

The Prestige oil – properties and weathering at sea

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ABSTRACT

The tanker *Prestige* sank off of Spain in November 2002. The oil recovery operation took several months and samples were regularly taken of the weathered oil by the recovery vessels. The long term weathering of the oil from *Prestige* incident has been documented at SINTEF's laboratories. The study included characterisation of the Prestige oil and of samples taken at sea over a period of 3 months. Chemical characterisation and physical measurements including rheological studies have been performed on the weathered samples to acquire more information on long term weathering of oils. The results showed that the evaporation of the oil was < 5% (weight). The Prestige oil emulsified up to 60 % volume water content, and the weathering processes resulted in a large increase in viscosity from 50 000 to 300 000 cP. The rheological measurements showed that the emulsions changed appearance and consistency over time at sea from viscous, but still flowing emulsion after few days to more rigid, rubber-like emulsions after months at sea.

BACKGROUND

The tanker *Prestige* was on its way from the refinery in Ventspils in Latvia carrying 77 000 tonnes of fuel oil. Outside the coast of Spain the *Prestige* suffered hull damage and started leaking oil on the 13 November 2002. The boat was towed out from the coast, broke in two and sank at a depth of 3500 meters on the 19 November 2002. The oil onboard the *Prestige* was a very heavy fuel oil (burner oil) with a viscosity of approx. 650 cSt at 50°C and density 0.995 kg/L, indicating that it is an equivalent bunker fuel oil grade would be IFO-650. (Since the oil was not for bunker purposes (i.e. to be used as fuel for a ship) it is better to say it was equivalent to an IFO-650 grade.)

The oil recovery operation took several months, and samples were collected continuously by the recovery vessels. It is important to take advantage of such incidents to obtain good data and knowledge on the long term weathering properties at sea for these heavy fuel oils. After an oil spill recovery operation it is also important to characterize the collected emulsions to gain experience and identify limitations of the oil spill contingency equipment used. Physical-chemical documentation of what is actually collected is essential to be able to plan later actions with the same equipment.

SINTEF has analyzed samples of the *Prestige* oil weathered at sea over a period of 3 months. These samples were taken in connection with the recovery of oil by the Norwegian oil spill contingency vessels *Normand Draupne* and *Far Scout* from December 2002 to February 2003. SINTEF also received a sample from one of the French oil spill contingency vessels taken in November shortly after the shipwreck. A sample of the cargo oil was supplied by CEDRE.

Chemical characterization and rheological measurements have been performed on the samples to acquire more information on long term weathering of oils. The rheological measurements both included simple viscosity measurements and and more complex

rheological parameters. SINTEFs Oil Weathering Model (OWM) was used to predict the weathering behaviour of the Prestige oil at sea.

EXPERIMENTAL METHODS

Instruments used to obtain data on the oil and the emulsions are given in Table 1.

Table 1 Instruments/methods used.

Property	Instrument / Method
Water content	Karl Fisher
Rheological properties	Physica MCR 300
	- viscosity measured 30 seconds on each different shear rate - elasticity measured in the linear viscoelastic area at $f = 10$ rad/s
Chemical analysis	GC-FID

RESULTS

Samples analyzed

The samples analyzed in this project are shown in Table 2.

Table 2 Samples analyzed

Date	Sampled by	Place
The oil	CEDRE	The tanks of <i>Prestige</i>
18.11.02	CEDRE	Off Spain
02.12.02	Norwegian Clean Seas Association for Operating Companies (NOFO)	Off Spain
06.01.03	Norwegian Coastal Administration (Kystverket)	Biscaya
15.01.03	Norwegian Coastal Administration (Kystverket)	Biscaya
11.02.03	Norwegian Clean Seas Association for Operating Companies (NOFO)	Biscaya

The date is that of sampling. The exact weathering time of each sample is not precisely known because the exact time of oil release of each sample of oil is not known. The time estimates in the rest of the report have to be regarded as rough estimates, but we suppose that the oil collected by the Norwegian vessels originates from the main oil spill prior to the sinking of the *Prestige* (Is this correct?). It is reasonable to expect that the samples taken in the Biscaya have drifted from the main release in November to the Biscaya by wind and currents, with a weathering time of approximately 2 and 3 months respectively.

Physical-chemical properties of the parent oil

Information from ITOPF, IFP and CEDRE shows that the oil originates from a refinery in Ventspils in Latvia where the refining process is based on atmospheric distillation.

Some selected physical parameters of the Prestige oil are shown in Table 3.

Table 3 Physical data of the parent Prestige oil.

	The Prestige oil
Density (kg/L)*	0,995
Pour point (°C)**	3
Viscosity at 50°C (cSt)**	655

* Measured by IFP in France.

**Reported by the refinery.

Figure 1 shows the viscosity as a function of temperature for the oils onboard the *Prestige* and, for comparison, the oil from the *Erika*, Heavy Gas Oil, IFO30, IFO180 and IFO 380 from the Mongstad refinery. According to the IFO-system for classification of bunker oils as fuel in ships, the viscosity is measured at 50°C, and the IFO grade of the oil is the viscosity in cSt (cP divided by density) at this temperature. The oil from “*Prestige*” has a viscosity of approx. 650 cSt and can therefore be characterized as equivalent to an IFO 650 grade bunker fuel oil. The viscosity of the *Prestige* oil increases 10 times with a drop in temperature from 50°C to 25°C, and increases by a factor of 4-5 times when the temperature decreases from 15°C to 5°C which are typical Norwegian summer and winter sea temperatures.

