

Oil Spill Dispersants Guidelines

These guidelines are applicable to the National Plan to Combat Pollution of the Sea by Oil and Other Noxious and Hazardous Substances

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Guidelines:

1. Scope

1. This specification covers importation, transport, storage, use and disposal of oil dispersant concentrate for the use in Ghanaian waters.

2. Applicable Documents

1. Reference is necessary to the latest issue (unless otherwise stated) of the following documents which form a part of this specification to the extent specified herein:
 - i. International *Standard* ISO 7827 "Biodegradability—Organic compounds in an aqueous medium"
 - ii. International *Standard* ISO 9000 series of Quality Assurance Standards
 - iii. International Maritime Organization - "International Maritime Dangerous Goods Code"
 - iv. EPA guidelines for transport of Hazardous Materials

3. Definitions

1. For the purpose of this specification, the following definitions apply:
 - i. EPA - The Environmental Protection Agency.
 - ii. Approved Dispersant - A dispersant which has been tested for toxicity and dispersal efficiency and which, having met acceptable toxicity and efficiency criteria, is suitable for use in Ghanaian waters.
 - iii. Batch - A quantity of some commodity made in one operation or lot
 - iv. Cloud Point - The temperature at which solid substances begin to separate from solution.
 - v. Dispersant – A chemical which reduce the surface tension between oil and water, and thereby facilitate the breakup and dispersal of the oil in the form of finely divided droplets throughout the water column.
 - vi. Dispersant Efficiency - The ratio expressed as a percentage of the volume of oil dispersed to the total volume of oil treated with dispersant.
 - vii. Flash Point - The temperature at which a liquid gives off sufficient vapour to flash in the presence of a naked flame.
 - viii. Shall and Should - *shall* is mandatory, *should* is desirable or advisory.
 - ix. Surfactant - *Surface Active Substance* -A substance which has the effect of altering the interfacial tension between oil and water.
 - x. The Agency - EPA.

4. Requirement

1. **General**- The requirement is for an approved dispersant concentrate for the dispersal of oil at sea. The dispersant shall be in the form of a liquid and the material offered against this specification shall, under normal operating conditions, contain no solid material, no suspended matter and no additional liquid phases. It should be non-corrosive to the storage containers and should not contain substances that are normally considered to be toxic to humans.
2. **Prohibited Ingredients** - The dispersant shall not contain benzene, carbon tetrachloride, or other chlorinated hydrocarbons, phenol, cresols, caustic alkali, or free mineral acid.
3. **Aromatic Hydrocarbons** - If hydrocarbon solvents are used in the manufacture of the dispersant, they shall be low in aromatic hydrocarbons, with an upper limit of three percent total aromatic hydrocarbons as determined by Gas Chromatography/Flame Ionisation Detection, Infra Red Spectroscopy or Fluorescence Detection.
4. **Stability** - The surfactants shall be wholly soluble in the solvent and shall remain uniformly distributed at all temperatures from -10°C to +50°C.
5. **Physical Properties**
 - i. **Flashpoint**- Importer shall advise the flashpoint of the tendered dispersant, as determined by the Pensky Marten closed cup method (ASTM D93, IP 34, BS 2834).
 - ii. **Cloud Point** - The cloud point of the dispersant as determined by methods (IP 219 or ASTM D2500) shall not be more than -5C. The dispersant shall not separate into layers at temperatures greater than -10C.
 - iii. **Viscosity** - The dispersant viscosity at 0°C shall not be more than 250 centistokes ($2.5 \times 10^{-4} \text{m}^2 \text{s}^{-2}$) at a shear rate of 103s^{-1} .

6. Ecotoxicity

- i. **Toxicity**- It is a mandatory requirement that each dispersant imported shall have been tested for marine toxicity. The toxicity of oil dispersants is characterized by the acute lethal concentration (hereinafter, LC50), as well as the MPC or approximately safe impact level (hereinafter, ASIL) for fisheries waters.
- ii. The testing shall involve two tropical marine fauna species, with the object of determining the dispersants 96 hour LC50 and to establish incipient lethal limits. The testing shall be carried out at a recognised and accredited testing laboratory and the importer shall forward a copy of the test results with the offer. A brief description of the required testing protocol is given at annex "A". A candidate product previously accepted under the requirements of this document will not be required to be tested under the revised protocol, providing the formulation remains

- iii. *Toxicity Limit* - The dispersant as tested under the current protocol shall have a 96 hour LC50 value on the order of magnitude of 10 mg/litre (ppm) as derived from the 96 hour semi static exposure regime.
- iv. *Biodegradability* -the dispersant shall be tested for biodegradability according to test protocols described in AS 4351.1 Part 6, and must meet the 'pass' criteria as described in AS 4351.1 Part 6.2.2 or Part 6.3.2. An equivalent standard for testing biodegradability may be used subject to approval by EPA.

