SINTEF REPORT

SINTEF Applied Chemistry

Address: N-7465 Trondheim, NORWAY
Location: Sem Sælands vei 2A
Telephone: +47 73 59 28 73
Fax: +47 73 59 69 95

Enterprise No.: NO 948 007 029 MVA

TITLE

Weathering properties of Endicott, Milne Point Unit, High Island Composite, the Alpine Composite, the Neptune Field Composite, and North Star oil samples

AUTHOR(S)

Frode Leirvik, Tina J. Schrader and Merete Øverli Moldestad

CLIENT(S)

U.S. Department of the Interior Minerals Management Service (MMS)

REPORT NO. STF66 A02114	CLASSIFICATION Unrestricted	CLIENTS REF. Richard Prentki	
CLASS. THIS PAGE Unrestricted	ISBN 82-14-02696-2	PROJECT NO. 661189.40	NO. OF PAGES/APPENDICES 131
ELECTRONIC FILE CODE MMS-report 151002.doc		PROJECT MANAGER (NAME, SIGN.) Merete Øverli Moldestad	CHECKED BY (NAME, SIGN.) Per S. Daling
FILE CODE	DATE 2002-11-07	APPROVED BY (NAME, POSITION, SIGN.) Tore Aunaas, Research Director	

ABSTRACT

Based on the findings from the Phase I review “Revision of MMS Offshore Continental Shelf Oil-Weathering Model: Evaluation,” OCS Study MMS 98-0031 for MMS, SINTEF Applied Chemistry has continued with Phase II and III; the “Revision of the OCS Oil-Weathering Model”. The main objectives of Phase II and III are:
to adapt the SINTEF Oil Weathering Model (OWM) to MMS needs,
to expand the OWM oil library to include oils of interest to MMS, and
to develop and collate data sets identified in Phase I from experimental oil spills for validation testing of algorithms and OWM’s.

During Phase II and III SINTEF have performed weathering studies of total six crude oils supplied by MMS. The results from these weathering studies have been added to the OWM library for use by MMS in Environmental Impact Assessment studies and presented in this final report.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
GROUP 2	Environmental	Miljø
SELECTED BY AUTHOR	Weathering	Forvitring

TABLE OF CONTENTS

1 Background

SINTEF Applied Chemistry completed the Phase I review “Revision of MMS Offshore Continental Shelf Oil-Weathering Model: Evaluation,” OCS Study MMS 98-0031 for MMS in 1998. This review recommended:

- upgrading to an existing state-of-the-art Oil Weathering Model (OWM)
- additional improvements needed to maintain state-of-the-art and to meet needs of MMS users
- spill data sets that would be suitable for algorithm and model testing and validation.

Based on these findings, MMS initiated the ongoing Phase II and III “Revision of the OCS Oil-Weathering Model”. The main objectives of Phase II and III are:

- to obtain and adapt the SINTEF OWM to MMS needs,
- to expand the SINTEF OWM oil library to include oils of interest to MMS

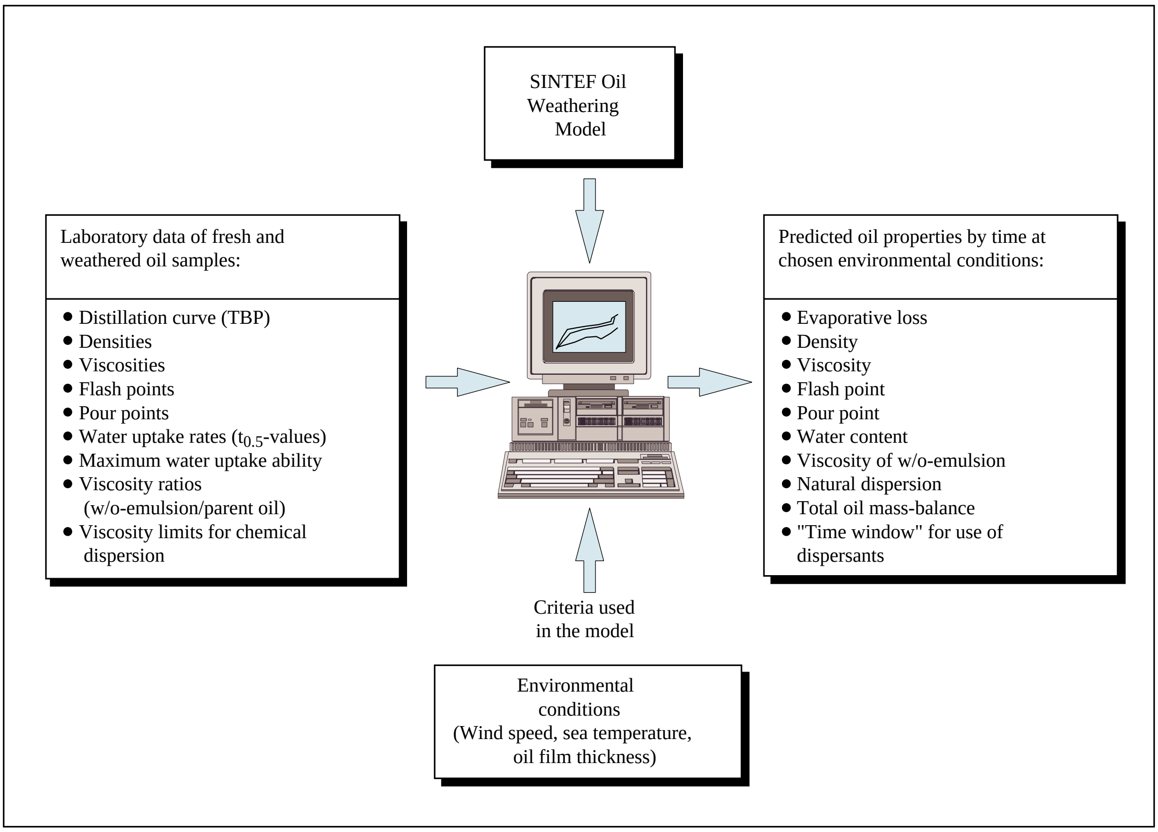
In Environmental Impact Assessment (EIA) studies and when planning the most effective response it is important to have reliable predictions of how specific oils properties will change during a spill. The efficiency of various oil spill combat methods (e. g. mechanical, dispersion and/or burning) depends greatly on the physico-chemical properties of the oil at the time of action.

In the literature, several approaches on how to predict oil properties have been established. SINTEF has chosen a direct empirical approach and in addition to crude oil data (Crude Oil Assay), the SINTEF OWM uses experimental weathering data obtained from both bench and meso-scale laboratory weathering testing of the actual crude oil as input data. Experience and data generated from full-scale field studies during the past 25 years has provided the basis for a continuous evolution of the algorithms used in the model. In recent years comparisons of the predictions obtained from the SINTEF OWM with field data have shown the strength in the prediction quality (Fiocco *et al.*, 1999 and Daling and Strøm, 1999).

SINTEF has performed weathering studies on the following six crude oils supplied by MMS: Endicott, Neptune Oilfield, Alpine Oilfield, High Island Oilfield, Milne Point Unit, and North Star. The Neptune Field and High Island oils are Gulf of Mexico oils, the rest are Alaskan oils. The results of these weathering studies will be added to the OWM library for use by MMS in Environmental Impact Assessment studies and are presented in this final report.

