
- vessels are suitable for treatment of smaller spills near the shore, but the aircraft 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;
- the dispersant spraying operation should be terminated when the oil reaches the state
 of weathering (viscosity, mousse formation) in which it is not readily dispersed any
 more.

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.

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 at the same time when oil is mechanically recovered on the other end of it.

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 in case of emergency application of products approved for use by each country.

Finally, countries which decide to use dispersants as a part of their oil pollution 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 DISPERSANT ACTION

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
- b) pour point

Only oils with viscosity at seawater (amblent) temperature of not more than 2000 cSt (most fresh crudes, medium fuel oils) are considered to be chemically dispersable by presently existing products. Chemical dispersion of oils with viscosity above 2000 cSt (heavy, weathered and emulsified crudes, heavy fuels) is very little or not effective. Even oils with low initial viscosity are likely to reach the limit of 2000 cSt quickly (approximately 24 hours from the moment of spillage), due to the weathering process.

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.

Water-in-oil emulsions ("chocolate mousse") do not react to dispersants.

5.2 Contact dispersant/oil

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 800 μ m, or approximately 500 μ m. 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. Although it is difficult to control precisely the size of droplets, most spraying systems presently in use are designed to produce droplets in the above-mentioned range.

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. Either natural or induced mixing energy is necessary to achieve this goal.

In most circumstances natural agitation of the sea surface (waves) will be sufficient for completing this process (sea state 2, Beaufort 3), however, if the wave energy is insufficient (very calm sea), the mixing of dispersant/oil system and water can be achieved:

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

by using specially designed devices for agitating the sea surface (breaker boards, plastic chains).

When the dispersant is applied from a bow-mounted ship's spraying system, mixing energy is provided by bow wave created by the spraying vessel itself

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 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 aircraft.

Waves generally help dispersion of treated oil. However beyond sea state 5 oil is likely to be covered by breaking waves, which results in a loss of product since the dispersant comes in contact with water rather than with oil.

Poor visibility affects dispersant action only indirectly through impeding spraying operations.

6. PHYSICAL CHARACTERISTICS OF DISPERSANTS

Physical properties of dispersants are only of academic interest to a user and the majority of countries which have established approval procedures do not use physical properties as a criteria. However, dispersants may be distinguished by the following main physical characteristics:

- viscosity

- pour point

- specific gravity

- corrosiveness

- flash point

- stability/shelf life

6.1 Viscosity

The viscosity of a liquid is defined as its resistance to flow. The unit most commonly used in the Mediterranean region for quantifying viscosity is "centistoke" (cSt).

The viscosity of dispersants ranges between 5 and 120 cSt. Conventional dispersants are less viscous than concentrates. Since viscosity has an effect on the dispersant droplets size, it has to be taken into account when aerial spraying is considered. An often quoted classification system divides dispersants into three groups:

A: viscosity less than 30 cSt. Typically hydrocarbon based products.

B: viscosity between 30 and 60 cSt. Usually conventional products with increased content of surfactants.

C: viscosity above 60 cSt. Normally real concentrates, with high surfactant content and non-hydrocarbon solvents.

Products in group C are most suitable, group B products may sometimes be used and group A products are not suitable for aerial spraying.

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.

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

6.3 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.

6.4 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.

6.5 Corrosiveness

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

6.6 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 for their product a shelf-life of 5 years or more. It is practically impossible to verify such a declaration and accordingly, the countries who request an indication of the shelf-life of the product in their approval procedure, usually rely on the statement of the manufacturer. (cf. Chapter 12).

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 is defined as the inherent potential of the capacity of a material to cause adverse effects in a living organism. It is a relative measure, influenced by many factors, including in particular concentration, duration of exposure, and type of organism.

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 as parts per million (ppm) or parts per billion (ppb) and these units are used interchangeably with mg/litre and µg/litre, respectively, minor differences in exact concentrations notwithstanding.

Toxicity of dispersants would be ideally tested *in situ* and on actually present organisms. 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, animals are exposed to more or less constant 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.