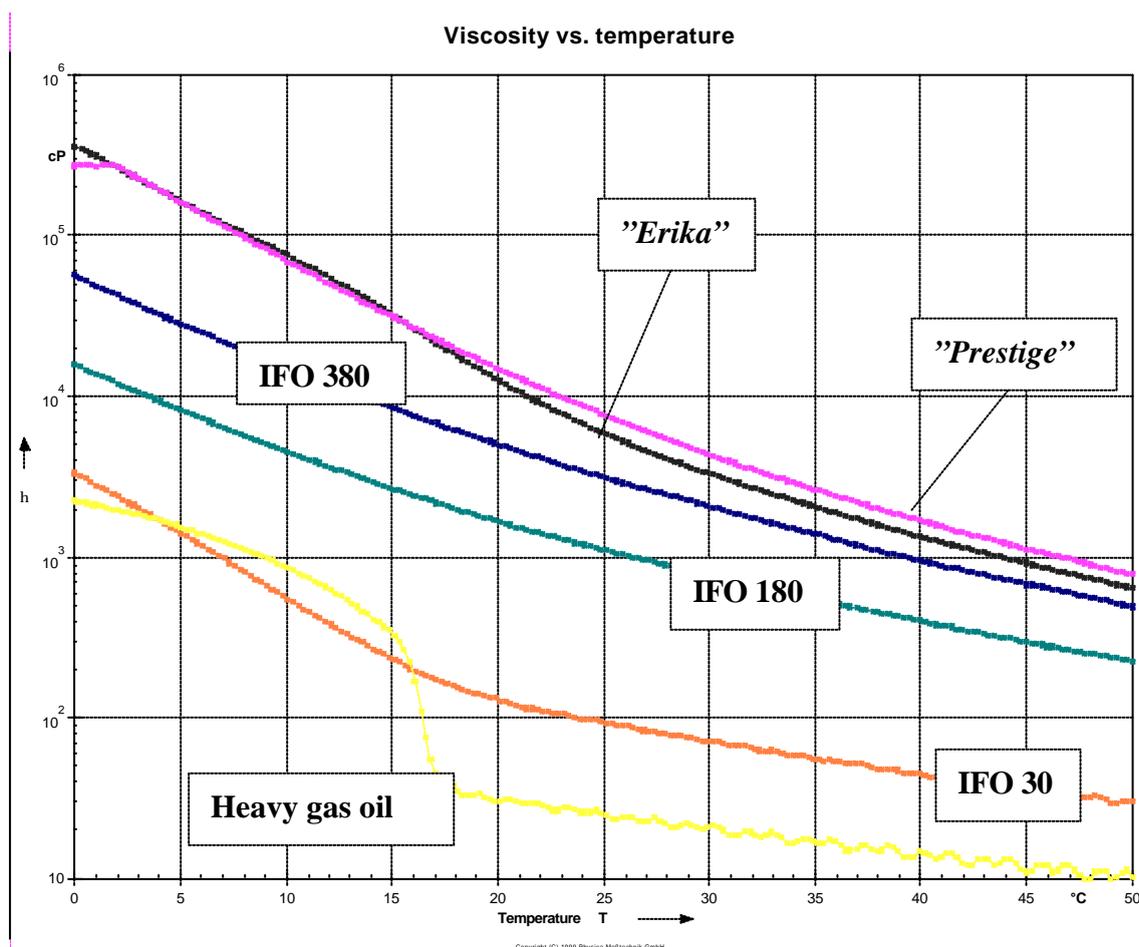


Figure 1 Viscosity at shear rate 10 s⁻¹ as a function of temperature for the oils onboard the “*Prestige*” and the “*Erika*”, and also IFO30 and IFO180 from Mongstad refinery.

Figure 2 shows that the viscosity of the parent Prestige oil is dependent on the shear rate, i.e. the Prestige oil is a non-Newtonian fluid both at 5 and 15°C. Light, water-free crude oils can be Newtonian, but waxy crude oils and heavier bunker oils generally show non-Newtonian behaviour at typical sea temperatures. The shear dependency of the Prestige oil is some larger at 5°C than at 15°C. Due to the Pour Point of the Prestige oil at 3°C, the oil may be partly solidified at 5°C. The Pour Point is the temperature at which the oil just flows when assessed under the conditions of the standard test method (ASTM-method D97-66). The temperature at which the oil does not flow is therefore 3°C (5 °F) below this value, since an assessment is only made at every 3°C. Wax precipitation starts to occur above the Pour Point.

The oil has more “structure” at low temperatures. Due to a probable yield stress, the measured viscosity will be more dependant on the shear rate used and the measured viscosity values will be proportionately higher at lower temperatures. This is of importance in considering the flow properties of the oil inside the sunken vessel at a depth of 3500 meters and at a temperature of approximately 3°C.