2 The weathering predictions obtained from the SINTEF OWM

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the change of an oils properties and behavior on the sea surface. The SINTEF OWM is schematically shown in Figure 2.1.



ik41961100\tegner\fig-eng\model.eps

Figure 2.1: 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. In this report the predictions are presented over a time period of 15 minutes to 5 days after the oil spill has occurred. This covers potential spill situations where the response time is short (e. g. close to terminals) to offshore spills where the response time can be several days.

2.1 Fixed and variable parameters used in the SINTEF OWM

2.1.1 Spill scenario

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. In this project a surface release at a rate of 1,33 metric tons per minute (i.e. 80 tons over one hour) was chosen as the spill scenario.

2.1.2 Oil film thickness

In the SINTEF OWM the oils are categorised into condensates, low emulsifying crudes, emulsifying crudes, heavy bunker fuels or refined distillates based on experimental results obtained in the bench-scale testing. A default for the initial oil and terminal w/o-emulsion film thickness is given for each category of oil in the model.

From the experimental results of the bench-scale testing (see Appendix C) Endicott, High Island Composite, Alpine Composite and North Star are described as emulsifying crude oils whereas, the Neptune Field Composite, which did not form stable w/o-emulsions, is described as a low emulsifying crude oil.

The spill conditions, oil categories and initial and terminal film thickness' are summarized in Table 2.1.

Table 2.1: The spill criteria chosen for Endicott, the Alpine Composite and the Neptune Field Composite crude oils in this project.

Oil	Oil Category	Initial film thickness [mm]	Terminal film thickness [mm]
Endicott	Emulsifying crude oil	20	1,0
Neptune Field Composite	Low emulsifying crude oil	20	0,5
Alpine Composite	Emulsifying crude oil	20	1,0
High Island Composite	Emulsifying crude oil	20	1,0
Milne Point Unit	Emulsifying crude oil	20	1,0
North Star	Emulsifying crude oil	20	1,0

2.1.3 Sea temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report, one at the average summer temperature the other at the average winter temperature for the area of interest. The temperatures are chosen on background of climate statistics for the two regions and are given in table 2.2.

Table 2.2: The average summer and winter sea temperatures used for Endicott, the Alpine Composite, the Neptune Field Composite, the High Island composite, the Milne Point Unit and the North Star crude oils in the SINTEF OWM.*

Oil type	Region	Summer temperature [°C]	Winter temperature [°C]
Endicott	Alaska	10	0
Alpine Composite			
Milne Point Unit			
North Star			
Neptune Field Composite	Gulf of Mexico	29	20
High Island Composite			

*Information provided from the Live Access to Climate Data server at the NOAA/ Pacific Environmental Laboratory.

2.1.4 Wind speed

The relationship between the wind speed and the significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown in Table 2.3.

Table 2.3: The relationship between the wind speed and the significant wave heights used in the SINTEF OWM.

Wind speed [m/s]	Beaufort wind	Wind type	Wave height [m]	Wave height [ft]
2	2	Light breeze	0,1-0,3	0.2-0.60
5	3	Gentle to moderate breeze	0,5-0,8	1-1.5
10	5	Fresh breeze	1,5-2,5	3-5
15	6-7	Strong breeze	3-4	6-8

2.2 Input data for the SINTEF OWM

In the bench scale laboratory testing, a systematic stepwise procedure developed at SINTEF (Daling *et al.*, 1990) is used to isolate and map the various weathering processes that take place when an oil is spilled on the sea surface. The experimental design for the bench scale studies is described in Appendix B and the results are presented in Appendix C. The input data to the SINTEF OWM is given in Appendix D.

The experimental weathering data obtained in the bench-scale testing are processed and used as input for the SINTEF OWM. The following oil/emulsion properties obtained in the bench-scale testing are used in the model:

- specific gravity
- pour point
- flash point
- viscosities of fresh and water-free residues (150°C+, 200°C+ and 250°C+)
- viscosities of the 50% and 75 % w/o-emulsions
- water uptake (maximum water content, stability and half-life-time)

The SINTEF OWM is described in more detail in Johansen, 1991 and in the users guide for the model.

2.3 Weathering properties related to response

The efficiency of various oil spill combat methods (e. g. mechanical recovery, dispersion and/or burning) depends greatly on the physical and chemical properties of the oil at the time of action. When planning the most effective response the predictions charts provide important information.

2.3.1 Mechanical response

Past experiences from Norwegian field trials have shown that the effectiveness of many mechanical clean up operations is reduced due to a high degree of leakage of the confined oil or w/o-emulsion from the oil spill boom (especially in high current). This leakage is especially pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 cP at a shear rate of $10s^{-1}$ (Nordvik *et al*., 1992). The **lower viscosity limit** for an optimal mechanical clean up operation has therefore been set to 1000 cP.

The **upper viscosity limit** for an optimal mechanical clean up operation depends on the type of skimmer used. For some disk-skimmers the collection capacity is reduced significantly at w/o-emulsion viscosities exceeding 10 000 cP (ITOPF, 1986), however ITOPF, 1986 does not state the shear rate.

Recent tests performed by SINTEF using a weir skimmer show that the efficiency may be reduced for semi-solidified oils, i. e. oils with a large wax content and high pour point values, and for oils with viscosities between 15000 and 20000 cP (Leirvik *et.al*.,2001).

2.3.2 Chemical dispersion

A dispersibility methodology, based on the viscosity increase due to weathering, was developed at SINTEF (Daling and Strøm, 1999) in order to determine the window of opportunity for the effective use of dispersants for different oils. Chemical dispersibility testing was not included in this study. General limits for dispersibility based on pour point values are given in table 2.4. These values are not valid for all oils and situations, and should only be regarded as guidelines.

Table 2.4: The chemical dispersibility used in the SINTEF OWM based on pour points.

Pour point [°C]	Chemical dispersibility
< 5°C above the sea temperature	Dispersible
5-15°C above the sea temperature	Reduced dispersibility
> 15°C above the sea temperature	Not dispersible

2.4 How to use the prediction charts, an example

If e.g. Endicott has drifted for a period of time on the sea surface the prediction charts can be used to determine the remaining oil's chemical, physical and emulsifying properties. Table 2.5 shows examples for the following scenario:

- Drift time: 24 hours
- Temperature: 0°C/10°C
- Wind speed: 10 m/s

Table 2.5: Weathering properties for Endicott obtained from the prediction charts.

Property	Winter temperature [0°C]	Summer temperature [10°C]
Evaporation	13 vol%	15 vol%
Pour point	15 °C	17°C
Viscosity of the water free oil	5 000 cP	3 000 cP
Water content	50 %	58 %
Viscosity of the emulsion	12 000 cP	9 000 cP

2.5 Prediction charts for Alaskan oils

2.5.1 Prediction charts and summary of the Endicott crude oil's weathering properties at sea

Detailed information of the Endicott crude oil sample

Area/block:	Alaskan North Slope
Common field name:	Endicott
Well number:	133 G-12-00

Summary of the Endicott crude oil's weathering properties at sea

Endicott is a heavy crude oil, with a density of 0,9131 g/mL. Endicott has a relative low content of lighter molecular weight compounds, and at 10 m/s wind speed only 10 % of its original volume will be evaporated 24 hours after the spill at summer temperatures.