Notwithstanding the above-mentioned restrictions, numerous studies carried out over the past 25 years clearly revealed the basic aspects of dispersant toxicology. Main factors influencing the toxicity of dispersant appear to be the following:

. Physicochemical factors:

Surfactants - All surfactants are toxic in high concentrations. Tests show that anionic surfactants are generally more toxic than nonionic ones or esters.

Solvents - Solvents were the most toxic components of early formulations due to their high aromatic hydrocarbons contents. Those used in current dispersants (see para. 3.4) are far less toxic. Toxicity decreases in the order: aromatic hydrocarbons > saturated hydrocarbons > glycol ethers > alcohols.

. Biological factors:

Species - different species show different sensitivity to dispersants. Sensitivity to water based dispersants falls in the order: crustaceans < bivalves < fishes. Sensitivity to petroleum based dispersants falls in the reverse order: fishes < bivalves < crustaceans.

Life history stage - it appears that young life stages (eggs, embryos) are more sensitive to dispersants than older ones.

Physiological factors - susceptibility to dispersants varies with seasonal variations, previous exposure, acclimation, health and feeding state.

Temperature:

Dispersants become less toxic with lowering of temperature. The same phenomenon occurs with dispersed oils. There are significantly higher sensitivities of organisms in warmer waters and in summer as compared to winter conditions.

Lethal concentrations of dispersants have always been the main concern and most toxicity tests aim at determining these. However certain sublethal effects including changes in reproduction, behaviour, growth, metabolism and respiration may also occur when organisms are exposed to levels well below lethal thresholds. Behavioural responses such as cessation of feeding, slowed swimming, disorientation, impaired locomotion and paralysis have been recorded. Surface membranes and tissues, particularly gills, are likely to be most affected by exposure to dispersants (surface active component).

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

Few reports exist of measurements of concentrations following the use of dispersants in the field, however, these suggest that even initial concentrations in the water column are below most, but not all, estimated lethal and sublethal 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.

The **combined effects of dispersant and oil** may be additive (a sum of effects caused by each of these separately), more than additive (synergistic) or less than additive (antagonistic).

Toxicity of oil is mostly related to that of its "water soluble fraction" (WSF), and there is evidence that the toxicity of WSF of oil and of dispersed oil is more or less the same. Unfortunately, about two thirds of literature published prior to 1987, instead of giving values for oil concentration in water phase, uses nominal concentrations, rendering results of these studies of little use. Tests in which WSF is measured and used as a basis for calculating toxicity generally show no difference between physically and chemically dispersed oil. Moreover, these tests rarely show the evidence of synergism between oil and dispersant, thus validitating the general conclusion that oil is as acutely toxic as dispersed oil.

Apparently greater toxicity of chemically dispersed oil is likely to be a result of exposure and not of a greater inherent toxicity.

Results of tests designed to compare dispersant toxicity to dispersed oil toxicity suggest that dispersed oil is more toxic when a relatively non-toxic dispersant is used and that a dispersant alone is more toxic when a toxic formulation is used.

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 able 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 aromatic fractions of oil are biodegradable, while for 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;
- . reducing the tendency of oil to form tar balls or mousse;
- enabling dispersed oil droplets to remain in the water column instead of beaching or sedimenting.

Dispersant may however, also reduce the rate of biodegradation by:

- . adding new bacterial substrate (the dispersant) that may be more attractive to microorganisms than oil;
- increasing dispersed oil concentrations in the water column, which may have temporary toxic or inhibitory effects on the natural microbial populations.

As in the case with 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 dispersed oil concentrations higher 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 remain undegraded despite the addition of dispersants.

7.3 Effects on Seabirds and Marine Mammals

Oil affects seabirds and marine mammals due to:

- 1. Toxic effects of either direct ingestion of oil from the sea surface or indirect ingestion through grooming or preening.
- 2. 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 indicates similar response of seabirds to oil components in chemically and mechanically dispersed oil. Response to oil and dispersed oil appears to be similar. 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 impairement 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, nevertheless suggests that use of dispersants may not reduce the physical threat of spilled oil to some fur-insulated sea mammals.

