

SPECIFICATION FOR OIL SPILL DISPERSANTS

1. Scope

This specification relates to oil spill dispersants for application at sea or on beaches and to the procedures adopted in the UK before any dispersant can be so used.

2. Procedures

(a) Qualification

A dispersant which has been found to conform to the requirements of the Specification when subjected to tests carried out by the Defra commissioned laboratory or independent laboratory selected by the applicant, will be granted a Certificate of Qualification, if the information required in Clause 5 below has been provided.

(b) Product Approval

No dispersant may be used on UK beaches or in, UK waters, as defined by the Food and Environment Protection Act 1985, unless it has been approved by the appropriate UK authority, the Secretary of State for the Department for Environment, Food and Rural Affairs (Defra), the Scottish Executive, the Welsh Assembly Government, or the Department of the Environment for Northern Ireland (DoE(NI)). The Department for Environment, Food and Rural Affairs deals with approvals in England and Wales, and the Scottish Executive (Agriculture and Fisheries Department) (SEERAD), with approvals in Scotland. Approval will only be issued in respect of a product which, (i) is the subject of a valid Certificate of Qualification and (ii) has been found to conform to the Defra requirements concerning toxicity to marine organisms, in tests conducted by Defra on a sample of the product supplied to the Defra commissioned laboratory. Defra's approval will normally be valid for a period of five years from the date on which it is granted.

Note: The authority of the UK approving authorities to approve oil spill dispersants relates to UK waters and UK ships and aircraft only. Dispersants should only be considered suitable for use outside the UK when the agreement of the appropriate National Authority has been obtained, even if carried by a UK ship or aircraft, and UK approval is held. A list of products approved by the UK approving authorities can be obtained from Defra.

(c) Charges and Samples for Qualification and Approval

The Qualification and Approving authorities impose separate charges for the work involved in their respective activities. These charges must be paid by the person or

organisation submitting a product for Qualification or Approval. That person or organisation must also provide, free of charge and carriage paid, such samples (normally 5 litres) of the product as are required by either authority.

The Department for the Environment, Food and Rural Affairs are the UK authority in respect of approval of oil dispersants under the Food and Environment Protection Act, and their address is given below.

(d) Correspondence

Correspondence concerning all aspects of UK approval testing should be sent to:

Department for the Environment, Food and Rural Affairs
Marine Consents and Environment Branch
Area 2D
3-8 Whitehall Place
London
SW1A 2HH

3. Types of Dispersant

This specification relates to three types of oil spill dispersant. These are:

Type 1: Conventional Hydrocarbon-base - for use primarily undiluted on beaches, but may also be used undiluted at sea from WSL spray sets using breaker boards or other suitable means of application and agitation.

Type 2: Water-dilutable concentrates - for use at sea after dilution 1:10 with seawater, and sprayed from WSL spray sets using breaker boards or other suitable means of application and agitation.

Type 3: Concentrate - for use undiluted from aircraft, ships or on beaches, using appropriate spray gear.

Notes: (1) Treatment rates would normally be one part dispersant to 2-3 parts of oil for types 1 and 2 dispersant, or one part of dispersant to 20-30 parts of oil for type 3 dispersant. The rate of application of type 3 dispersant applied undiluted should not exceed 110 l ha^{-1} , when applied in UK waters or from UK ships or aircraft.

(2) Use of a dispersant is subject to the conditions in the Approval Certificate, including the prior approval of Defra for any use in water of 20m or less in depth, or within 1 mile of such depths; this includes use on beaches.

4. Materials

(a) The oil spill dispersant shall consist of suitable ionic, non-ionic or a blend of such surfactants dissolved in a suitable solvent. It shall not contain compounds which could expose the user to an unacceptable toxicological hazard during the normal spraying or handling operations when wearing a closely fitting face visor.

(b) It is unlikely that dispersants containing more than 3%wt. of aromatics will pass the toxicity requirements. In addition, the following ingredients are prohibited: benzene, chlorinated hydrocarbons, phenols, caustic alkali and free mineral acid.

(c) The surfactants shall be wholly soluble in the solvent and shall remain distributed uniformly at all temperatures from -10°C up to +50°C when stored for periods of up to 7 days.

(d) Type 2 dispersants shall be miscible with seawater at 1:10 concentration to form a solution or emulsion which has a viscosity not greater than that of the original dispersant alone.