Endicott will form w/o-emulsions with a maximum water content of approximately 60 % at winter temperatures and 65 % at summer temperatures doubling the original spill volume. The w/o-emulsions formed are very stable and in order to effectively dehydrate the w/o-emulsions when using an emulsion breaker (e. g. Alcopol O 60 %) a minimum dosage of 2000 ppm should be applied.

After approximately three hours at winter temperatures and half an hour at summer temperatures the Endicott w/o-emulsion will have a viscosity of over 1000 cP which is the recommended lower viscosity limit for an effective mechanical response. Viscosity of the Endicott emulsion will exceed 20 000 cP within 1-3 days at high wind speed. This might cause lowered efficiencies in a mechanical recovery operation using e.g. a weir or disk skimmer. At lower wind speeds this should not be a problem.

Given the high viscosity of the Endicott emulsions, a limited time window for the use of dispersants could be expected. A dispersibility study should be performed on the Endicott oil in order to establish the time-frame in which the use of dispersants are feasible, and to determine the optimal dosage of dispersants for an effective chemical treatment operation.

Due to the high viscosity of the Endicott emulsions a high "lifetime" should be expected for the slick on the sea surface. At low wind speeds natural dispersion is almost neglectable, and even at higher wind speeds the slick will endure for several days on the sea surface.

The prediction charts for the weathering of the Endicott crude oil at sea are given in Figure 2.2 to Figure 2.7. The mass balance for Endicott at the mean summer and winter temperatures in the Alaskan North Slope region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figure 2.8 to Figure 2.11. These figures illustrate the degree of natural dispersion at varying sea conditions.

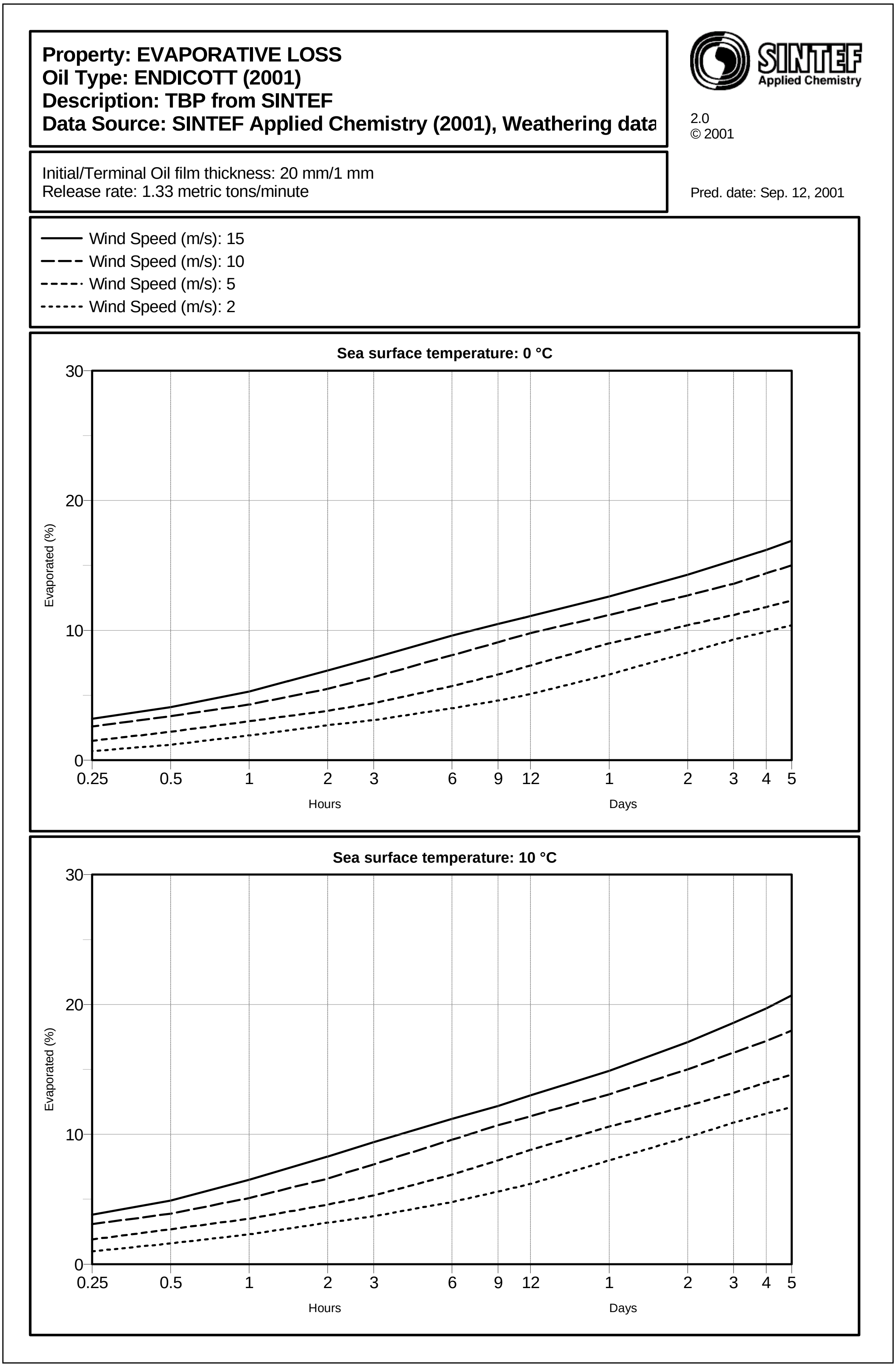
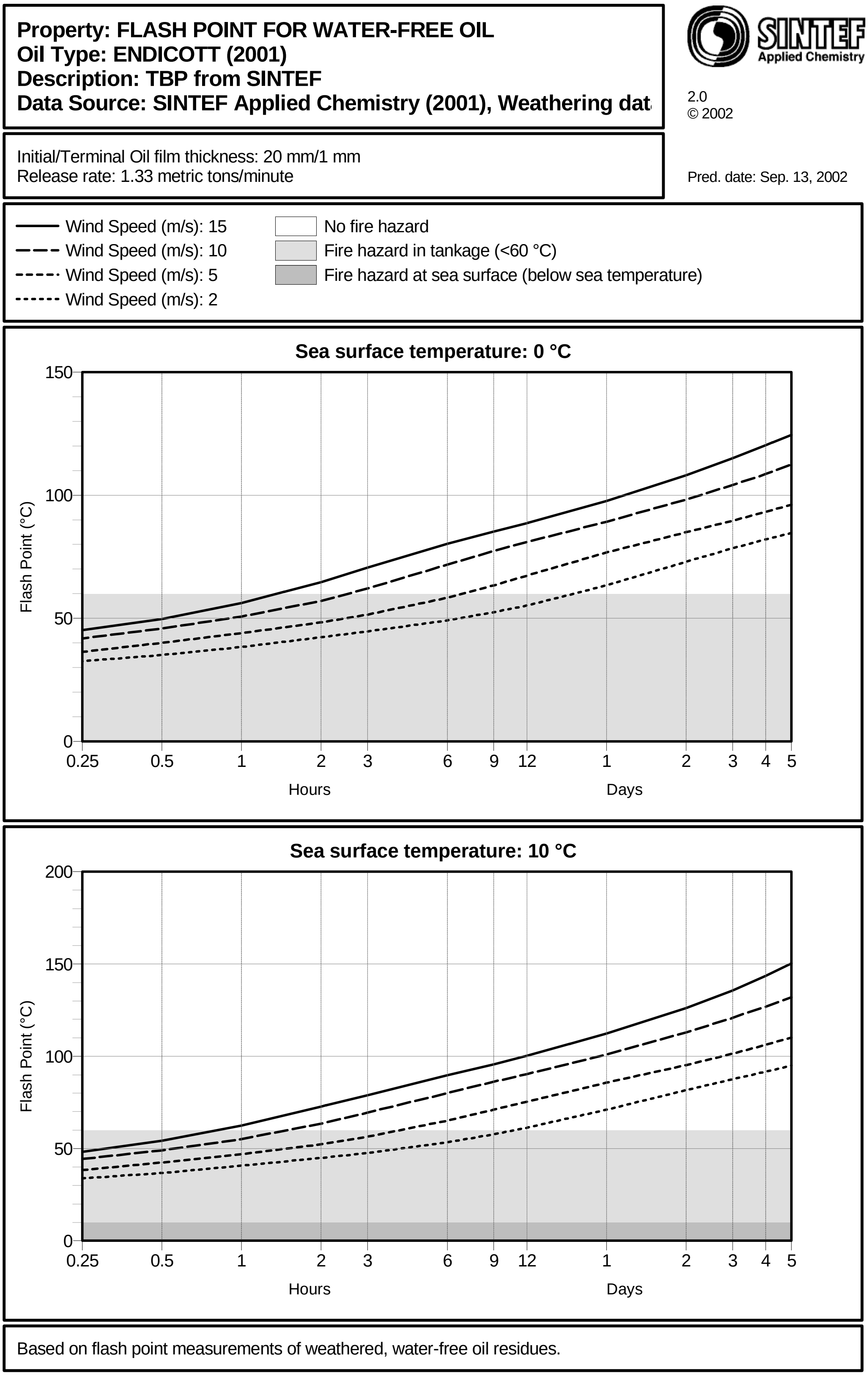