Note:

LC₅₀ – the concentration of oil dispersant at which 50% of organisms die in a certain time (24-96 hours, as a rule). This parameter characterizes an acute toxicity and it can be used to screen a number of dispersants for the purpose of selecting the least toxic compound for subsequent practical use. When oil dispersant is applied to an oil slick during OSR its concentration must not exceed LC₅₀

MPC – the maximum concentration of a given compound in the water at which no consequences occur that would reduce the fisheries significance of the body of water.

7. Operational

- i. *Efficiency Testing* - It is a mandatory requirement that each dispersant tendered against this specification shall have been tested for dispersal efficiency. For the purposes of this specification, the "Mackay Dispersant Performance Test" is the only efficiency test acceptable to EPA. See annex "B" for a description of this test.
- ii. *Efficiency*- The dispersant shall be more than 75% efficient at an application ratio of 20:1, ie. twenty parts oil(light Arabian crude which has been artificially weathered), to one part dispersant, when tested by the Mackay dispersant performance test.
- iii. *Test Report* - The efficiency testing shall be performed by a recognised and accredited testing laboratory and the importer shall forward a copy of the test report with the tender.

8. Storage

- i. *Storage Requirements* -The importer shall advise on their storage requirements for the imported product. This advice shall also include information as to whether or not there are special conditions or legislative requirements applicable to storage of the imported dispersant.
- ii. *Stability in Storage*- In storage the dispersant shall not separate, gel or solidify.
- iii. *Storage Life* - The dispersant when stored according to the manufacturer's recommendations, in the original sealed containers, with ambient temperatures ranging between -10c and +50c, should have a storage life of not less than ten (10) years.

- iii. *Maintenance in Storage* - The importer shall advise if any maintenance procedures are recommended or are required in order to achieve the desired storage life of not less than ten (10) years.

9. Packaging

- 1. *Container Volume* - The importer shall ensure that the specified dispersants are in:
 - i. 200 litre drums, and;
 - ii. 1 000 litre intermediate bulk containers (IBC).
- 3. *Storage Life* - The drums and IBCs shall provide safe sound storage for the dispersant for a minimum storage period of not less than ten (10) years. See clause 7.6.
- 4. *Transport Codes*- The imported containers shall be suitable for the transport of the dispersant by all transport modes (land, air and sea) and shall therefore meet the packaging requirements of the following transportation codes:
 - i. International Maritime Dangerous Goods Code
 - ii. International Air Transport Dangerous Goods Code
 - iii. EPA guidelines for transport of Hazardous Materials
- 5. *Corrosion Resistance* - The containers shall be suitable for use in a marine environment and should not be degraded by exposure to temperatures in the range of - 30c to + 50c, humidity up to 100% and high levels of UV radiation.
- 6. *Batch Numbers* - The dispersant's batch number and year of manufacture shall be clearly marked on the side of each container.
- 7. *Labelling* - The dispersant containers shall be labelled in accordance with international standards labelling requirements. The label shall be in the specified format and shall provide all the information required by the guidance note (e.g. GHS for classification and labeling of chemicals). The label shall be weatherproof, UV stable, not affected by dispersant and truly permanent.

10. Material Safety Data Sheet

- i. *Material Safety Data Sheet* - it is a mandatory requirement that a material safety data sheet (MSDS) be submitted with each tender. The MSDS shall be the latest issue for the tendered product.
- ii. *Format*- The format is flexible however it is desirable that it should conform to international standards.
- iii. *Information* - The MSDS should be complete in all detail and shall provide as a minimum all the information listed as core entries in Appendix 6 - "Material Safety Data Sheet Checklist", of the guidance note.

