Observations And Conclusions From 10 Years Of Periodic Quality Controls On Operational Dispersant Stockpiles.

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Abstract

For the last 10 years, the French operational stockpiles of oil dispersants owned by the Navy, have been periodically checked to control their good preservation; similar controls were also performed on dispersant stockpiles of some oil companies.

The main criteria considered for these controls were the physical characteristics as well as the efficiency.

Cedre, which is in charge of these controls, performed more than 70 controls and gathered an interesting set of data on various batches of conventional and concentrated dispersants, some of them aged up to 20 years.

These data were statistically analysed to get a better understanding of dispersants medium and long term ageing, and to identify the effects of storage conditions on the quality of dispersants: drums or bulk storage, climatic conditions.

The criteria used in this study are the density, the viscosity, the pour point, the flash point and the efficiency of the dispersants as well as their appearance, colour, presence of a deposit or separation into phases.

1.0 Introduction

The French oil spill response policy includes, besides oil recovery using booms and skimmers, the use of dispersants, taking into account the characteristics of each spill.

As a basic rule, dispersant use is encouraged if the oil is still dispersible and if there is sufficient possibility of dilution for the dispersed oil at the spill location to avoid any adverse toxic effect of the dispersed oil on the environment. To help the decision-making regarding the use of dispersant, geographical limits have been defined along the French coasts considering the depth and the distance to the shore.

In this respect the French Navy which is in charge of the operations at sea, maintains application means capabilities in its harbours and a large dispersant stockpile, around 1200 tons, distributed along the French coasts, English Channel, Atlantic Ocean and Mediterranean sea; this stockpile is kept in drums, in tanks or onboard some ships likely to take part in a dispersant application operation.

Different control procedures have been put in force in the past 15 years :

- a procedure for approving dispersant has been set up in the eighties and updated in 1986; this approval procedure is based on laboratory assessment of efficiency, toxicity and biodegradability of the dispersant.
- a control of the stockpiles of dispersants; in 1988, the French Navy decided to establish a quality control on each batch of dispersant every 5 years.
- since 1990 each new batch of dispersant purchased by the Navy is checked for efficiency and physical parameters.

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Acting on behalf on the French Navy, *Cedre* has defined the methodology for these controls (sampling procedures and analyses).

These periodic controls involve a verification of the physical characteristics and the measurement of the of the dispersant's efficiency; in some cases, an additional control on the toxicity of the product may be undertaken.

In addition, some efficiency controls were performed on private dispersant stockpiles owned by oil companies.

This presentation intended to summarize the results obtained from these controls.

2.0 Principles Of The Controls Of The Dispersants Stockpiles

2.1 Control Of The Physical Characteristics

This control involves density, viscosity, flash point and pour point measurements. These measurements, easy to perform, are used as a pre-screening to detect any change in a batch and also to check its homogeneity; they are performed on several samples taken from each batch : when the product is kept in drums, several drums are selected at random; when it is stored in tanks on land, 3 samples are taken respectively close to the bottom, in the middle and in the upper part to detect any decanting; unfortunately, for dispersant stored in tanks on ship, it is often not possible to take more than one sample per tank (due to the geometry of the tank itself).

The sampling was performed by the operational staff in each harbour while the measurements of these physical parameters were carried out by the local laboratories of the Navy.

2.2 Control Of The Efficiency

The efficiency is measured at *Cedre* following the standard method NF90-345 (IFP dilution test) which is also used for dispersants approval:

> this test occurs in a 5 liters tank equipped with a wave generator (supplying a moderate agitation), and a circulation of water to continuously renew the tank content, (supply of sea water and overflow).
>
> Oil (around 4 g. of reference oil #1000 cSt at 20°C) is treated by the dispersant (dispersant/oil ratio: 5%) in the tank. Then, the system is let running for one hour.
>
> The effectiveness is represented by the amount of dispersed oil which has been eliminated from the tank through the outflow during the test; effectiveness ranges between 0 and 100% corresponding to the maximum theoretical quantity which would be eliminated if it was substance purely dissolved. The reasonable accuracy of the method is $\pm$ 3.
>
> Usually tests are carried out at least twice to obtain an average value.

2.3 Additional Control Of The Toxicity

The procedure for the periodic control considers the possibility of performing a toxicity control using the French standard method NFT90-348 (acute toxicity on marine shrimps) in case of a significant batch of dispersant proved to have changed; this additional information is to help in deciding to discard or not the altered dispersant.