Note: Type 1 and 3. dispersants have no requirement to be miscible with water since they will be applied undiluted.

5. Formulation

(a) Details of the formulation must be submitted (in confidence) to AEA and Defra at the time of application for Qualification and Approval respectively. The details shall include the percentage, chemical name (when applicable) and function.

Note: For Qualification purposes AEA will send a form on which the information can be entered when the contract for the work is sent.

(b) After a product has been Qualified, no change in the formulation will be permitted unless the change is approved in writing both by the Qualification Authority and the Approving Authority.

6. Qualification Testing

Note: The units quoted in this specification are consistent with the practice applied at present in the Chemical and Petroleum industries.

(a) Test Methods

Unless otherwise stated, the test methods to be used shall be the latest published editions of those given in this specification.

(b) Tolerance of test methods

Requirements contained herein are absolute and not subject to corrections for tolerance of test methods. If multiple determinations are made by the Qualification Authority, average results are to be used except for those test methods where repeatability data are given. In those cases, the average value derived from the individual results that agree within the repeatability limits given for the test method, may be used if the Authority permits.

(c) Additional test requirements

The Qualification Authority reserves the right to require additional testing of the product.

(d) Requirements

A sample taken from any portion of the product shall comply with the requirements of Table A1.

TABLE A1

TEST No	TEST	TYPE 1	TYPE 2	TYPE 3	METHO D
1	APPEARANCE	CLEAR AND HOMOGENEOUS, - VISUAL INSPECTION			
2	DYNAMIC VISCOSITY AT 0°C (mPa s maximum)	50	250	250	ASTM D445 IP 71 BS 4708
3	FLASH POINT (°C minimum)	60	60	60	ASTM D93 IP 34 BS2839
4	CLOUD POINT (°C maximum)	-10	-10	-10	ASTM D2500 IP 219
5	<u>EFFICIENCY INDEX</u> (at 10°C) 2000 mPa s fuel oil %minimum	30	30	60	ANNEX 1
6	500 mPa s fuel oil % minimum	N/A	N/A	45	
7	MISCIBILITY WITH WATER	N/A	Pass	N/A	Para 4d

7. Quality Assurance

(a) The manufacturer shall certify that each batch of the product is of the same formulation as that qualified in accordance with clauses 6 and 7 of this specification.

(b) The Qualification Authority reserves the right to sample and test the product at any time. For bulk supplies, the Qualification Authority may require a 25 litre reference sample to be taken at the time of blending.

(c) If any sample taken from a consignment is found not to comply with the requirements of this specification, the whole consignment may be rejected.

(d) The provisions of this clause apply equally to the manufacturer and any sub-contractor.

8. Keeping Qualities

The product, when suitably stored in its original sealed containers, shall retain the properties described in this specification for a period, from the date of despatch, of not less than two years in temperate climates (-20 to + 30°C).

9. Containers and marking of containers

(a) The product shall be supplied in sound, clean, dry containers, or bulk carriers suitable for the product and in accordance with the requirements of the contract or order.

(b) Coatings, paints, and markings of the containers shall comply with the requirements of the contract or order, and shall be to the satisfaction of the purchaser.

(c) It shall be the responsibility of the supplier to comply with any legal requirements for the marking of containers.

(d) Details of current procedures for the testing of the toxicity of oil dispersants can be obtained by application to the Department for Environment, Food and Rural affairs at the above address.

April 1983

(revised 1989, 2005 and February 2007)

**THE DETERMINATION OF THE EFFICIENCY INDEX
OF OIL SPILL DISPERSANTS.**

INTRODUCTION

The method for the determination of the Efficiency Index of oil spill dispersants is defined in the report LR 448 (OP). This revision expands on that method and incorporates the analytical procedures currently in use.

DEFINITION

The Efficiency Index of an oil spill dispersant is defined as the percentage, by weight of the test oil which has been transferred, as small droplets into the water phase under the conditions of the test, assuming complete and even distribution at the time of sampling.

SUMMARY OF THE METHOD

The oil spill dispersant is added, dropwise, to a measured volume, (by weight) of the test oil on the surface of seawater at 10°C in a conical separating funnel.

The separating funnel is rotated about its horizontal axis, at right angles to its longitudinal axis, for a period of 2 minutes at 33 ± 1 rpm. After rotation has ceased, the stopper is removed and after 1 minute standing time, 50ml of oily water are run off through the bottom tap. The quantity of oil present in the sample is then determined spectrophotometrically after extraction into chloroform.