Figure 2.2: The predicted evaporative loss for Endicott at summer (10 °C) and winter (0 °C) mean temperatures in Alaskan North Slope region.



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

SINTEF Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

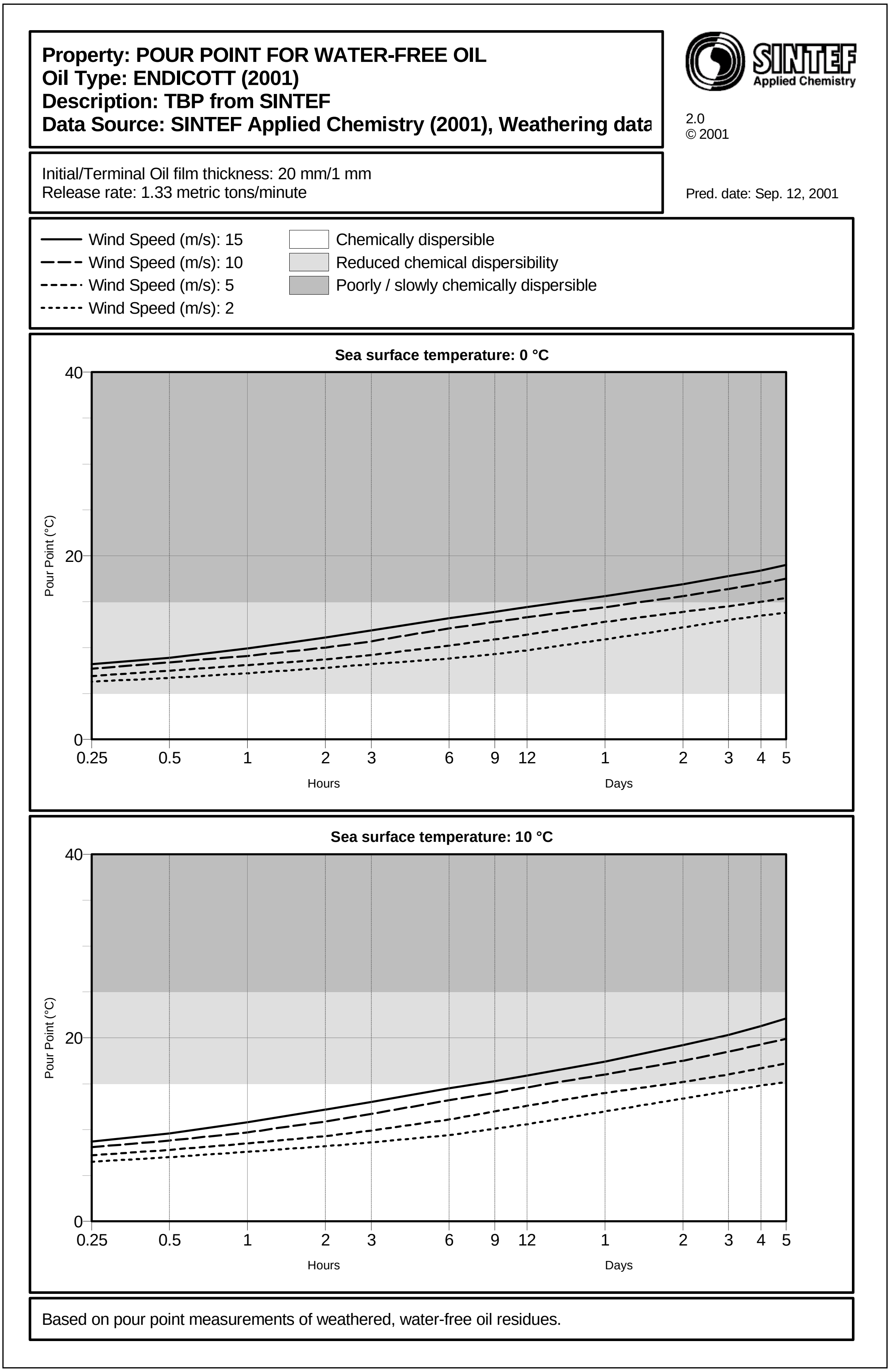
Pred. date: Sep. 13, 2002

Wind Speed (m/s): 15
Wind Speed (m/s): 10
Wind Speed (m/s): 5
Wind Speed (m/s): 2

☐ No fire hazard
▨ Fire hazard in tankage (<60 °C)
■ Fire hazard at sea surface (below sea temperature)

Based on flash point measurements of weathered, water-free oil residues.

