

<p style="text-align: center;"><b>THE NEW FRENCH APPROVAL PROCEDURE FOR SHORELINE CLEANING AGENTS</b></p>
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by

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### ABSTRACT

Different products can be used to help the cleaning operations of oil polluted rocks or piers. Some cleaning agents are designed only to help the desorption of the pollutant from the solid support : these non emulsifying agents are used when the pollutant has to be collected after being released. Some are designed to help the desorption of the pollutant and then to emulsify the pollutant in the water column underneath : the emulsifying cleaning agents . As for the dispersants, these products which are use in a natural sensitive environment, the shoreline, need to be checked prior to their application.

In this respect, a new approval procedure is being set up in France. This procedure takes into account the finality of the cleaning products and is based on laboratory tests. The first one, the control of the emulsifying capability, is to classify the products into emulsifying and non emulsifying agents ; all intermediary products which do not clearly belong to one of these two categories will be rejected because they do not respond to any cleaning strategy.

From this point the non emulsifying agents are tested for their efficacy (desorption), and their toxicity ; as these products are used with the view to collect the oil afterward, an additional test is performed to check the ability to sorb the treated oil with classical sorbents.

The emulsifying products are also tested for their efficacy (desorption) and their toxicity. However, because they are released with the oil in the environment, two additional tests are performed to assess their biodegradability and to check that the cleaning agent does not affect the oil biodegradability.

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## I. Introduction

In the event of oil spills, solid oiled surfaces such as rocks and port installations may have to be cleaned, when they are not exposed enough to permit a natural cleaning by wave action, or if they require a rapid restoration for touristic reasons or other purposes.

The methods to be used should be adapted to the degree of weathering of the oil. With time, and due to the effect of the sun, the oil loses its lighter fractions (through evaporation). It adheres more strongly to the rock or port installation, (adsorption), and acquires an increasingly hard surface (photo-oxidation). All these phenomena lead to the creation of a hard crust which becomes more and more difficult to remove.

For this reason, it is often necessary to use specific products, called "rock cleaning products", to facilitate the cleaning operations. These products are spread on the surface to be cleaned (usually at a rate of 30% product/oil) to soften the pollutant and diminish its adherence before undertaking the actual cleaning operations using a high-pressure water spray.

The cleaning products to be used should be chosen in function of whether or not the pollutant will be recovered after washing. There are two types of products :

\* **Emulsifiers** which contribute to the surface cleaning process and then, to the dispersion of the removed oil within the water column in order to facilitate its elimination or natural degradation.

\* **Non-emulsifiers** which simply reduce the adhesive capacity of the pollutant on the rock or pier to be cleaned without further dispersion, in order that the removed oil can be more easily recovered (by pumping and using sorbents).

When using non-emulsifying cleaning products, the cleaning operations do not generally endanger the environment since the pollutant is subsequently removed.

When using emulsifying cleaning products, this is not the case since the technique involves releasing the removed pollutant in the surrounding environment, and may result in relatively large quantities of oil being returned to coastal waters. For this reason the use of emulsifying cleaning products should be limited to cases when :

- removal or collection would be impossible after cleaning,
- the quantity of pollutant is small (small spill, scattered pollution),
- the water currents and tides are sufficient to induce a rapid dilution of the pollutant,
- and there are no sensitive areas close by (fish farms, water intakes, marsh, lands, etc)

As we are dealing with products to be applied in the environment, it is necessary to evaluate the substances before their use, to assess their effectiveness and relative harmlessness.

CEDRE had published a list of cleaning products which had been tested for their effectiveness and their toxicity. However, part of this list, based on information from 1985, has become outdated;

Just as dispersants have needed to be approved for their potential effectiveness and/or toxicity, it has become necessary to set up an actual approval procedure for the various cleaning products to be used in France.

## **II. Description of the Approval Procedure**

### **II-1 General principles**

An approval procedure must take into consideration the concept of the use for which a product is intended. In this manner, the first step should discriminate between the non-emulsifiers and the emulsifiers, and then consider each case separately.

The Approval Procedure begins with a primary test to measure the emulsifying ability.

This test is performed in a closed flask as follows: in a separating funnel, a small amount of topped crude oil (1 g, density = 0.88 g/l) is dropped on the surface of 250 ml of sea water; then the oil is treated with 0.4 ml of cleaning product.

The flask content is vigorously mixed by rotating the separating funnel.

Once the mixing is completed, the separating funnel is stopped for 6 minutes ; then a sample of 10 to 12 ml is taken through the tap of the separating funnel.

The oil concentration in the sample is measured to evaluate the quality of dispersion.

According to the results obtained from this initial test, the cleaning product is classified as being non-emulsifiers (if the oil concentration is <5 % ) or emulsifiers (if the oil concentration >30%).

When the results are intermediate (between 5 and 30%), the cleaning products are rejected since they do not meet the possibilities for a clear cut concept of use.

Once a product has been classified in terms of its emulsifying ability, the approval procedure continues as described below according the type of cleaning agent.

### **II.2 - Non-emulsifying products**

#### **II.2.1 Cleaning effectiveness evaluation**

The cleaning effectiveness test is performed on glass slides (cf fig 1) as follows :

A known quantity of heated Bunker C oil is spread on a glass slide. Once this oil has been allowed to cool to room temperature, it is treated by a spray of the cleaning product. The oil is subsequently removed by a spray of sea water performed in well controlled condition (nozzle, pressure); the amount of removed oil is measured ; at least 60% of the oil should be removed.