The method may be used for determining the efficiency index of any of the three dispersant types, (types 1, 2 or 3).

APPARATUS

SEPARATING FUNNELS

(1) A conical separating funnel of nominal capacity 250ml, (Fig 1). After use the funnel should be rinsed thoroughly with chloroform to remove any oil remaining inside, then washed in a laboratory glasswasher. The washing programme should include a thorough rinse with distilled water to ensure that all traces of detergent are removed. The funnel should then be allowed to drain and cool before being placed in the temperature controlled cabinet ready for use.

(2) A separating funnel to BS 2021 with a nominal capacity of 100ml.

MOTOR DRIVEN RACK

A motor driven rack, into which can be fitted and clamped the 250ml separating funnel. The rack should rotate about a horizontal axis approximately 15-20 mm below the level of the seawater in the separating funnel.

SYRINGES

(1) A glass syringe, fitted with a needle, capable of accurately dispensing 0.2ml of dispersant in drops of 5 to 10 microlitres.

(2) A glass syringe capable of accurately dispensing 5.0ml of the test oil.

(3) A glass syringe, fitted with a needle, capable of accurately dispensing 2.0ml of Type 1 dispersant, and 2.0ml of Type 2 dispersant in drops of 5 to 10 microlitres

SPECTROPHOTOMETER

A spectrophotometer capable of measuring absorbance at 580nm, and equipped with glass cells of 10mm path length.

Stopclock

Measuring cylinders-, 250ml and 50ml

REAGENTS

TEST OILS

(1) An oil of known density and having the following characteristics:

Dynamic viscosity at 10°C: 1800 to 2200 mPa s at 4s⁻¹ shear

Asphaltenes (IP 143/78): 6.0% by weight, maximum.

Pour point (IP 15/67): <5°C

(2) An oil of known density having a dynamic viscosity at 10°C of 450 to 550 mPa s at a shear rate of 4s⁻¹. This oil is prepared by diluting the higher viscosity oil, referred to above, with kerosine to reduce its viscosity to the required value.

KEROSINE

Odourless Kerosine to BS2869 Ams 1 and 2, Class C1

SEAWATER

Seawater taken from the sea and having a total solids content of 3.3 - 3.5% Synthetic seawater is also permissible.

Sodium sulphate, anhydrous

Chloroform

METHOD

CALIBRATION

Transfer 0.1, 0.2, 0.3, 0.4 and 0.5g of the test oil, accurately weighed, into separate 100ml volumetric flasks. Dissolve the oil in chloroform and make each flask up to volume.

Measure the absorbance of each solution at 580nm in glass cells of 10mm path length, using the chloroform as a reference solution.

A graph may be plotted of absorbance against concentration of oil in the chloroform solution. Alternatively the line of best fit of the calibration points may be calculated to give linear regression coefficients.

PROCEDURE

The test procedure is carried out in a temperature controlled cabinet maintained at 10°C. All reagents, test materials and apparatus should be kept in the cabinet for 24 hours before conducting the test.

Place the unstoppered separating funnel in the motor driven rack. In a measuring cylinder, measure 250ml of seawater and transfer to the separating funnel.

Using the syringe, transfer 5ml, by weight, of the test oil to the surface of the seawater and start the stopclock. Weigh the syringe before and after use to calculate the weight ($\pm 0.001\text{g}$) of the 5ml of the oil.

Using the appropriate syringe, take the required volume of the dispersant to be tested, (0.2ml of type 3 dispersant, 2.0ml of undiluted type 1 dispersant and 2.0ml of freshly diluted type 2 dispersant). 1 minute after completing the addition of the test oil to the seawater, transfer the dispersant to the oil. The addition of the dispersant to the oil should be done dropwise, starting from the centre of the oil lens and working radially outwards so that the dispersant is distributed as evenly as possible. Place the stopper in the separating funnel and clip on the retaining cap of the motor driven rack. Close the door of the temperature controlled cabinet.

When the time of the stopclock shows 2.5 minutes from the addition of the oil to the seawater, start the rotation of the separating funnel, and continue for 2 minutes.

After 2 minutes switch off the motor driven rack and allow the separating funnel to stand, undisturbed for exactly 1 minute. Remove the stopper, and run off from the bottom tap, 50ml of oily water into a measuring cylinder. The taking of this sample should take no longer than 10 seconds.