Figure 2.3: The Flash point for water-free Endicott at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

SINTEF Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

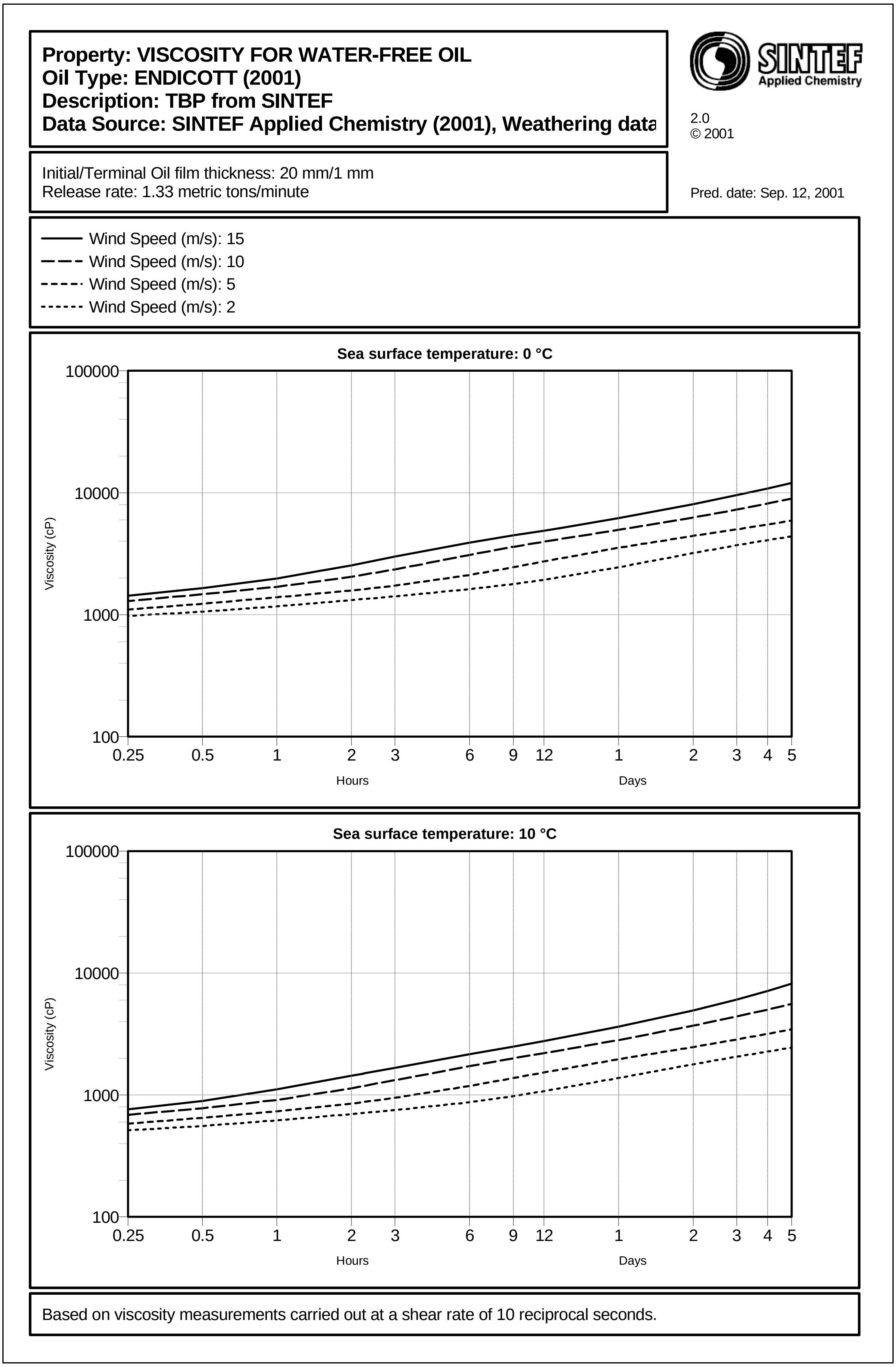
Pred. date: Sep. 12, 2001

—— Wind Speed (m/s): 15
— — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
------ Wind Speed (m/s): 2

☐ Chemically dispersible
░ Reduced chemical dispersibility
▒ Poorly / slowly chemically dispersible

Based on pour point measurements of weathered, water-free oil residues.

Figure 2.4: The predicted pour point for water-free Endicott at different wind speeds at the summer (10℃) and winter (0℃) mean temperatures in the Alaskan North Slope region.



Property: VISCOSITY FOR WATER-FREE OIL
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 12, 2001

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.5: The predicted viscosity for water-free Endicott for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures in the Alaskan North Slope region.