11. Test Certificates

- i. *Test Certificates*- Information regarding the physical, chemical and toxic properties, and efficiency of the tendered product shall be provided in the form of test certificates issued by recognised and accredited testing laboratories.

5. Quality Assurance

- i. The importer of the dispersant shall use an inspection system conforming to the ISO 9000 series of quality standards which shall ensure that the dispersants offered to the Agency for acceptance conforms to the specified requirements. The inspection system shall be documented and available for review.
- ii. The dispersant manufacturer shall use a quality control system conforming to the ISO 9000 series of quality standards which will ensure that each batch of dispersant delivered is the same formulation and quality as that tendered and that which has been subjected to the specified testing protocols.
- iii. EPA reserves the right to take samples of dispersant for examination and or testing to ensure that supplies conform to the requirements of this specification.
- iv. EPA reserves the right to reject any dispersant supplies which fail to meet the requirements of this specification.
- v. Acceptance of the dispersant shall be subject to agreement by the Inspecting Officer that the quality requirements of this specification have been met.

6. Transportation Requirements

The importer shall advise of the requirements to transport the tendered product in compliance with the following transportation codes.

- i. International Maritime Dangerous Goods Code
- ii. International Air Transport Dangerous Goods Code
- iii. EPA guidelines for transport of Hazardous Materials

7. Net Environmental Benefit Analysis (NEBA)

- i. Technologies - Used technologies must be in compliance with Ghana's legal requirements in the field of environmental protection, as well as with all appropriate international agreements that Ghana is party to;
- ii. In order to reduce environmental damage and expenses for OSR operations, as much oil as possible should be collected, eliminated, and recovered at sea prior to reaching shore or any natural territories requiring special protection;
- iii. Mechanical methods for removal of oil from the surface of the water are preferred if the hydrological and meteorological conditions at the spill site permit the use such methods; sorbents shall only be used when the absorbed oil

- can be removed from the surface of the water in a timely manner (within a single working shift); the use of sinkable agents is prohibited;
- iv. When combating large oil spills, all methods (both dispersants and mechanical equipment) for cleanup sea surface shall be used, since practical experience shows that no more than 20-30% of the spilled oil can be collected using mechanical equipment;
 - v. These various OSR technologies can be applied in parallel: some slicks are treated with dispersants, and some are collected using mechanical OSR equipment;
 - vi. The decision to apply dispersants shall be made solely on the basis of a Net Environmental Benefit Analysis (NEBA) for the regions that have become contaminated or that are under a threat of pollution. Only preliminary approved dispersants shall be used in those cases where results of NEBA indicate that failure to use dispersants will cause more severe impact on biological resources and economic facilities.
 - vii. ***Preliminary approval*** by state nature protection agencies confirms that the dispersant in question has "in principle" been authorized for use in the inland and territorial seas, exclusive economic zone of Ghana and may be included in particular site or regional or national oil spill contingency plans. The preliminary approval means that dispersant toxicity is tested by specialized research centers and dispersant has duly established maximum permissible concentrations (hereinafter, MPC) for sea areas.
 - viii. Planning and justification of the use of oil dispersants, as one possible OSR method should be made in advance when developing the Oil Spill Contingency Plan, hereinafter referred to as "OSR plans" (regional, for a specific port or a specific facility). NEBA for the region in question shall be included (along with a description of the oil spill scenarios considered) in OSR Plan, prepared and approved by the EPA.
 - ix. The following factors must be taken into account in the planning process and scenarios:
 - risk assessment of possible oil spills and the volume of oil spills;
 - factors influencing the oil's behavior on the water (properties of the oil, typical meteorological conditions);
 - the sensitivity of the most valuable ecosystem components (VEC) to oil pollution;
 - physicochemical characteristics of the dispersants;
 - the results of the NEBA conducted according to the Regulations;
 - Possession of a properly approved MPC of specific dispersants.
 - x. If oil dispersants are applied on bodies of water used for public water supply or recreation, they must have properly approved MPC or approximately permissible levels (hereinafter, APL), which are included into international hygienic standards, such as WHO standards.

The purpose of an NEBA is to prepare recommendations concerning the choice of environmentally and economically optimal oil spill response technique(s) in a real-life situation. An optimal technique is defined as one that will minimize a spill's adverse impact on a region's environment and economy.