8. 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 a 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 agreements between national authorities on these criteria, although certain steps have been taken in this direction within, for example, the Bonn Agreement.

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 decided 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 expenence 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 dispersants' use was their toxicity. It is understandable when some disastrous effects of using first generation products (having a high aromatic contents) is taken into consideration. With the development of new, much less toxic formulations, more and more attention has been paid to dispersants' efficiency. 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 criteria 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.

8.1 Effectiveness tests

Most of these tests measure the degree of dispersion (droplet size distribution) either by visual observation or by some kind of analytical technique, after mixing oil and dispersants under standard conditions. Mixing energy can be introduced into the water/oil/dispersant system by:

- a pump which circulates the mixture;
- . waves created by a moving plate or ring;
- . waves generated by an air stream;
- . rotating a specified shape flask at a fixed speed;
- . various types of stirrers.

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

The effectiveness is sometimes assessed also on the basis of measuring the speed of resurfacing of dispersed oil after mixing.

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, etc.).

8.2 <u>Toxicity testing</u>

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:

- a) to determine the relative toxicity of a certain dispersant versus other previously tested products;
- b) to assure that dispersants do not significantly increase acute (or chronic) toxicity of dispersed petroleum hydrocarbons;
- c) to determine factors that modify dispersant toxicity, or enhance or ameliorate oil toxicity under natural conditions.

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

Measure of LC 50 in a determined period (usually 24 or 48 hours) is the most common criteria used in toxicity tests.

8.3 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.

Control of the non-inhibition of biodegradability (cf. paragraph 7.2) was introduced by France several years ago, in addition to testing biodegradability alone.

8.4 Other tests

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

9. DISPERSANTS' DOSAGES 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 **dose** (oil/dispersant ratio) recommended by the manufacturer or determined by experiments.

Although recommended doses vary from one dispersant to the other and for each dispersant with the type of oil and its viscosity, in spill situations it is often necessary to apply approximate quantities, calculated on the basis of certain average figures.

In general terms **hydrocarbon based dispersants** 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** are in the range of 5 - 10% for oils of up to 1000 cSt, and 10 - 15% for treatment of oil between 1000 - 2000 cSt. Treatment of oils with viscosities of more than 2000 cSt is considered ineffective.

Required application rates also depend on the type of spilled oil, its thickness and prevailing conditions. Since an oil slick does not have uniform thickness and moreover it is difficult to determine it precisely, it is necessary to calculate application rates 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). 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 either

- a) selecting the appropriate discharge rate of the dispersant pump, or by
- b) 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.

10. <u>DISPERSANT APPLICATION SYSTEMS</u>

Selection of the dispersant 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:

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

10.1 Portable units for individual use:

Light weight, cheap and easily available back pack units, normally used in agriculture can also be used for application of dispersants to small spills near the shore or for cleaning rocks. 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.

10.2 Boat mounted spraying systems:

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

10.2.1 Systems for spraying diluted dispersants

Systems for spraying hydrocarbon based dispersants (2nd generation) 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, which need to be stern mounted and thus necessitate the use of cumbersome breaker boards.

Eductor systems are designed to work with the ship's built-in fire-fighting system. The eductor, which is 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.

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

Only concentrate dispersants can be used with it.

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 there are units for installation on either the vessel's bow or stern.

Stern mounted units generally require the use of breaking boards or similar devices for the agitation of the surface on which the dispersant was applied. When the spraying gear is bow mounted, mixing energy is provided by the bow wave.

Injection type systems are suitable only for spraying diluted concentrate dispersants.

10.2.2 Systems for spraying neat dispersants

Systems for spraying neat concentrates 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.

These units are specifically designed for the application of undiluted concentrate dispersants.

- The ducted-fan air blower system is a relatively new addition to boat mounted equipment. Neat concentrate dispersant is injected into a ducted-fan air blower through specially designed nozzles. These units are removable and are usually put on a vessel's bow. Spray can be directed by the operator. Wind strongly affects the direction of the spray.