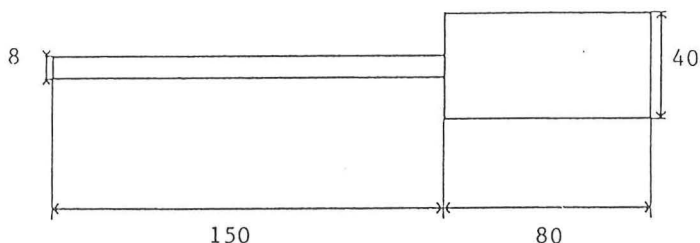


Fig. 1 : Glass slides

For each tested cleaning agent, the test is performed on 3 glass slides in order to check the variability of the results ; in addition, 3 more oiled glass slides which are not treated with the cleaning agent, are washed with water to check that the test has been performed in proper conditions.

### II.2.2 Toxicity test on sea shrimp :

The toxicity of the cleaning agent is assessed on marine shrimp by *comparing*, in the same batch of shrimps the mortalities (Lethal concentrations), caused by the cleaning agent and a reference toxic product : a population of shrimps is divided into small batches (30 individuals); these batches are exposed either to the known toxin (Noramium DA 50, a well-known surfactant substance), or to the tested cleaning products for 6 hours (a tidal delay).

For a concentration equal to 10 times the LC50 rate of the reference toxin, a cleaning product should not produce a toxicity significantly more than 50 %.

This method has been chosen because it avoids problems caused by any eventual resistance variations in batches of shrimp populations.

### II.2.3 Other tests :

A test for the biodegradability of the product is not planned since the wash-water run-off is to be recovered.

However, as sorbents are often used to recover the oil contained in the cleaning operation effluents, it would be interesting to test the effect of the cleaning product on the sorption of a typical sorbent ; an additional test is planned for this consideration, however its results will not be actual criteria for product approval but will be provided simply as additional, complementary information.

### II.3 - Emulsifying products

In this case, since the removed pollutant and cleaning products will remain in the environment, the approval procedure has copied the procedure used for dispersants, especially in terms of the biodegradability tests.

#### II.3.1 Cleaning Effectiveness Evaluation (see Paragraph II.2.1)

#### II.3.2 Toxicity Test on Sea Shrimps (see Paragraph II.2.2)

#### I.3.3 Product's Biodegradability Evaluation

This test is a modified "Sturm" test: it is the measure of the percentage of degradation over a 28 day period by measuring the CO<sub>2</sub> released by the bacteria which have only the sample of the cleaning product as their carbon source (NF-T-90-346).

The biodegradability must be at least 50% over the 28 days.

#### II.3.4 Evaluation of the inhibiting effects of the product on the biodegradation of Oil

It is important to check that the cleaning agent does not affect the oil biodegradation : this test compares the amounts of residual oil after 21 days of incubation on samples of oil which are both treated and untreated by the cleaning product (NF-T-90-347) ; the cleaning product should not decrease the oil biodegradation

### III. Tested products performances

#### III.1 - Effectiveness

A summary of the test results for the emulsifying ability and the cleaning ability for a number of tested cleaning products is presented in the table below.

PRODUCT	EMULSIFYING EFFECTIVENESS	CLEANING EFFECTIVENESS
Corexit 7664	20	1
Corexit 9580	21	84
Dispolene S90	51	6
Enersperse 700	25	6
Envirosolv	0	86
Gamlen OSR 2000	38	70
Gamlen OSR 4000	40	85
Gamosol	30	84
Ketrul 210	0	84
Ketrul 211	0	77
Sea Clean	54	75
Sofrasol	23	96

Taking into consideration the approval levels which were retained for a product's emulsifying ability (< 5% or > 30 %) and for a product's cleaning ability (> 60%), the following products meet the requirements of the approval procedure concerning the efficiency tests (emulsification and cleaning effectiveness):

- Non-emulsifiers : Ketrul 210, Ketrul 211 and Envirosolv
- Emulsifiers : Dispolene S90, Gamlen OSR 4000, Gamlen OSR 2000, and Sea Clean

### III.2 - Toxicity

In terms of their toxicity, a series of products were evaluated : the LC 50/6 hours was determined for Ketrul 210, Ketrul 211, Gamlen OSR 4000, Dispolene S90, and Corexit 9580, despite the fact that this latter product was not retained due to its "intermediate" emulsifying ability.

The toxicity of Gamlen OSR 2000 had been previously determined.

The table below provides a summary of the Toxicity test results.

PRODUCTS	LC 50 per 6 Hours (ppm)
Gamlen OSR 4000	4 400
Gamlen OSR 2000	10 000
Dispolene S90	3
Corexit 9580	15 400
Ketrul 210	6 300
Ketrul 211	13 900
Reference Toxin	64

It can be seen that the Dispolene S90 is quite toxic, and this is probably due to its high aromatic content. The difference in toxicity observed between the Ketrul 210 and Ketrul 211 products is also related to their aromatic contents (which are respectively less than 5 and 1 %).

### IV. Conclusions

As a result of this study, we have determined a specific Approval Procedure for rock cleaning agents.

This procedure, which will be officially put into force very rapidly, discriminates between two types of cleaning products :

- non-emulsifying cleaning products which are designed to allow the oil recovery after the clean-up operation,
- emulsifying cleaning products designed to clean and disperse the oil in the water column.

The many tests made in order to define the Approval Procedure have enabled us to select the best products among those tested, and to up-date the list of recommended products.

Updated List of Recommended Cleaning Products (Updated in January, 1994)

- Non-Emulsifying Cleaning Product
  - KETRUL 211
  - KETRUL 210
- Emulsifying Cleaning Product
  - GAMLEN OSR 4000
  - GAMLEN OSR 2000

It is necessary to note that these products have not yet been tested for biodegradation.

This list is provisional, awaiting the enforcement of the approval procedure ; as soon as sufficient number of cleaning agents have been approved a definite list will be published.

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