NEBA shall include weighting and comparison of the advantages and disadvantages of dispersant use for environmental protection of the area under consideration, as well as an assessment of whether it is possible to prevent significant damage to biological resources. NEBA will include priority levels for protection of particularly rare and valuable species of birds and aquatic animals. Preparation of the assessment of overall environmental benefit shall take into account the fact that fish stocks are restored within 1—3 years, while stocks of plankton are re-stored within 2—3 weeks, while bird colonies and grounds inhabited by aquatic animals may be permanently destroyed. NEBA is conducted in the stage of preparing OSR plans (preliminary), as well as when a decision is being made at the time of an oil spill (actual).

The following factors shall be taken into account during preparation of NEBA protocol:

- The list of environmentally and economically valuable components that must be protected on the basis of their priority.
- Seasonal variations of environmentally valuable components.
- Results of oil spill behavior mathematical modeling, the nature of the spilled oil's and physicochemical changes of it.

- Weather conditions
- The effect of floating and emulsified oil on environmentally valuable components.
- The advantages and disadvantages of different available oil spill response techniques.
- Only preliminary approved dispersants must be considered.

Certain OSR technologies can be immediately eliminated from consideration in a NEBA because they are not effective or usable under the conditions in question; all other technologies shall be ranked by effectiveness and preference. The proposals advanced may include the use of different technologies in different portions of the slick. As far as pollutant dispersal is concerned, the recommendations should also include determination of whether it is or is not feasible to use dispersants in this situation, determination of which sections of the slick are best treated with dispersants, determination of the DOR and description of the measures to be used in monitoring application of the dispersant(s). The results of the environmental analysis shall be documented in an agreed statement and approved by the On-Scene Commander (hereinafter, OSC) and the office of the territorial Environment Protection Agency.

The NEBA must be conducted by a group, which must include:

- representatives of the territorial unit of the Environment Protection Agency;
- specialists from fishing industry and/or scientific fisheries organizations who are well acquainted with the characteristics of the region or area under consideration;

- specialists in oil spill response technologies;
- specialists in the use of oil dispersants;
- Representatives of agencies of the state sanitary and epidemiological surveillance (MMDAs and Health Authorities).

These groups are established in advance by the developer of an OSR plan for a facility or region. The list and names of the experts recruited during actual conditions must be approved by the OSC of the facility or region.

They should have experience and knowledge in the following fields:

- state of the environment in the area of the accident and the requirements of sanitary and epidemiological surveillance;
- distinctive characteristics of the biology, breeding conditions, habitat and migration routes of birds, mammals, fish, benthic and other aquatic organisms living in the vicinity of the oil spill and adjacent areas; and calculation of the damage to living resources;
- behavior of spilled oil on the water;
- OSR technologies and resources;
- use of oil spill dispersants.

Decision-making on the use of pre-approved oil dispersants in an actual situation is to be made by the OSC in agreement with the territorial office of the Environment Protection Agency.

In the event of an oil spill, a NEBA must be conducted for the actual situation. If a preliminary NEBA has been conducted, the NEBA of the actual situation is done in an abbreviated form. Its purpose is only to make sure that the actual situation corresponds to the scenarios given in the OSR plan, and also to refine the recommendations on the choice of OSR technology (technologies).

On the basis of real-time information, the leader of the NEBA group, who is appointed by the IC, organizes a comparison of the scenarios for which the preliminary NEBA was made to the actual situation at the site of the spill.

If the actual and preliminary scenarios coincide or are similar, the authorized representatives of the territorial units should endorse the use of oil dispersants in the given situation.

If the actual situation deviates significantly from the preliminary scenarios the OSC shall convene the NEBA group as quickly as possible and conduct a NEBA to carry out a complete assessment of the actual situation.

8. Requirements to a technique of dispersant application

When treating oil slick with a dispersant, the initial concentration must not exceed the dispersant's LC_{50} . All dispersants preliminary approved in Ghana have equal LC_{50} corresponding to 10 ppm.

Calculation of the initial concentration is based on the amount of dispersant applied, assuming that dispersion takes place in a volume of water equal to the surface area of the oil slick to be treated multiplied by a factor of 10 (the depth of penetration of dispersed oil; it may reach 10 m).