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.

10.3 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), 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.

10.3.1 Airplanes

- Crop spraying airplanes are readily available. However, it is advisable to modify the spraying nozzles because the application rate of dispersants is 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.
- Fixed systems for converted multi-engine aircraft comprise storage for dispersants,
 a pump including powerpack spray arms with nozzles and a remote control system.
- 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.

10.3.2 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.
- Helicopter spray buckets can be used with any helicopter having a cargo hook for understung loads. Units are self contained (tank, pump, power pack, spraying arms) and remotedly controlled from the cockpit.

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 underslung 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. 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. This aspect becomes particularly important when dispersants are used for the treatment of massive spills relatively far offshore. Since mechanical recovery of oil also necessitates 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 chose.

If the maximum efficiency of the dispersant treatment operation is expected, particular attention needs to be paid to its logistic aspects:

treatment of oil with dispersants necessitates the use of significant quantities of the product. It may range from a minimum 10% of the volume of oil which is planned to be treated when concentrate dispersants are used, up to almost the same volume as the volume of oil (100%) to be dispersed, when conventional, hydrocarbon-based products are used. This explains why nowadays concentrate products are almost exclusively used for the treatment of large spills at sea, and the use of hydrocarbon-based products is limited only to small spills near shore.

Stockpiles of dispersants existing in most of the countries are usually planned to be sufficient only for initial response. It is necessary to make in advance arrangements with manufacturers and/or distributors to provide additional quantities of the product at an extremely short notice. The problems arise with smaller manufacturers who usually do not keep large enough supplies and hence are unable to provide sufficient quantities when necessary.

Transportation of these additional quantities of dispersant from the site 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 operations base, needs to be properly planned and precisely executed.

- If large quantities of dispersants are utilized, 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.
- Wear and tear of spraying equipment may be significant and proper maintenance is necessary. This is usually done during the night, when the operations need to be interrupted anyway. The same applies to the maintenance of vessels or aircraft included in the operation. 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 aircraft are used, necessary arrangements for fuel supply are made in advance through the contingency planning process. If aircraft are requested through international assistance, availability of specified fuel needs to be checked prior to making the request.

- 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 aircraft 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.

12. STORAGE OF DISPERSANTS

12.1 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 11). 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 (cf. Chapter 6, paragraph 6.5), 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 who 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.

12.2 Ageing

Dispersants are a complex mixtures 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.

These processes are still not clearly understood. However, it is certain that they may lead to reversible or irreversible deterioration of the original properties of the product. Most often, this deterioration is reflected as a loss of effectiveness of the product.

In the most simple case, the effectiveness can be restored by mixing the contents of the containers in which the dispersant is stored. If one of the components has lost its activity, the manufacturer might be able to reactivate the product by adding additional active components. In the worst case, the product cannot be recuperated and it therefore has to be disposed of, destroyed or used for another purpose (e.g. as a solvent).

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 6.6). 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.

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ANNEX 2

POLICY OF THE MEDITERRANEAN COASTAL STATES REGARDING

THE CONDITIONS AND RESTRICTIONS ON USE OF DISPERSANTS

This Annex includes preliminary and summary information on policies regarding the use of dispersants in response to accidental marine oil pollution, adopted by the Mediterranean coastal States. A major part of the information included in it is based on information received through contacts between the Regional Centre and persons responsible for oil pollution combating in their respective countries. Since the nature of most of these communications was informal and unofficial, the information summarized below should not necessarily be considered correct and certainly not complete.

ALBANIA No information.

ALGERIA No information.

CYPRUS - Use of dispersants in the open sea (off shore) is one of the main components of the national response strategy.

- Dispersants approved by EEC countries (in particular by Warren Spring Laboratory in U.K.) are accepted.

- Authorization of the Director of Fisheries Department required prior to use.

EGYPT - Dispersants are generally not used.

- Authorization of the Academy of Scientific Research and Technology is required prior to use.

Official testing procedure has not been defined.