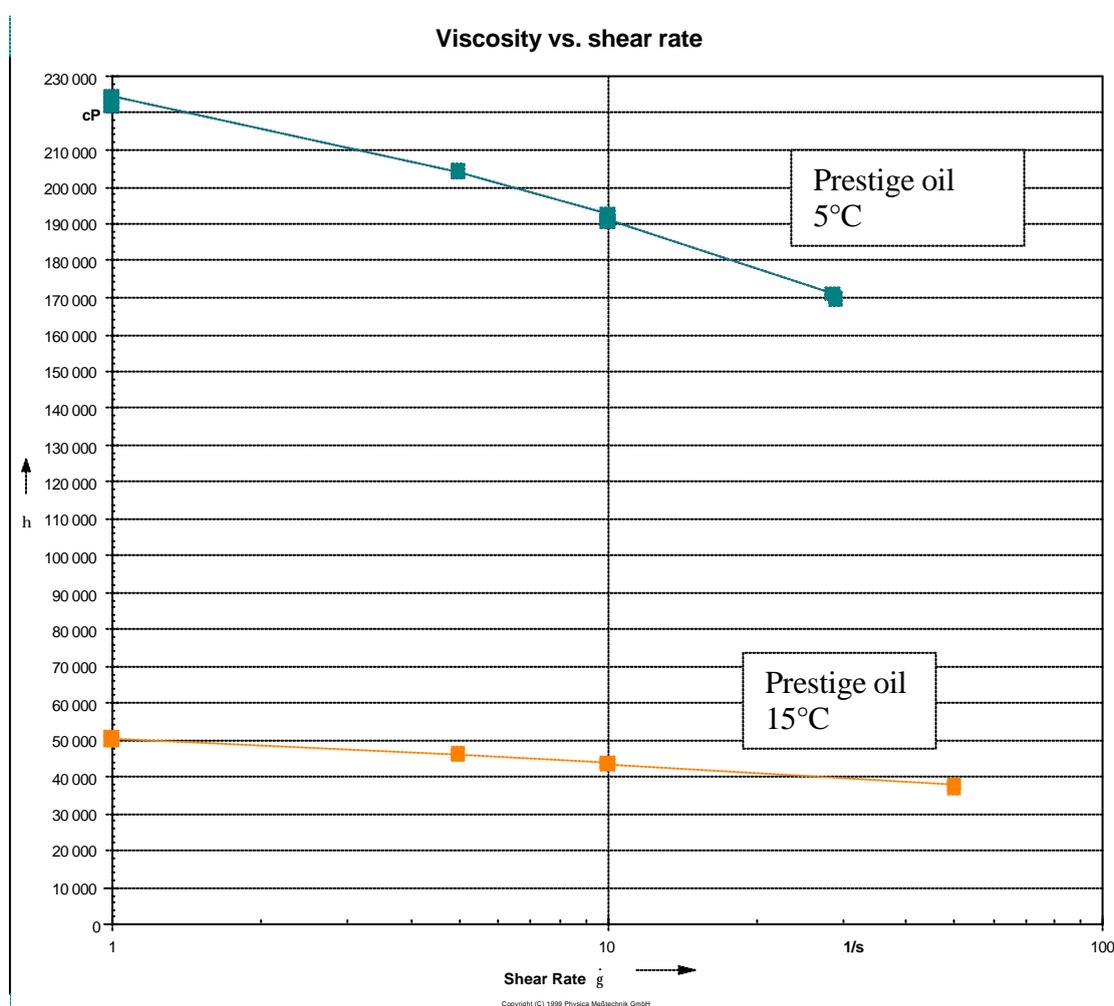


Figure 2 Viscosity of the parent Prestige oil at 5 and 15°C.

Evaporation of the oil at sea

GC-analyses of the parent Prestige oil and emulsions taken after approximately 3 months at sea are shown in Figure 3. The analysis results from all the emulsions are shown in Appendix A. The lightest components in the oil evaporate when the oil is at sea. The GC-analyses gives an overview of the weathering, and particularly the degree of evaporation of the emulsions compared to the oil. The marked areas in Figure 3 A and B shows that the content of light components is slightly lower in the emulsion (B) compared to the parent oil (A). The evaporation of heavy fuel oils as the Prestige oil is generally low because of the generally low content of volatile components. Due to the extreme high “film” thickness (up to 50 cm reported), the evaporation of the Prestige oil at sea was low. The degree of evaporation was quantified to be <5% after 3 months weathering at sea.

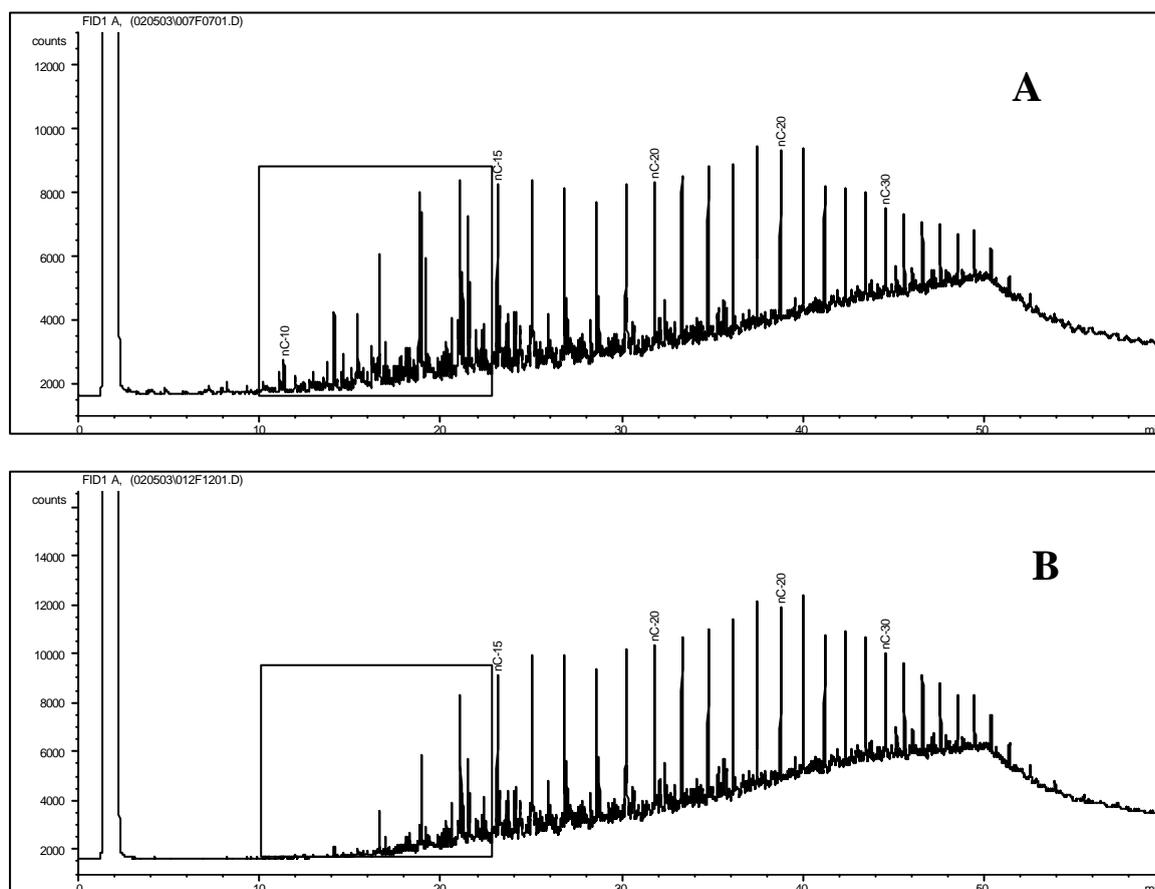


Figure 3 GC-analyses of the parent Prestige oil (A) and emulsion taken 11 February 2003 (B).

Change in the physical properties of the emulsion over time at sea

Results from the physical measurements on the Prestige oil and emulsions are shown in *Table 4*.

Table 4 Physical properties of the Prestige emulsions.