It is recommended to use undiluted dispersants, but in practice water solutions of dispersants are sometimes used (usually in a concentration of 10-30%), especially for treating thin films and low-viscosity grades of oil (less than 500 cSt). In this case, a vessel's fire-fighting system can be used, and the dispersant is ejected into the fire main.

Oil dispersants are not recommended for use in enclosed regions of the sea with a low water exchange rate (inlets, lagoons), in shallow waters.

To increase the efficiency of dispersion of a viscous and water content oil slick, it is recommended to use two-stage treatment. The first treatment, for the purpose of de-emulsifying water from the oil slick, is effected with $DOR = 1/30$, and then 3-4 hours later the treatment is repeated with DOR equal to $1/20$. It is not advisable to treat iridescent thin oil films with dispersant.

9. Assisting tools for oil spill dispersant application

a. Sensitivity Maps

Oil spill response operations success substantially depends on time required for decision making. In order to reduce it and increase a quality of NEBA a development of environmental sensitivity maps is essential. It is recommended to use GIS for this purposes. Rare species of wild plants and animals, specially protected natural territories, valuable economic objects and types of shores must be included among the VEC. They have to be shown on maps of the potential sensitivity to oil pollution of resources in the marine area under consideration.

Some coastal areas are more sensitive to oil pollution than others. Factors that determine the sensitivity are e.g. presence of important natural resources, marshes and economic activities. In planning the response to oil spills, an in-depth knowledge of the coastal sensitivities in the threatened area will enable an optimized use of response resources. Furthermore, priorities for protection strategies can be identified through application of maps showing ecological sensitive coastal areas.

The maps must show the seasonal distribution of VEC. The map's explanatory notes shall contain the sensitivity of VEC to the impact of surface and dispersed oil and the priority of protecting them from oil pollution. It is also recommended that the maps indicate areas of the sea where the use of dispersants is inadvisable at any time of the year (for example, fish-hatchery enterprises and facilities, water intakes), where their use is possible in certain seasons of the year, and where dispersants can be used at any time of the year after a NEBA has been conducted (for example, to prevent oil pollution of specially protected natural territories).

In the absence of the maps, the OSR plan must include the characteristics (fisheries, environmental and sanitary-epidemiological) of the sites of possible accidents, which should be obtained from the appropriate regional Environmental Protection Agency Office.

b. Mathematical Models of Oil Behavior on the Sea Surface.

Along with the sensitivity maps, they serve as decision-making tools forecasting zones at risk, direction and velocity of spilled oil (oil slicks) thereby allowing for decisions for selection of strategy and means to be applied for the spill response.

Wide ranges of mathematical models are available today including both forecasting and backtracking features. Some models also offer a three-dimensional approach allowing for evaluation of evaporation/dispersion of the oil depending on the type of spilled oil. The key and crucial issue for all models is the quality of simulation/verification of the local current regime.

Annex A

Testing Oil Dispersants For Toxicity

1. Test Species

Tropical

- a. *Liza vaigiensis* - a species of tropical reef mullet (fish)
- b. *Penaeus monodon* - a banana prawn (crustacean).

(Or reasonable alternative species which (1) are common and representative of a typical tropical marine community, (2) are available throughout the year and readily collectable from the field, (3) are of an appropriate size, and (4) are adaptable to laboratory conditions).

2. Test Method

Tests are to be semi static tests involving daily renewal of test solutions. They should conform to the normal requirements of bioassay procedures and in particular there should be:

- a. At least one control chamber and six test chambers each having a different concentration of the test dispersant.
- b. Full randomisation of chambers and animals.
- c. Test chambers are to be gently aerated to prevent stratification of test media. At least ten animals per test chamber but the biomass should not exceed one gram per litre and the dissolved oxygen should not fall below four milligrams per litre in twenty four hours.

Test data should be reported as toxicity response curves showing the LT value at each concentration tested. 96 LC₅₀ values shall be determined from the response curves and incipient LC values should be determined if possible.

In order to determine LT50 value for the lower concentrations, it may be necessary to extend the test period beyond the basic 96 LC₅₀ test up to and for no more than seven days. During the extended period, daily animal observations, feeding and medium changes should be carried out for each of the concentrations requiring extension as well as for the control.