So far, physical parameters and efficiency have proved to be sufficient to manage the stockpiles.

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3.0 Analyses Of The Data Obtained From Quality Controls

3.1 Available Data From Quality Controls

Since 1988, *Cedre* performed 5 series of quality controls on different parts of the French stockpile, covering 168 samples examined for their physical characteristics, and 88 for their efficiency.

These controls extended over 11 different trademarks of dispersants :

- two conventional ones: BP 1100X and Gamlen LT126 (aged up to 20 years old),
- old concentrated dispersants non approved according to the current approval procedure (dispersants acquired before 1986), Shell DC, BP 1100 WD, Finasol OSR7 (aged between 7 and 15 years old), and Finasol OSR5, Dispolene 32S (aged between 3 and 15 old),
- approved concentrated dispersants (according to the current procedure, 1986): Dispolene 36S, Inipol IP 80, Finasol OSR52 and Gamlen OD4000 (aged between 0 to 6).

These data have been examined in order to get a better understanding of dispersants ageing process. This study was conducted mainly on the concentrate dispersants, considering the following factors :

- the dispersant trademark, to check whether some product are more likely than others to become tainted,
- the age of the dispersant (at the date of the control) to see whether, generally speaking, dispersant are affected by age,
- the storage type, to see whether dispersants are better preserved in drums, in tanks on land or in tanks on ships,
- the storage site, to see whether the climate could influence the preservation of dispersants (differences of climate between the South and North of France), or if all staffs in charge of stockpiles work the same way

The characteristics taken into considerations were efficiency, density, color, phase separation in the product, deposition at the bottom of the storage capacities, viscosity, pour point and flash point.

The characteristics of the samples were compared with the reference characteristics obtained either from the suppliers or the results obtained during the approval process: while these reference values were well defined for the recently approved products, some characteristics of the older products, as efficiency and color, were not always known with accuracy.

In addition, the dispersants' manufacturers were required to explain, when possible, the changes observed on their products.

3.2 Observed Variations On The Characteristics:

3.2.1 Conventional Dispersants:

On conventional dispersants, clear phase separations has been observed generally, solvent on the upper layer, surfactant on the lower; this was confirmed by efficiency tests carried out on each phase: these tests gave very low values for the upper part and rather high efficiency values for the lower one. These products were early removed from the stockpiles.

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3.2.2 Concentrate Dispersants:

On the concentrate dispersants, except for few batches, the preservation was much better than for conventional ones.

3.2.2.1 Efficiency (Table 1):

The variability of the efficiency was higher for the old concentrate dispersants (non approved dispersant in the current approval procedure); for these dispersants, significant variations of efficiency (>±3) were often observed.

For the more recent concentrates (approved), the variations of efficiency were not really significant (≈±3). However the majority these batches were only between 0 and 6 years; for longer period of time, we had very few samples; few controls on a 15 -19 years old batch of an efficient dispersant (Finasol OSR5) suggested the efficiency to remain acceptable over such a period of time.

Table 1. Periodic Quality Control Of The French Dispersant Stockpiles: Results Of The Efficiency Testing

Dispersant	Average Efficiency	Standard Deviation	Number Of Batches Controlled
Finasol OSR 7	23	20.6	7
BP 1100 W D	25	17.2	9
Shell D C	28	12.6	10
Dispolene 32 S	58	6.1	8
Finasol OSR5	59	1.8	8
Finasol OSR 52	70	2.9	4
Dispolene 36 S	70	4.6	6
Inipol I P 80	71	1.7	9
Gamlen OD 4000	73	2.5	6

3.2.2.2 Density (Figure 1):

Generally, there were little variations in the density, usually between 0.01 to 0.03, except on some batches for which the difference was up to 0.06. It is interesting to observe that the variations of density are always positive (except for one batch): when altered, the density is always higher than the reference one; this could be possibly explained by a little evaporation of the solvent or of water included in the formulations.