Sample date	Time at sea (Days)	Density (kg/L) calculated	Water content (%)	Viscosity (cP v/10s ⁻¹)		Elasticity (Pa)
				5°C	15°C	15°C
The Prestige oil	0	0,995	0	191000	43400	25
18.11.02	5	1,009	45	208000	83500	846
02.12.02	19	1,012	55	491000	105000	2570
06.01.03	54		-	500000	206000	7110
15.01.03	61	1,013	60	510000	205000	7550
11.02.03	88	1,013	60	906000	297000	7170

- Not measured due to lot of free water in the sampling bottle.

The density of the oil is 0.995 kg/L. The density of the emulsions was calculated due to problems by measuring density of so highly viscous samples. The calculations were verified by buoyancy testing in sea water and fresh water. The emulsions float in salt water (density lower than 1,025) and sink/float very low in fresh water (density higher/in the area around 1).

The Prestige oil emulsified to a 60% water content. The emulsification/mixing of water and evaporation make the viscosity increase significantly, as shown in Figure 4.

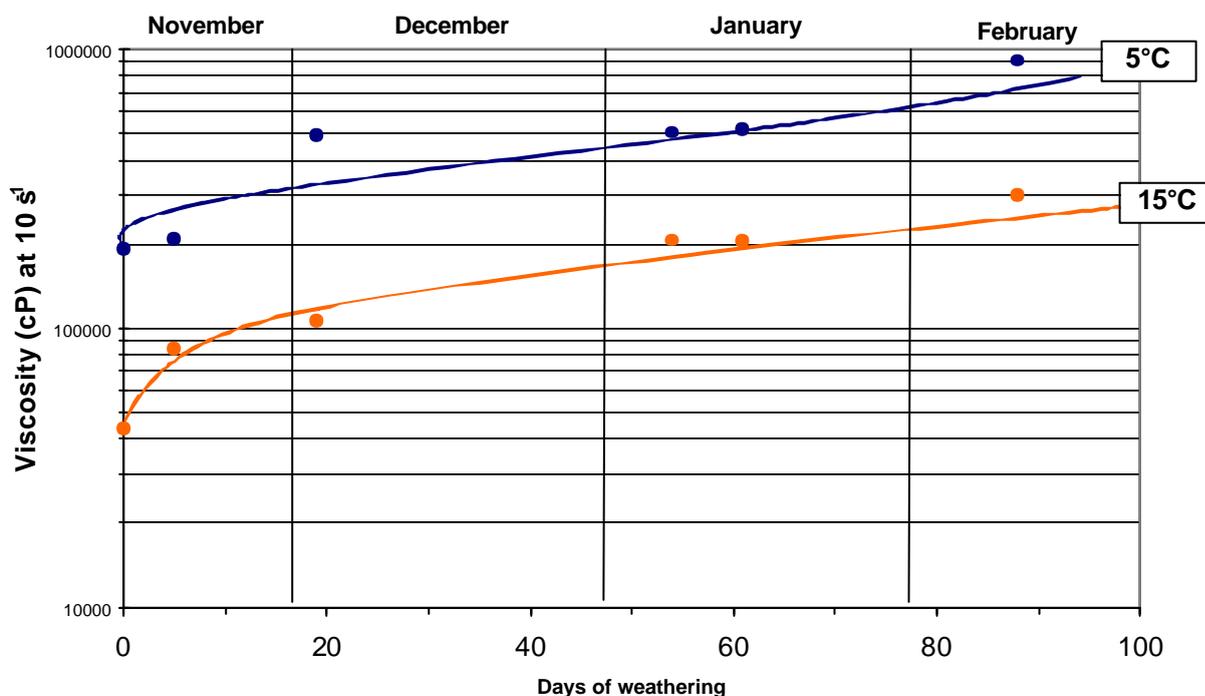


Figure 4 Development of viscosity at sea.

The viscosities were measured at both 5°C and 15°C and at a shear rate of 10s⁻¹. The sea temperature in the actual time period of the incident was reported to be around 15°C. After one month at sea the viscosity at 15°C was approximately 100 000 cP at 10 s⁻¹, after two months approximately 200 000 cP at 10 s⁻¹ and after three months approximately 300 000 cP at 10 s⁻¹. These are very high viscosities, and explain very well the difficulties when handling the emulsified oil during the mechanical recovery operation. The measurements are also performed at 5°C which would be a typical Norwegian winter sea temperature. It is difficult to know if this heavy oil would emulsify as much as 60% water at 5°C, however, these values give an indication of what the oil viscosities would have been if the *Prestige* had broken up 5 days earlier when passing through the Baltic and Skagerak area. Figure 1 show that the viscosity of the oil increases approximately 5 times as the temperature decreases from 15 to 5°C. It is therefore reasonable to expect that an oil with the same properties as the *Prestige* oil would be considerably worse to handle at “Norwegian winter conditions” compared to the same oil spilled off of Spain.

As discussed in Figure 1, the water-free oil show “shear dependency”. Figure 5 shows that the “shear dependency” was higher for the *Prestige* emulsions than for the *Prestige* oil. The viscosities of emulsified crude oils and bunker oils are typically shear dependent, and it is therefore important that the shear rate is reported together with the viscosity both for the oils and the emulsions. The viscosity development of the two emulsions also showed that the shear dependency was different and that each emulsion has to be measured at different shear rates to know what viscosities are applicable for different shear rates.