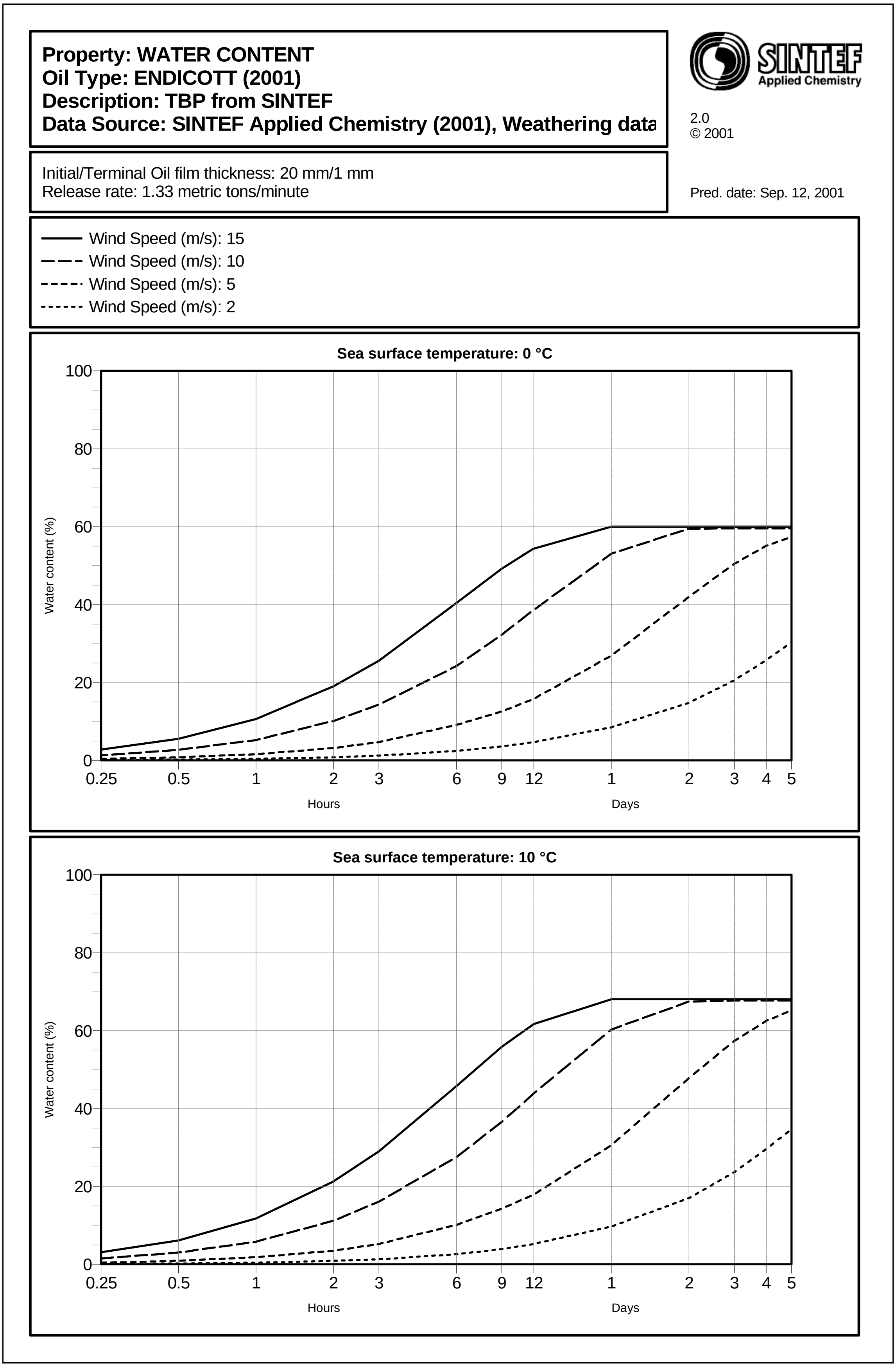
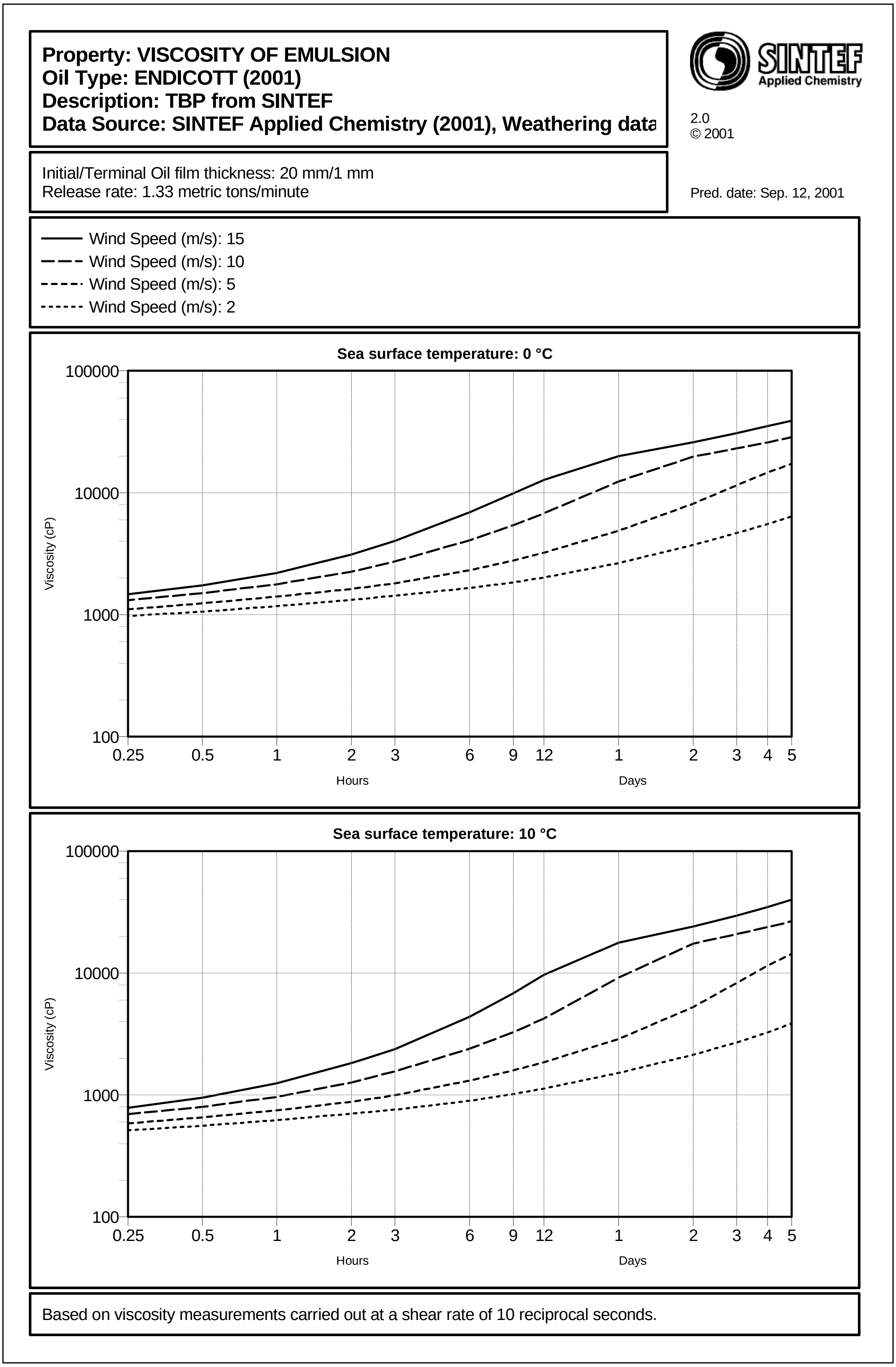


Figure 2.6: The predicted water content in the Endicott w/o-emulsions for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures in the Alaskan North Slope region.



Property: VISCOSITY OF EMULSION
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.7: The predicted viscosity of the Endicott w/o-emulsions for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures in the Alaskan North Slope region.