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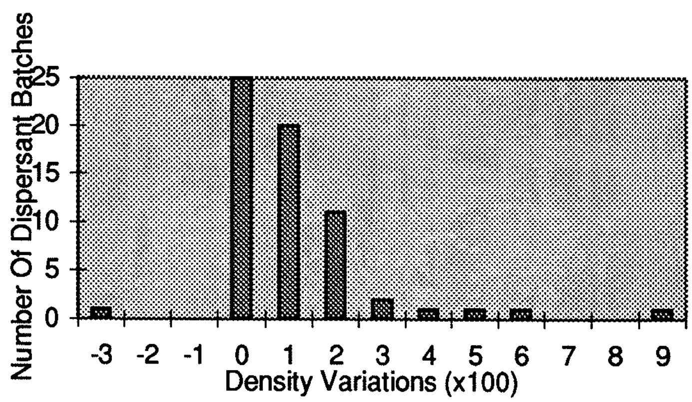

Figure 1 : Distribution Of The Variations Of Density On The Controlled Batches

3-2-2-3 Viscosity:

The variations of viscosity were obviously dependant on the dispersant; on the recent dispersants (for which we know the reference viscosity), the variations were rather homogeneous for each product (see table 2)

Table 2. Variation Of Viscosity On Some Recent Dispersants

Dispersant	Observed Variation Of Viscosity (At 20°C)
Finasol OSR 52	moderate decrease (≈ -30 cSt)
Inipol IP 80	small decrease (≈-3 cSt)
Gamlen OD 4000	no real change
Dispolene 36 S	moderate increase (≈ 40 cSt)

3.2.2.4 Pour and flash points:

These data proved to be very variable from one batch to another; even the controls performed on brand new dispersants purchased by the Navy showed large variations of pour and flash points; however the flash point always kept over savety limits, and the variations of these characteristics were in the range of the manufactoring specifications. In fact, there was no real reference value for each dispersant and it would be necessary to record the data for each batch of product.

Therefore, these characteristics were not very useful to demonstrate any evolution of the stockpiles.

3.2.2.5 Color:

The variations of color appeared to be very dependant on the dispersant:

- some dispersants, as Finasol OSR52 got darker with time,
- some, as Gamlen OD 4000, do not really change,
- Inipol IP80 proved to change differently from one batch to another (sometimes darker, sometimes clearer); these changes, which often occurred with the apparition of phase separation, seemed to be due to the storage itself (it could be transfer from a tank to another which was

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not cleaned enough, corrosion of the wall of the tank...); these change of color where not observed for the batches which were kept in drums.

3.2.2.6 Phase Separation:

As already mentioned, large phase separation were observed in the conventional dispersants.

Concerning the concentrate, some phase separations occurred on the surface layer for few batches of some products, as BP 1100WD or Inipol IP80; however the surface phase represented only a small volume of the dispersant (<5%). Again, as this phenomena occurred only in few batches, it could be mainly due to the storage conditions.

3.2.2.7 Deposition:

Different types of deposition have been found in most dispersant batches; these depositions were either white crystals for Finasol OSR52 (explained by the manufacturer Fina by the presence of corrosion inhibitor), either brown deposition which could be attributed to storage and handling conditions (mixing with other products, residual dirt in the tanks, inner coating of the tank more or less melt by the dispersant...).

3.2.2.8 Global Examination Of Data

The whole data related to the concentrated dispersants was examined, using a non parametric test (Kruskal Wallis), to see the general effect of each factors, dispersant trademark, age of the sample, type of storage and storage location, on the variables, variations of efficiency, of density, of color, phases separation and deposition; (Kruskall Wallis test: Bruno Scherrer- Biostatisque, Gaetan Morin edition.1984, p.534; the use of a non parametric test is rather easy as it requires no special conditions for the data).

The results are reported in the table #3, below:

- the dispersant has at least a highly significant influence on all variables except efficiency; this confirmed the observations mentioned.
- the age has also a just significant influence on the efficiency and on the density (however, the differences are relatively small)
- there is no significant effect of the storage type and the location

Even if it did not appear as significant in the statistical tests, the examination of the data suggests that drum storage is safer than tank storage; however this feeling could result from the sampling strategy used for these quality controls, which was different for the tanks (3 samples, surface, middle and bottom) and for the drums (one sample per drum).

The possible dependence between the different variables was examined: only the variations of efficiency and density showed some little correlation (r^2 = 11%); (r^2 calculated between the other variables were never more than few %).

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Table 3. Concentrate Dispersants; Effects Of Factors On The Variables Using Kruskal Wallis, Ns: Non Significant, *: Significant, **: Highly Significant, ***: Very Highly Significant.

	Efficiency	Density	Color	Phase Separation	Deposition
Dispersant Trademark	ns	**	****	*	**
Age Of The Sample	*	*	ns	ns	ns
Type Of Storage	ns	ns	ns	ns	ns
Storage Site	ns	ns	ns	ns	ns

4.0 Management Of The Dispersant Stockpiles

In fact, the concentrate dispersants, particularly the recent ones, were quite stable and well preserved with time: generally speaking, as regards efficiency, the observed differences between the batches of the same dispersant were low in comparison with the differences of efficiency between the dispersants themselves.