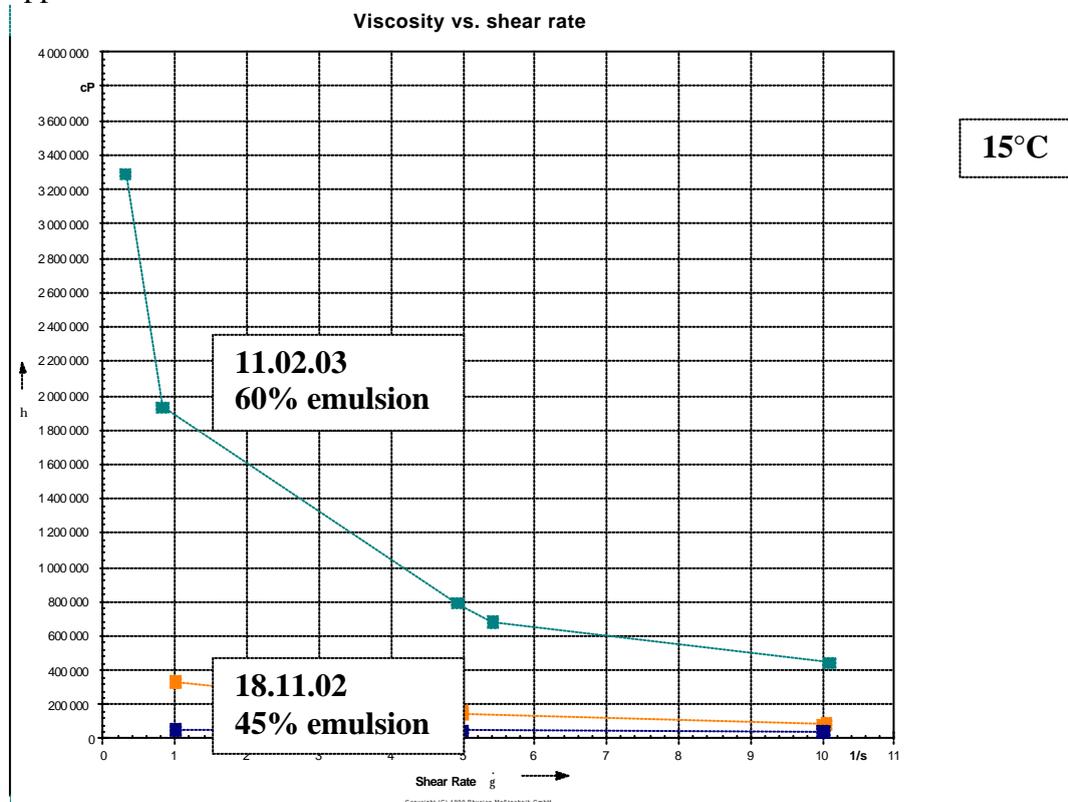


Figure 5 Oil viscosity as a function of shear rate at 15°C for the *Prestige* oil and emulsions of the *Prestige* oil.

Other rheological measurements have also been performed on the emulsions. Oscillatory stress-sweeps have been performed on the samples, and elasticity (G') and phase angle have been calculated. As opposed to viscosity measurements, measurements of the elasticity yields information about the internal strength of a *non flowing substance*. In some cases this "internal strength" would be high enough to prevent the substance from flowing. Whether a substance is predominantly viscous or predominately elastic is defined by the phase angle. Elastic substances have phase angle between 0° and 45° , viscous substances between 45° and 90° . The phase angles of the *Prestige* samples are plotted as a function of weathering time in Figure 6. A change from predominately viscous properties (flowing) to predominately elastic properties (non-flowing) was observed after approximately 1 month of weathering for the *Prestige* oil.

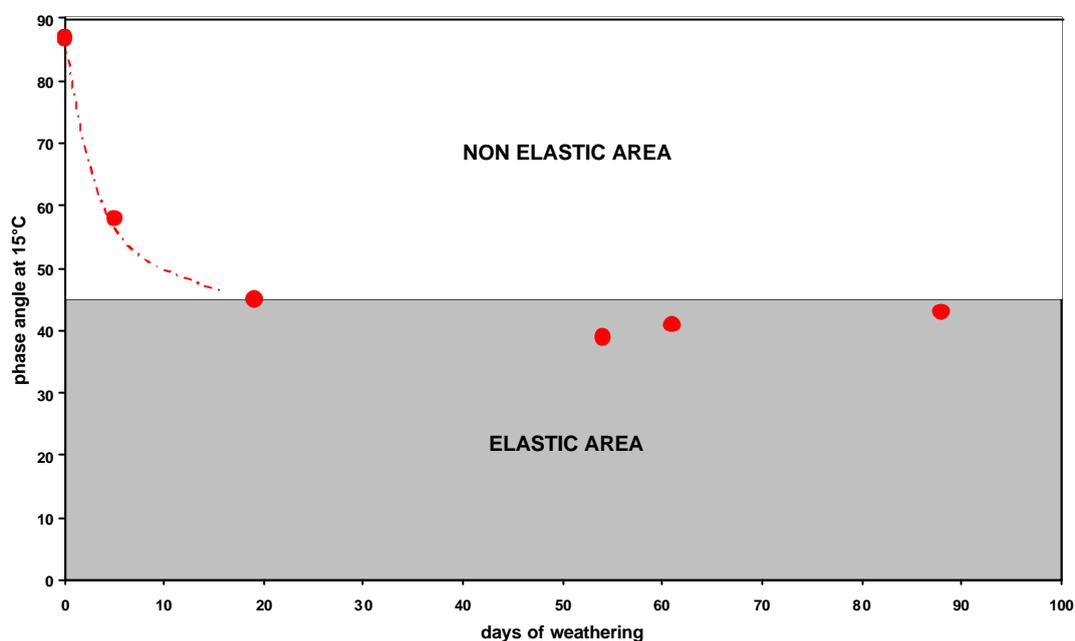


Figure 6 Phase angel as a function of weathering time of the Prestige oil at 15°
The modulus of elasticity and viscosity are plotted as a function of weathering time in Figure 7.

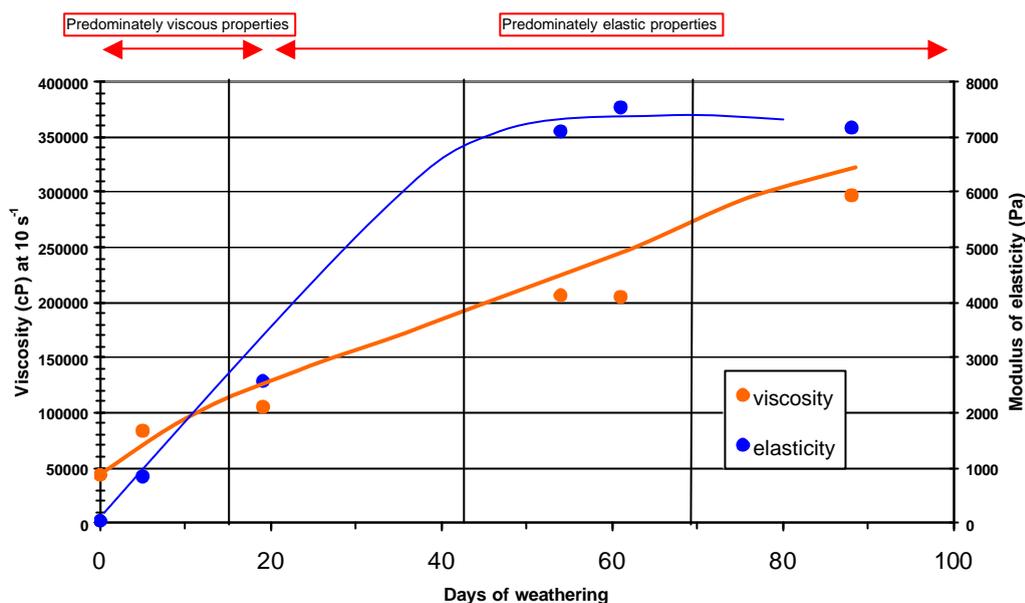


Figure 7 Modulus of elasticity versus viscosity plotted as a function of weathering time for the Prestige oil at 15°C.