Full details of the test animals, acclimation procedures, test conditions and derivation of results should be reported. Dispersant concentrations should be reported as nominal (added) values, because the qualification of exposure concentrations would require detailed surfactant analyses beyond the scope of most laboratories.

The salinity should be 35 0/00 in all tests. The temperature for tropical tests should be 30C 3.

Annex B

Mackay Dispersant Performance Test

Introduction

The Mackay dispersant performance test is used to determine :-

- a. How well various chemical dispersants work on various types of oil under given energy conditions, water salinities and temperatures.
- b. The relative performance of different chemical dispersants under the same conditions.

In the Mackay test a circulating air current imparts energy to the water surface in the test chamber. This method of generating turbulence is believed to simulate ocean conditions more accurately than do shaking, stirring or pumping methods. This method does not attempt to simulate subsurface ocean hydrodynamics. The focus is on approximating the mixing at the surface, since this is where oil dispersal occurs.

Outline of the procedure

The equipment and procedures described are those developed by Dr Donald Mackay of the University of Toronto.

The Mackay method of testing oil dispersants allows for the variation of air and water temperatures, mixing energy, water salinity and dispersant to oil ratios.

The Mackay tester, figure 1, consists of a cylindrical glass vessel with an internal diameter of 300mm and a height of 300mm. The vessel is covered with a plexiglass lid which is fitted with a gasket to provide a good seal between the lid and vessel. Lugs on the lid ensure that it is located concentrically on the vessel.

In the lid are:

- a. air inlet and outlet tubes
- b. ports through which oil and dispersant are introduced into the test chamber
- c. glass sampling tube
- d. oil containment ring and rod

The containment ring prevents uncontrolled spreading of oil over the water surface inside the test vessel prior to the introduction of the dispersant under test.

The test vessel is positioned in another vessel in which temperature controlled water is circulated. Temperature controlled airflow from a variable flow airpump is circulated

through the test vessel. Six litres of synthetic seawater or fresh filtered seawater (adjusted) to a specified salinity is used in the test. The volume of oil used is 10ml.

When the seawater temperature in the test vessel has stabilised to within 1°C of that specified, air is circulated through at the required velocity. When the air temperature is within 1°C of that specified and wave motion in the vessel is established and stable, 10ml of the test oil is introduced into the vessel and released in the containment ring. The desired amount of dispersant under test is applied to the oil surface and is allowed to penetrate through the oil film for 1.0 minutes. The containment ring is then lifted and dipped into the water two or three times to dislodge as much adhering oil as possible. After ten minutes the airflow is stopped and a 500ml sample of the oil, dispersant and water mixture is taken through the sample tube the inlet of which is positioned 45mm above the bottom of the test vessel. The first 50ml is discarded and the balance retained as the test sample. After a further five minutes a second 500ml sample is taken and the first 50ml is discarded as before.

The samples are treated with dichloromethane (CH_2Cl_2), and filtered through anhydrous sodium sulphate (Na_2SO_4). The concentration of oil in the sample(s) is determined by UV-spectrophotometer. The values obtained are compared to a calibration curve. 100% effectiveness corresponds to an ideal situation where all of the oil has been dispersed into the water column.

The shearing and mixing forces necessary to break up the dispersant treated oil and drive it into the water column in finely divided droplets are generated by the wind driven wave action created by the flow of air over the water's surface. To give a quantitative measurement of the mixing energy, and to correlate the energy level to sea state, oxygen transfer coefficients are determined. Oxygen transfer coefficients are, in the main, dependent on the amount of air flow immediately over the water's surface. Determination of oxygen transfer coefficients are done by first deoxygenating the water to about 10% saturation. This is achieved by either bubbling nitrogen through the water or by the addition of a small amount of a saturated solution of sodium sulphite (Na_2SO_3). An airflow of the desired velocity is circulated through the chamber. Using a dissolved oxygen meter, oxygen concentrations are plotted as a function of time. This is done for all desired energy levels.

Mackay has suggested that there is a correlation between turbulence levels in the test vessel and sea conditions (Mackay et al, 1980). This makes it possible to perform laboratory tests at approximately desired sea states. It is pointed out, however, that an exact simulation of environmental conditions in any laboratory is virtually impossible.

EPA, March 2008

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