FRANCE - No legal regulations; approval procedure designed by CEDRE which also issues recommendations on the subject.

- Geographical boundries for use of dispersants have been precisely defined, beyond which the use of dispersants could be considered.

 Outside these boundaries, dispersants are used without specific restrictions when the need arises; inside the boundary, the use of dispersants is limited and subjected to particular control and prior authorization by competent national authorities.

- Standard testing procedures exist for efficiency, toxicity, biodegradability and non-inhibition of oil degradation.

List of approved products is regularly updated by CEDRE.

GREECE - Dispersants are used when the need arises.

Only products authorized by the National Centre for Marine Rresearch can be used.

- In addition to the Hellenic Coast Guard, private companies can also use dispersants, following the authorization by local maritime authorities (Harbour Master).

ISRAEL

- Specific regulations are currently under development.
- Use of dispersants requires a prior written authorization from Ministry of Environment and can be executed only under supervision of Marine Pollution Inspectors.
- Only dispersants approved by CEDRE, France (new testing procedure, 1988) are permitted. Tests conducted: efficiency, toxicity, biodegradability and noninhibition of biodegradation of oil by the dispersant.
- Use of dispersants in water shallower than 30 m offshore coastal national parks, manne reserves and specially protected areas, is not permitted.
- Outside these regions, use of dispersants may be considered with specific judgement for each case.

ITALY

- Dispersants can be used, following an authorization by competent national authorities only in extreme cases and especially when there is a grave and imminent danger for human life or the environment and it is not possible to respond by using mechanical removal of oil and its physical distruction.
- Only dispersants tested and approved by the "Istituto Superiore di Sanità" can be used.
- List of approved products exists and is regularly updated by the Ministry of Mercantile Marine.

LEBANON No information.

LIBYA No information.

MALTA - Dispersants accepted for use by EEC countries can be applied.

MONACO No information.

MOROCCO - Dispersants approved by the administration can be used.

SPAIN -

- Use of dispersants is envisaged when mechanical recovery of oil is not possible.
- New regulations are currently under study, including official national testing and approval procedures.
- Local use is controlled by local maritime authorities.
- Authorities only recommend the use of selected products.

SYRIA No information.

TUNISIA No information.

TURKEY - Priority is given to mechanical recovery.

- No specific policy regarding the use of dispersants these are never used.
- Research in the field has been undertaken.
- Official testing procedure does not exist.

YUGOSLAVIA - Policy regarding the use of dispersants has not been officially defined.

- Occasional use, when mechanical recovery is not possible, is subject to the approval of the Harbour Master's offices.
- Official testing procedure does not exist.

ANNEX 3

LIST OF APPROVED DISPERSANTS IN THE MEDITERRANEAN COASTAL STATES

ALBANIA Information not available.

ALGERIA Information not available.

CYPRUS Information not available.

EGYPT Information not available.

FRANCE Dispersants approved in accordance with the new French procedure (in force

since 1 January 1988), for use either neat or possibly diluted with sea water

(corresponding to Type 3 products).

Dispolene 36 S Dispolene 38 S Finasol OSR 52 Inipol IP 80 Inipol IP 90

Gamlen O.D. 4000 (PE 998)

Bioreico R93

Dasic Slickgone NS Emulgal C 100

GREECE Information not available.

ISRAEL Type 3 products only approved by CEDRE, France according to the new

French procedure.

Dispolene 36 S
Dispolene 38 S
Finasol OSR 52
Inipol IP 80
Inipol IP 90
Gamlen OD 4000
Bioreico R 93
Dasic Slickgone NS
Emulgal C 100

ITALY Conventional dispersants (2nd generation)

Albisol BPD
Finasol OSR 2
Gamlen OSR 2000
Gamlen OSR LT 126
Nalco D 4105
Prodesolv 128/D
Rochem OSR L.T.
Rochem OSR W.S.A.
Shell Dispersant LTX

TC 66

Vecom B 1425 GL

ITALY (cont.) Concentrate dispersants (3rd generation)

AP - 2 BP 1100 WD Clean M Corexit 9600 Dispolene 34 S Finasol OSR 5 Hoe S 1708 Nalco D 4106

Nokomis 3 - C (Slik-A-Way)

Safety Sea Cleaner

Sımar 80

Spill Off Magnotox IMX 103

Urruty Ecopis

LEBANON Information not available.