An increase in both viscosity and elasticity is observed for the emulsions with the increased weathering time. This results in a change of the appearance of the emulsion from the highly viscous, but still flowing “few days emulsion” to the rigid, rubber-like “three month emulsion”. This means that the emulsion exhibited a stiff and solid structure, in addition to high viscosity, as shown in Figure 8. Taking into account both the increase in viscosity and elasticity, the emulsions would be easier to handle after few days and weeks weathering compared to two and three months.



Figure 8 Emulsion taken at 15 January 2003.

The change in consistency and appearance of the emulsions over time are probably due to changes in water droplet size and the water droplet size distribution, together with an increased precipitation with time of asphaltenes and wax as the “skin” around the water droplets. Precipitation of wax and asphaltenes in the oil might also change the stabilising shell or “skin” around the water droplets, and may explain the changed elasticity. Also weathering processes like oxidation and biodegradation can further changed the properties of this “skin” resulting in an increased emulsion stability. This has not been studied, but will be important to focus on later in connection to studies of long time weathering of oils. Microscope examination has been used to get an impression of the water droplets in the emulsions. Since the oil is so dark it was difficult to get good pictures of the water droplets, and it was also difficult to get the emulsion distributed in a sufficiently thin layer. Figure 9 shows pictures taken of *Prestige* emulsions. A change was observed in the droplet sizes over time. The average size of the water droplets became smaller over time; a higher proportion of larger water droplets were observed in the earlier, less weathered, emulsions. Large droplets were not observed in the later emulsions (water drops were present in all emulsions, but these were assumed to have entered during the sampling).

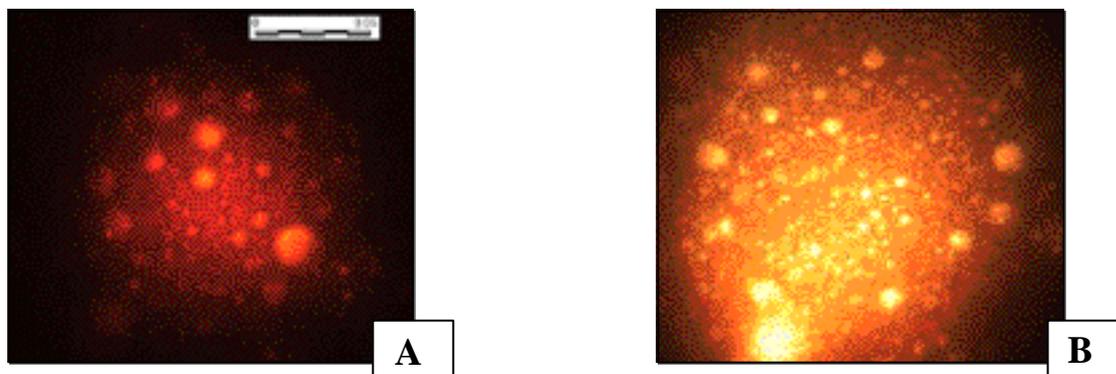


Figure 9 Microscope images of *Prestige* emulsions. Samples taken 18th November 2002 (A) and 15th January 2003 (B).

Prediction of the oil weathering properties at sea

The behaviour of spilled crude oils and refined oil products on the sea surface depends on the prevailing conditions (e.g. temperature, sea-state, current) and on the chemical composition of the oil. Large variations in oil properties cause them to behave differently when spilled at sea. The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the rate in change of an oils properties and behaviour on the sea surface (Aamo *et al.*, 1993, Daling *et al.*, 1997). The input data is based on the laboratory weathering studies of the oils (Daling *et al.*, 1990). The SINTEF OWM is schematically shown in Figure 10.

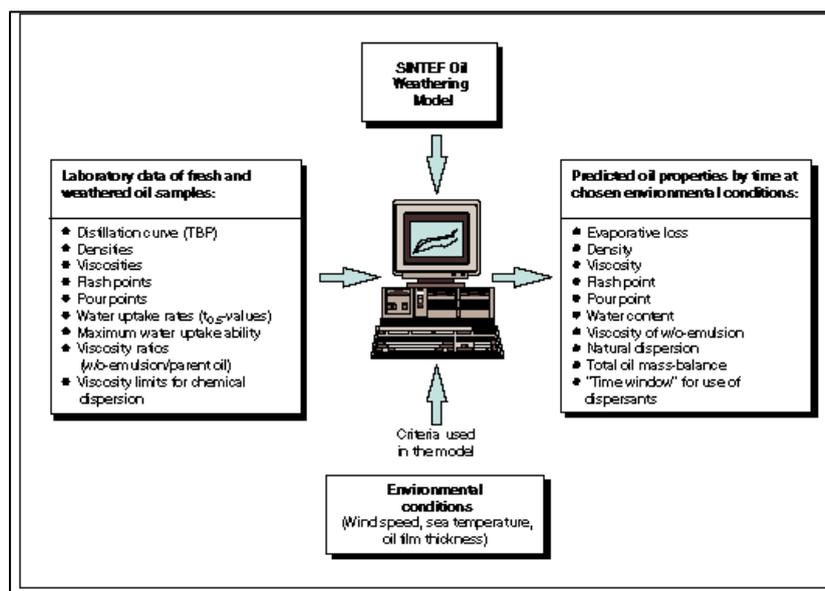


Figure 10 Schematic diagram of the input data to the SINTEF OWM and the predicted output oil properties.