The remainder of this determination may be done outside the temperature controlled cabinet.

Transfer the 50ml sample from the measuring cylinder to a 100ml separating funnel. Wash the measuring cylinder twice with 10ml of chloroform and add to the 100ml separating funnel. Stopper the funnel and shake for 1 minute. Allow the phases to

separate completely and run off the chloroform layer into a 100ml volumetric flask through a 75mm glass filter funnel fitted with a 9.0cm Whatman No 1 filter paper and into which has been placed no more than 1.5g anhydrous sodium sulphate. Repeat the chloroform extraction twice more, using 20ml chloroform on each occasion. Thoroughly wash the filter paper and sodium sulphate, with chloroform and then dilute to the mark on the volumetric flask. Stopper the flask and shake well.

Measure the absorbance of the sample solution using glass cells of 10mm path length and a spectrophotometer set to a wavelength of 580nm. The calibration standards prepared from the test oil should be measured at the same time as the sample solution.

Using either the graph or the calculated regression coefficients convert the absorbance measurement from the sample solution into concentration figures expressed as 'grams of oil per 100ml of chloroform'. This is equivalent to the weight of oil contained in the 50ml sample of oily water taken from the 250ml separating funnel.

CALCULATION

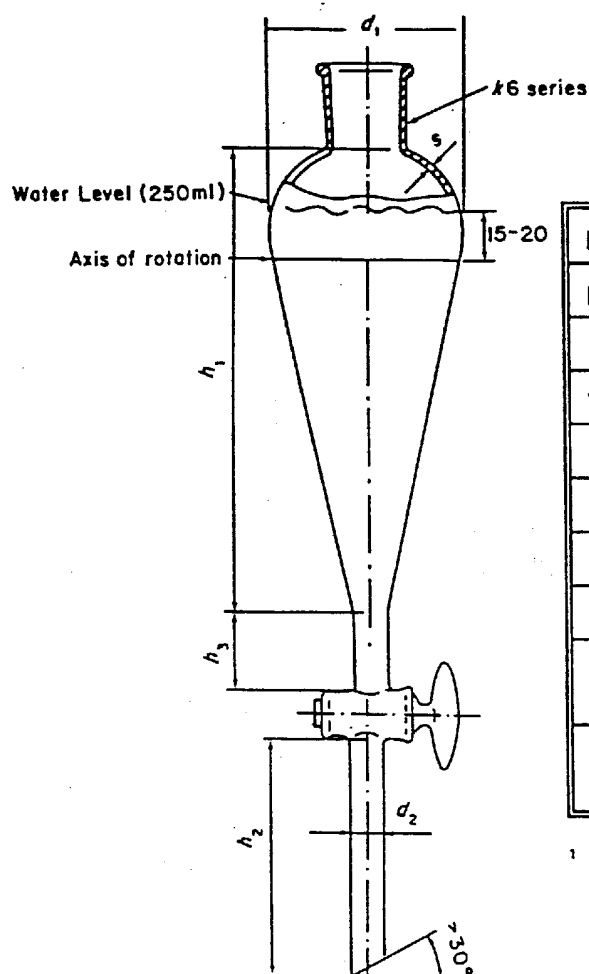
Calculate the efficiency index as follows:

$$\% \text{ Efficiency} = \frac{\text{weight of oil in 50ml sample of oily water} \times 500}{\text{weight of test oil added to the 250ml separating funnel}}$$

REPORT

The Efficiency Index is the average of three separate determinations. The calculated average is reported to one decimal place for each of the two reference fuel oils.

ANNEX 1, FIGURE 1



Nominal capacity	250ml
Height of body, h1	185mm
Diameter of body, d1 max	83mm
Wall thickness of body, s min	1.2mm
Diameter of stem ¹ , d2 ± 0.5	12.5mm
Length of stem, h2 ± 10	70mm
Nominal bore of stopcock min	3mm
Size of stopper (see ISO 383)	k6 series
Length of tube between bulb and stopcock, h3 max	20mm
Wall thickness of tube between bulb and stopcock min	1.5mm

¹ Medium walled tubing (see ISO 4803)

STANDARD CONICAL SEPARATING FUNNEL 250ml CAPACITY

NB. The distance between the seawater level when filled with 250ml seawater at 10°C and the axis of rotation of the flask should be between 15mm and 20mm.