LIBYA Information not available.

MALTA Information not available.

MONACO Information not available.

MOROCCO Information not available.

SPAIN Concentrate dispersants (3rd generation)

Corexit 9527 Finasol OSR 12 Finasol OSR 121

SYRIA Information not available.

TUNISIA Currently under development.

TURKEY Information not available.

YUGOSLAVIA Information not available.

ANNEX 4

DELIMITATION ZONES FOR THE USE OF DISPERSANTS ESTABLISHED BY THE MEDITERRANEAN COASTAL STATES

FRANCE (sample)

LE DELTA DU RHONE ET SES ABORDS

Map No.2: Geographical limits for massive use of dispersants *

A geographical limit has been defined, outside which it is possible to envisage the use of dispersants without major risk for the marine environment. This limit takes into account the currents' strength, and therefore dilution potentials, slicks' trajectories and biological resources in the envisaged sectors.

Inside the limit, it is recommended to consult CEDRE beforehand. In agreement with concerned scientific bodies, it will decide whether the dispersant treatment could start, taking into consideration local conditions (wind, currents, extent and type of pollution).

SPAIN

Initial studies are being prepared.

TUNISIA

Currently under development.

CEDRE; Atlas pour la prévention et la lutte contre les pollutions accidentelles par le pétrole : Le Delta du Rhône et ses abords, CEDRE, Brest, 1983.

^{*} The text and the map are reproduced from the study:

ANNEX 5

DISPERSANT TESTING PROCEDURES

At the time of the preparation of the document, only the description of the French testing procedures was available at the Centre.

FRANCE

EFFECTIVENESS:

Principle: The test (NF T 90-345) takes place in a 5 litre test tank with a seawater

current flow which enables a dilution of the tank contents (tank equipped with seawater inlet and overflow). The rate of dilution is fixed and the tank is also equipped with a system for vertical oscillations (wave beater) which can create

a moderate agitation.

Method: At the beginning of a test, the oil is placed on the water surface, and after

several minutes the dispersant (or mixture water/dispersant in a proportion of 90:10) is applied to the oil just before the agitation system is turned on.

The ratio dispersant/oil is 0.5 and the oil is a mixture of heavy fuel and light oil which has been adjusted to obtain a viscosity close to 1000 cSt at ambient

temperature.

The effectiveness is represented by the amount of oil dispersed and eliminated in the overflow during 1 hour. Effectiveness is between 0 and 100, where 100 corresponds to the maximum theoretical quantity which would be eliminated

in the case of a totally dissolved substance.

Requirements: For approval the effectiveness must be not less than 60%.

TOXICITY

Toxicity tests are made on shrimps in order to assess the acute toxicity of a dispersant on shrimps after 6 hours of exposure (after which time, the test organisms are placed in a tank of non-recycled seawater for 24 hours). The test is performed either with white shrimp (*Palaemonetes varians*) or on grey shrimp (*Crangon crangon*).

<u>Principle:</u> The testing consists of a comparison between the mortality induced by the

exposure of a same population of shrimps to a reference chemical (a well-known surfactor). NORAMI (M.D.A. 50) and to the dispersent

known surfactant: NORAMIUM D.A. 50) and to the dispersant.

In this way the method avoids the problems caused by possible variations of the shrimp's resistance (e.g. due to breeding or moulting season, ...). Method: The test involves 2 simultaneous steps:

1. Control of the sensitivity of the batch of shrimps: determination of the LC50 of the NORAMIUM D.A. 50/6h on 30 shrimps from the population to be tested.

 Control of the toxicity of the dispersant: a batch of 30 shrimps is exposed during 6 hours to the dispersant in seawater at a concentration ten times the "LC50 of NORAMIUM/6 h" previously determined.