Property: MASS BALANCE
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

SINTEF Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

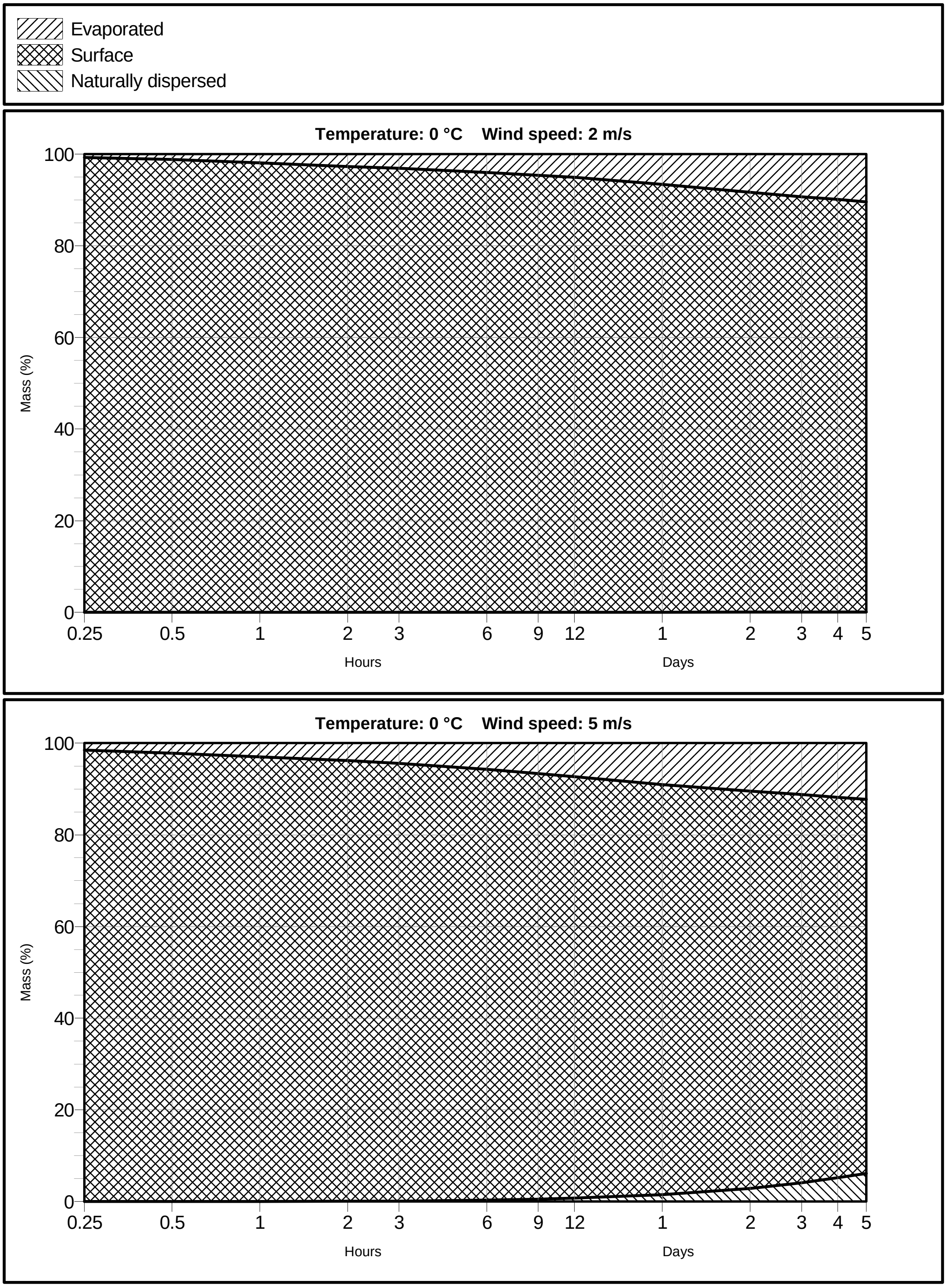
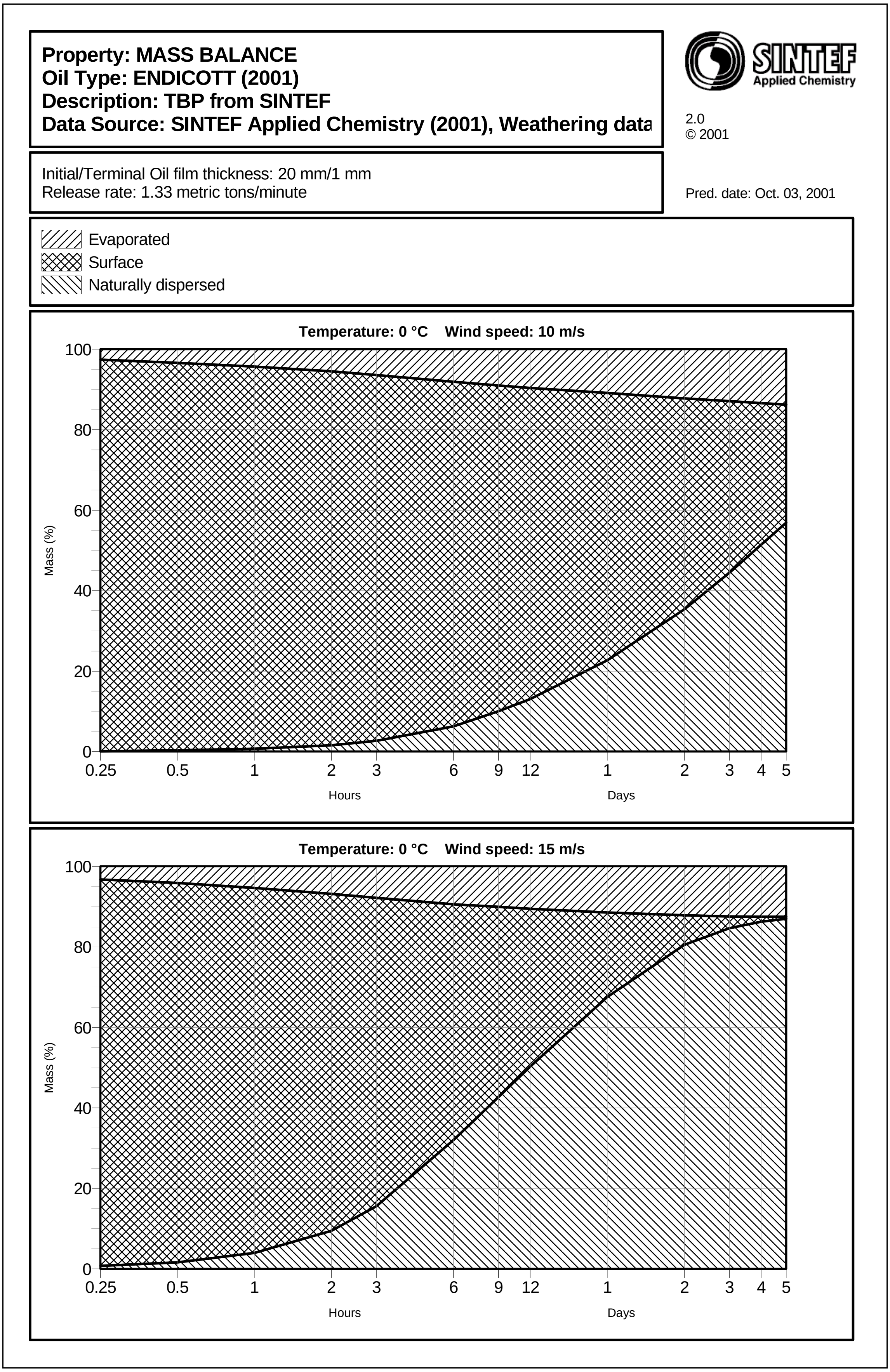


Figure 2.8: The mass balance for Endicott at the mean winter temperature (0 ℃) in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.