When, on few batches, the dispersant proved to be clearly spoilt, (decrease of efficiency, important phase separation or large deposition on the bottom, color or corrupted appearance), this could be mainly attributed to storage problems.

These problems can be listed as follows:

- problems due to the corrosion of the tanks or of the drums; it has been necessary to transfer several batches of dispersant into new tanks or drums; (however, it is not clear whether the corrosion of tanks, and particularly of drums, comes from the outside or the inside).
  In addition, especially on ships, it happened that batches of dispersant corrupted the inner coating of their tank (e.g. paint) and were therefore polluted.

  Concerning the plastic drums they proved to be subjected to alteration, as large deformations were observed (depression); however, these deformations did not affect the dispersant itself
- problems resulting from storage operations on tanks: transfer operations of dispersant from a tank to another were required for maintenance (e.g. repainting the tanks) or for the management of the stockpile (gathering different tank contents); during these operations dispersant batches may have got mixed with some other products.
  Moreover, some tanks could be insufficiently cleaned before receiving the dispersant.

  Some tanks onboard ships were also subjected to mishandling operations on the valves, and their dispersant polluted by external products, (water, oily wastes or various residues).

Taking into account the results of the quality controls, it was decided to renew progressively the stockpiles of dispersant with more recent products and to remove the batches of dispersant according to their efficiency : first the conventional, then the dispersants which efficiency was below 20 (mainly Finasol OSR7), then those which did not reach 40 (mainly Shell DC and BP 1100 WD).

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Now the stockpile is composed of dispersants which efficiency is over 50 % (in comparison to the approval limit of 60 %); except for few batches of Finasol OSR5 and Dispolene 32S, these are recent products, approved according to the current procedure, Finasol OSR52, Gamlen OD 4000, Dispolene 36S, Inipol IP 80.

5.0 Conclusions And Recommendations

From the quality controls carried out on the dispersant stockpiles in France (approval, control when purchased and periodic control every 5 years), an important set of data was gathered on the efficiency and on the physical parameters of these products.

The examination of these data shows that:

- conventional dispersants are subjected to phase separation,
- some ageing can be observed on old concentrate dispersants
- recent dispersants formulations seem to be quite stable and to keep their efficiency with time, at least in the range of 0 to 6 years; few observations suggested they can keep a acceptable efficiency over longer period of time as 15 years, but this will have to be clearly confirm on more sample during the future controls.
- the variations of efficiency observed on the different batches of each concentrate dispersant (variations which could be attributed to products' ageing), are generally small in comparison with the discrepancies between the dispersants themselves; therefore, for the recent products, when some change is observed on a batch, problems of storage can be suspected,
- among the physical parameters measured during these controls, density is the more interesting, as this measurement, easily performed, can give some interesting information on the state of conservation of the dispersants; changes of efficiency are often associated with changes of density. On the contrary, the pour and flash points are not very useful for documenting the ageing as they are quite varying. The other characteristics, viscosity, color, phase separation and deposition seem clearly dependant on each dispersant,
- the sampling strategy followed for the tanks, (3 samples taken, surface, middle and bottom), is useful and often shows the possible problems of storage, (dispersant contaminated by another product...); it should be extended to all storage sites when possible (even dispersants stored in drums).
- to reduce the risk of phase separation, periodic recirculation of the content of the tanks (or rolling the drums on ground) could be considered.

These quality controls allowed a rational management of the stockpiles: all the old and poorly efficient dispersants have been removed, and now the stockpile is composed of products which efficiency is over 50% according to the efficiency dilution test.method (NF T90 345).

Some problems of storage have been observed on few batches, resulting from the corrosion of the tanks or of the drums, or from handling mistakes, (pollution of the batch by a third product or tanks insufficiently cleaned). The maintenance practices could be improved.

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Finally, some improvements could also be made in the sampling procedure, to generalise to all the batches the sampling strategy proposed for tanks (3 samples surface middle and bottom), and to well apply the same methodology for sampling (protocol, sampler, sampling bottles..): so far, the sampling is carried out by the local staff in charge of each storage who has never been specially trained for this task. The recourse to the laboratory staff who is already in charge of the measurements could improve this point.

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