The predictions obtained from the SINTEF OWM are a useful tool in Environmental Impact Assessment studies and for determining the most effective response. The validity of the predictions has in recent years been documented by correlation studies to field data from experimental oil spills (Daling *et al.*, 1999). The spill scenario (e. g. sub-sea or surface blowouts, tanker spills, pipeline leakage etc.) and release rate chosen when using the SINTEF OWM is of importance. The Oil Weathering Model has earlier been verified in a field trial with crude oils at weathering times up to 3,5 days (Daling *et al.*, 1989 and Daling *et al.*, 1999), and can calculate the development in weathering properties for up to 30 days. Predicted properties after 2 and 3 months as for the latest samples, are therefore not possible with the present version of the model.

A surface release at a rate of 1.33 metric tons per minute was chosen as the spill scenario for modelling the release of oil from the *Prestige*. An initial film thickness of 20 mm and terminal film thickness of 20 mm was used. The predictions were made at 15°C, and at a wind speed interval regarded as representative for the wind conditions in the area in question from 18 November to 18 December (Meteo Galica, 2003).

Predicted evaporation, water content, and emulsion viscosity for the *Prestige* oil are shown together with measured field data in Figure 11, Figure 12 and Figure 13, respectively.

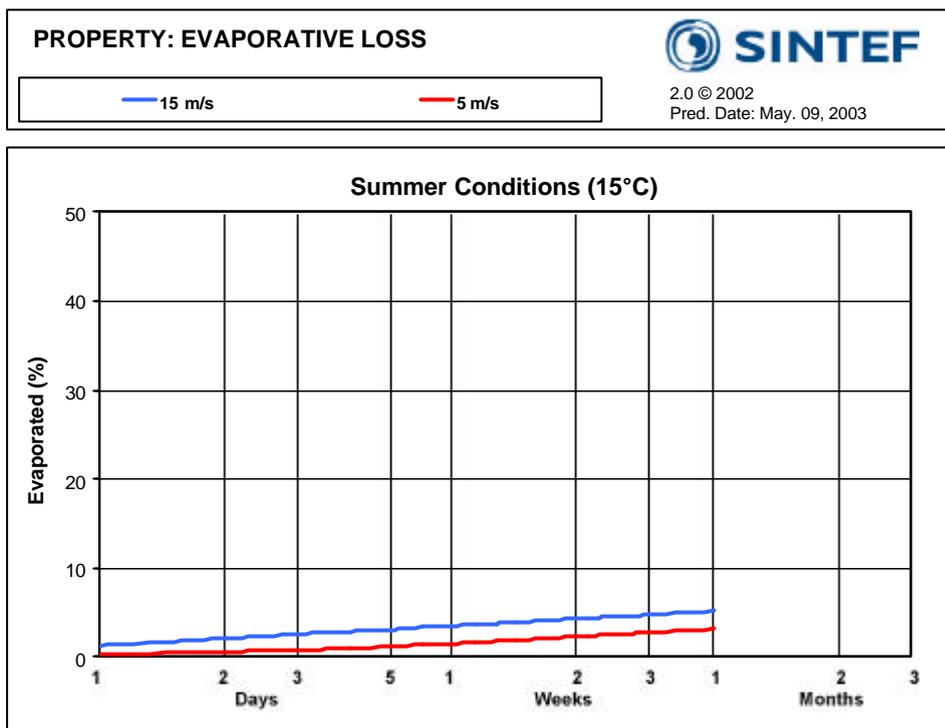


Figure 11 Predicted evaporation at sea at 15°C.

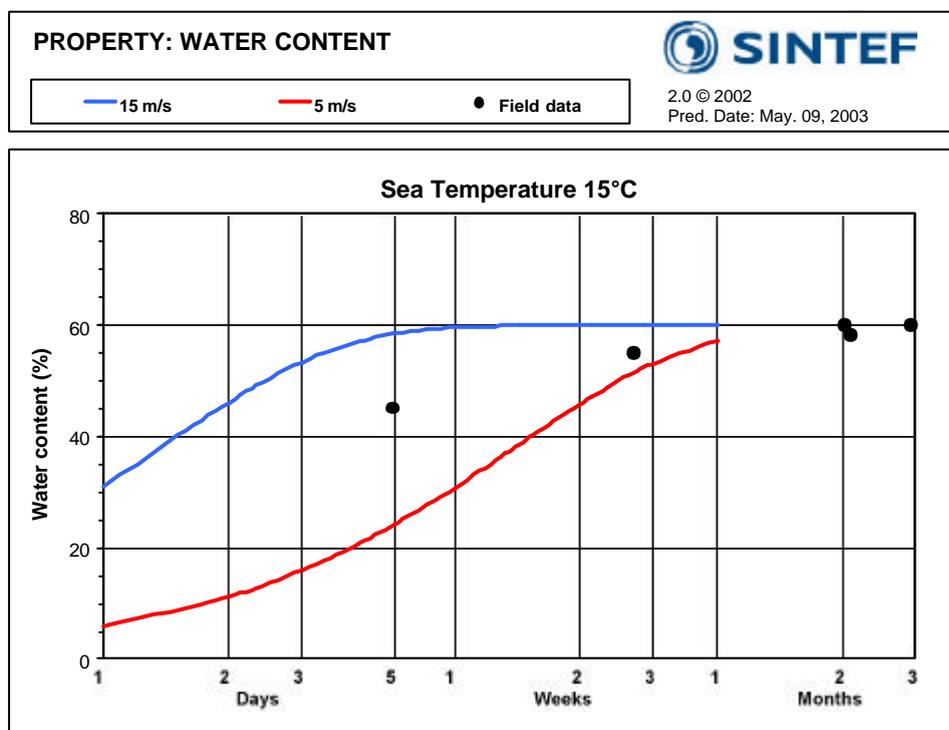


Figure 12 Predicted water uptake for the Prestige oil at 15°C sea temperature plotted with measured field data.