These two steps are performed in 16 I cylindrical tanks in which a propeller induces a generalized water current; the propeller is located in a vertical cylinder which has two sets of openings at the water surface and at the bottom.

Following each step in the procedure, after exposures (6 hours), the shrimps are left for 24 hours in clear water before the dead shrimps are counted.

Requirements: For approval, the mortality induced by the dispersant must not be higher than 50%.

BIODEGRADABILITY

Biodegradability is assessed by two laboratory tests: the first one to test the biodegradation of the dispersant; and the second one to check that the dispersant does not significantly affect the biodegradation of oil.

TESTING THE BIODEGRADATION OF THE DISPERSANT (NF T 90-346)

Principle: The CO₂ produced by aerobic bacteria (using the dispersant components as

carbon source) is measured. The test is 28 days long, at 22 °C temperature, and the quantity of dispersant is initally adjusted in order to reach a

concentration of organic carbon betwen 10 to 20 mg/l.

Requirement: For approval, the dispersant must show a biodegradability of at least 50% for

the first 28 days.

TESTING THE NON-INHIBITION BY THE DISPERSANT OF THE BIODEGRADABILITY OF OIL (NF T 90-347)

Principle: A comparison of remaining oil after a 21 day incubation period with and

without dispersant. The oil is referenced: BAL 110 (Arabian Light topped at 110 °C). The test temperature must be constant within \pm 1 °C between 20 and 28 °C. The oil-dispersant ratio is 10%. At the end of the test, the remaining

oil is measured by Infrared Spectrometry.

Requirement: For approval, the dispersant must not decrease the oil biodegradability by

more than 10%.

ANNEX 6

LIST OF COMPETENT LABORATORIES IN THE MEDITERRANEAN COASTAL STATES

ALBANIA Information not available

ALGERIA Information not available.

CYPRUS Information not available.

EGYPT Information not available.

FRANCE Efficiency testing

CEDRE (Centre de Documentation, de Recherche et d'Expérimentations sur les Pollutions Accidentelles des Eaux)

B P. 72

29263 Plouzane

Tel: +33 (-) 98.49.12.66 Fax: +33 (-) 98.49.64.46 Tix: 940145 CEDRE F

IFP (Institut Français du Pétrole)

B.P 311

92506 Rueil Malmaison Cedex

Tel: +33 (1) 47.49.02.14 Fax: +33 (1) 47.49.04 11 Tix: 203050 IFP A F

Toxicity testing

CEDRE (same address as above)

Evaluation of the biodegradability

- IRCHA (Institut National de Recherche Chimique Appliquée)
B.P. 1
91710 Vert-Le-Petit

Tel: +33 (1) 64.93.24.75 Fax: +33 (1) 64.93.43.32 Tix: 600820 IRCHA F

Evaluation of the possible inhibitory action on the biodegradability of oil

MNHN (Laboratoire de Cryptogamie)
 12 rue de Buffon
 75005 Paris

Tel: +33 (1) 47.07.08.64

Fax: -

- IRCHA (same address as above)

GREECE - National Centre for Marine Research

Agios Kosmas Hellinikon 16604 Athens

Tel: +30 (1) 982.02.14

982.92.37

Fax: +30 (1) 983.30.95

Tlx: -

ISRAEL Information not available.

ITALY Information not available.

LEBANON Information not available.

LIBYA Information not available.

MALTA Information not available.

MONACO Information not available.

MOROCCO Information not available.

SPAIN - MOPT - CEDEX

Centro de Estudios y Experimentaciones C/ Alfonso XII, 3 y 5

28071 Madrid

Tel: +34 (1) 467.37.08 Fax: +34 (1) 528.03.54

527.60.13

Tlx: -

Instituto Espanol de Oceanografia

Avda. de Brasil, 39 28071 Madrid

Tel: +34 (1) 597.08.64

597.44.43

Fax: +34 (1) 597.47.70

Tix: -

SYRIA Information not available.

TUNISIA Information not available.

TURKEY Information not available.

YUGOSLAVIA Information not available.