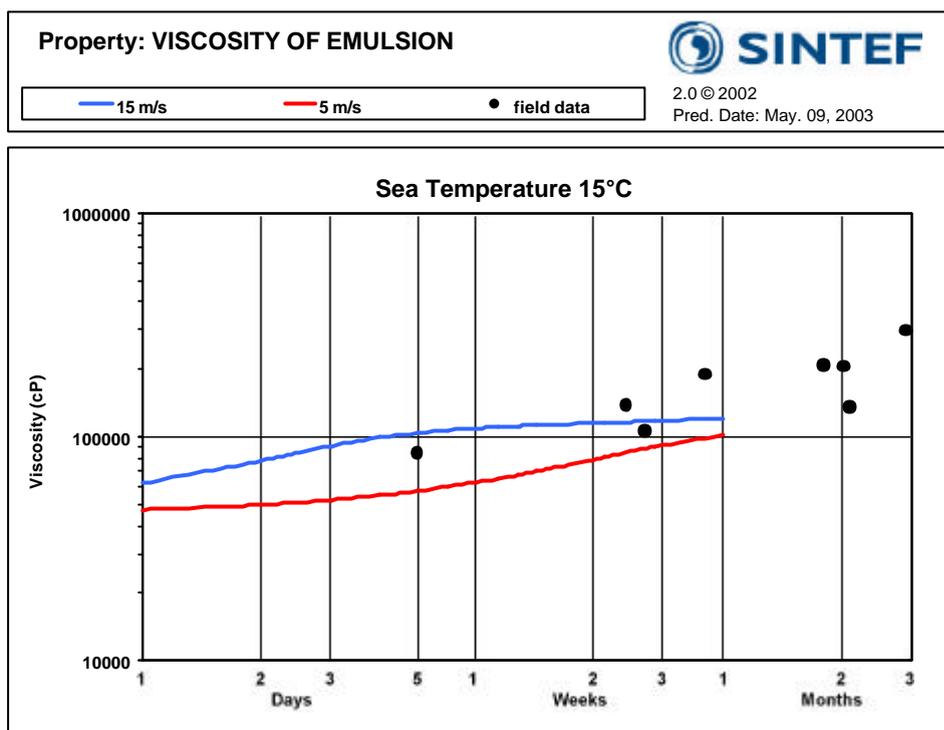


Figure 13 Predicted emulsion viscosity for the Prestige oil at 15°C sea temperature plotted with measured field data. The predictions are shown based on measurements done at shear rate 10 s^{-1} . This also applies to the plotted field data.

Predictions made based on the data of the parent *Prestige* oil show that calculated emulsion viscosity comply relatively well with measured field values for approximately 3 weeks. After this time, the field values are considerably higher than the predicted values. This may be due to the mechanisms involved at sea at long-term weathering, which is not accounted for in the weathering model. Such mechanisms may be oxidation, change in the emulsion droplet sizes, and biodegradation leading to increased rigidity of the skin formed between the water droplets and the oil phase. As discussed earlier, this may change other rheological properties than viscosity. More comprehensive studies of long term weathering of both crude oils and bunker oils should be carried out in the future to increase the knowledge about the changes in oil properties during long weathering, and thereafter further develop the existing models to enable predictions over longer time periods. Using this extended model, it will be easier to predict the changes over longer time and at the same time get information about how critical it may be if the oil stays on sea considering further handling.

CONCLUSIONS

Measurements have been carried out on a selection of emulsions taken in connection with the recovery response operation of the *Prestige*. The samples have been taken during a period of approximately three month's weathering at sea and show the following:

- ◇ The evaporative loss of the *Prestige* oil at sea was very low (<5%). This due to
 - very low content of volatile components in the parent oil
 - extremely high emulsion thickness at sea. The oil / emulsion layer was so thick that the evaporation was prevented.
- ◇ The *Prestige* oil emulsified to approximately 60% water content during the long period of weathering at sea.
- ◇ The *Prestige* oil reached very high viscosities when weathered at sea. After one month at sea the viscosity was approx. 100 000cP at 10 s⁻¹, after two months approx. 200 000 cP at 10 s⁻¹, and after three months approx. 300 000 cP at 10 s⁻¹.
- ◇ The emulsions changed appearance and consistency over time at sea. A change from highly viscous, but still flowing emulsions after few days to more rigid, rubber-like emulsions after months at sea was observed.
- ◇ Changes in consistency over time showed that the emulsions are more difficult to handle after months at sea, and that it is easier to work with the emulsions after few weeks at sea.
- ◇ Predictions of the emulsion viscosity with the SINTEF Oil Weathering Model showed agreement with the field values for the first three weeks. After this, field values of emulsion viscosity were considerably higher than the predicted values. This may be due to mechanisms involved in the long-term weathering that are not currently modelled.

ACKNOWLEDGEMENTS

This project was funded by the Norwegian Coastal Administration (Kystverket) and the Norwegian Clean Seas Associations for Operating Companies (NOFO). Francois Merlin (CEDRE) supplied a small, uniq sample of the cargo oil onboard *Prestige* and also a samples taken at sea few days after the accident.

REFERENCES

Aamo O.M., Reed M., Daling P.S. og Johansen O., 1993: A laboratory-based weathering model: PC version for coupling to transport models. *In Proceedings of the 16th AMOP seminar*, Environment Canada.

Xunta de Galica <http://www.cmmm-prestige.cesga.es/>

Daling P.S., Brandvik P.J. and Almås, I.K. 1989 : Weathering of surface oil-experimental oil spill at Haltenbanken 1989. IKU rapport no. 22.1934.00/03/89, 23 p.

Daling, P.S., Brandvik, P.J., Mackay, D., Johansen, Ø., 1990. Characterisation of crude oils for environmental purposes. *Oil and Chemical Pollution* 7, pp 199-224.

Daling, P.S., Aamo, O.M., Lewis, A., Strøm-Kristiansen. T., 1997. IKU Oil Weathering Modell-predicting oil's properties at sea. 1997 International Oil Spill Conference, Fort Lauderdale, Florida, 2-10 April, pp. 297-307.

Daling, P.S. and Strøm, T. 1999 : Weathering of oils at sea : Model/Field Data Comparisons. *Spill Science & Technology*, Vol. 5 No. 1, pp 63-74.

Cedre : <http://www.le-cedre.fr>

IFP : <http://www.ifp.fr>

ITOPF : Data from the refinery in Ventspills.