Property: MASS BALANCE
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

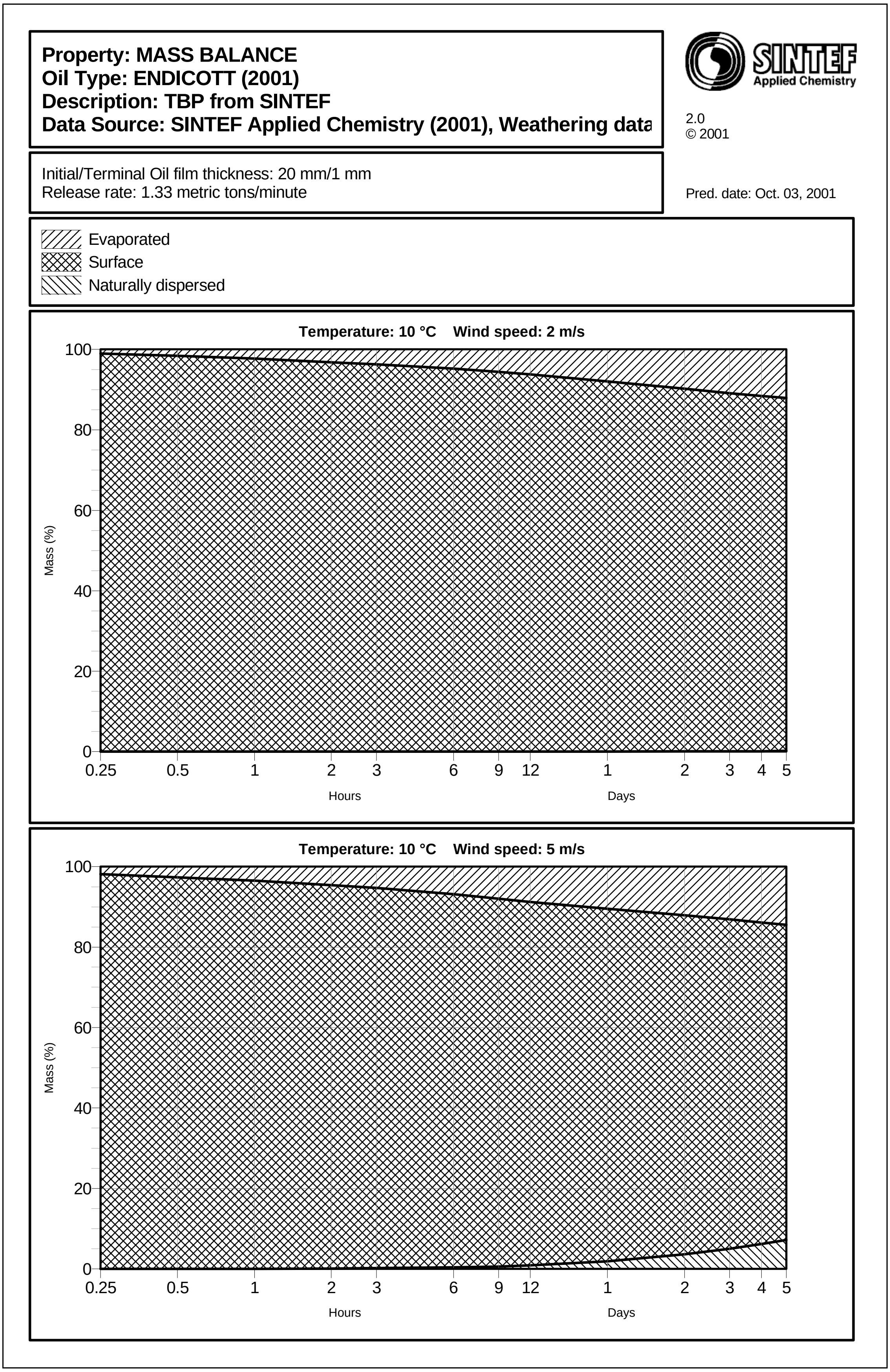
Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Figure 2.9: The mass balance for Endicott at the mean winter temperature (0℃) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.



Property: MASS BALANCE
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

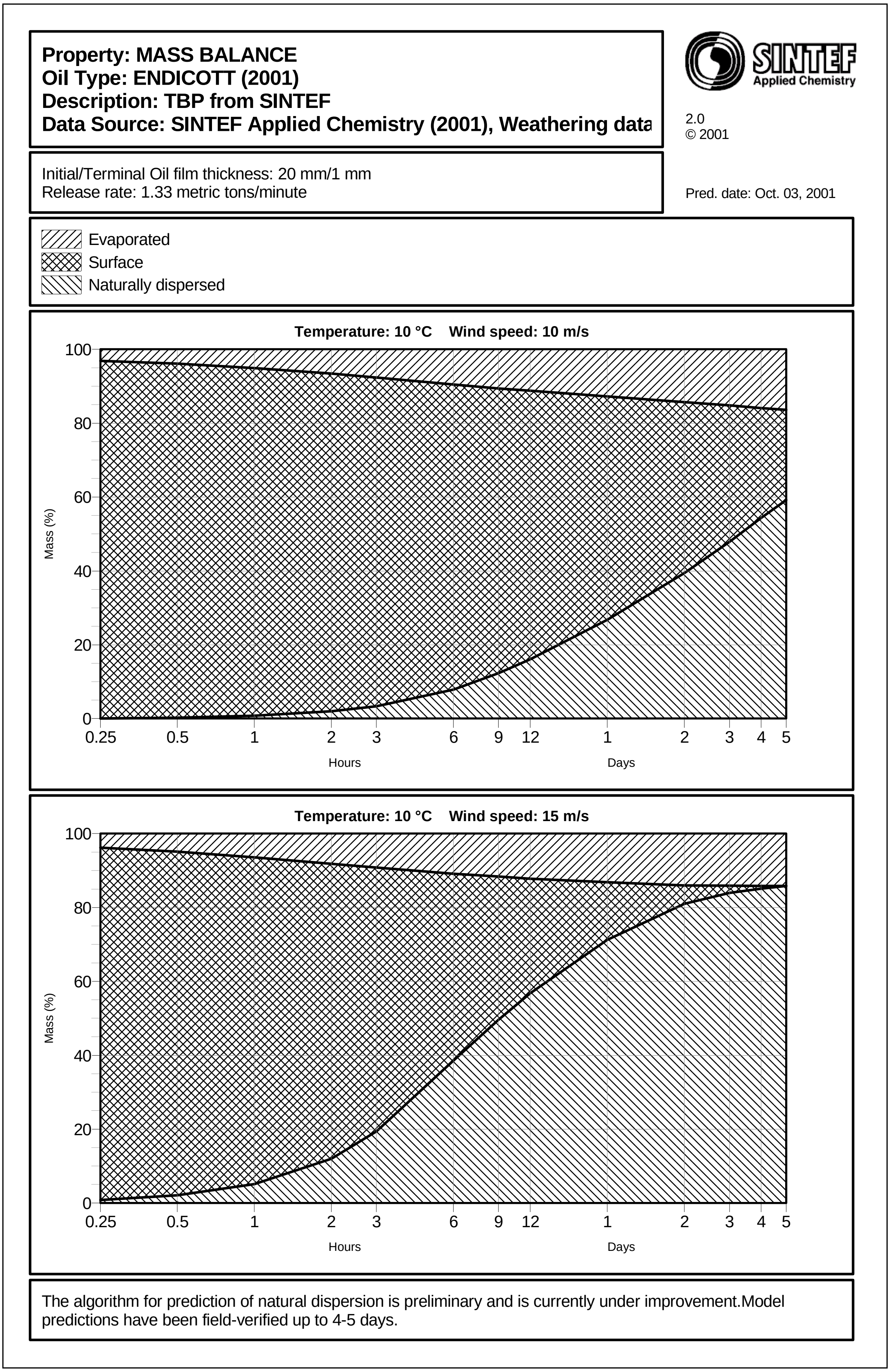
SINTEF Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Figure 2.10: The mass balance for Endicott at the mean summer temperature (10°C) in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.



Property: MASS BALANCE
Oil Type: ENDICOTT (2001)
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

▨ Evaporated
▩ Surface
▧ Naturally dispersed

The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Figure 2.11: The mass balance for Endicott at the mean summer temperature (10°C) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.

2.5.2 Prediction charts and summary of the Alpine Composite oil's weathering properties at sea

Detailed information of the Alpine Composite

Area/block:	Alpine Central Production Facility
Sample date:	07-23-2001
Company name:	Phillips

Composite sample from all of the producing wells at Alpine.

Summary of the Alpine Composite's weathering properties at sea

The Alpine Composite is a paraffinic crude oil, with a density of 0,834 g/mL. The Alpine Composite contains a relatively large amount of lower molecular weight compounds and approximately 25% of its original volume will be evaporated 24 hours after the spill at both summer and winter temperatures.

The Alpine Composite contains approximately 4 wt% wax and less than 0,1 wt% asphaltenes. The fresh oil has a pour point of -18°C and increases rapidly with weathering to approximately 10°C and 15°C at the mean winter and summer mean temperatures at a wind speed of 10 m/s.

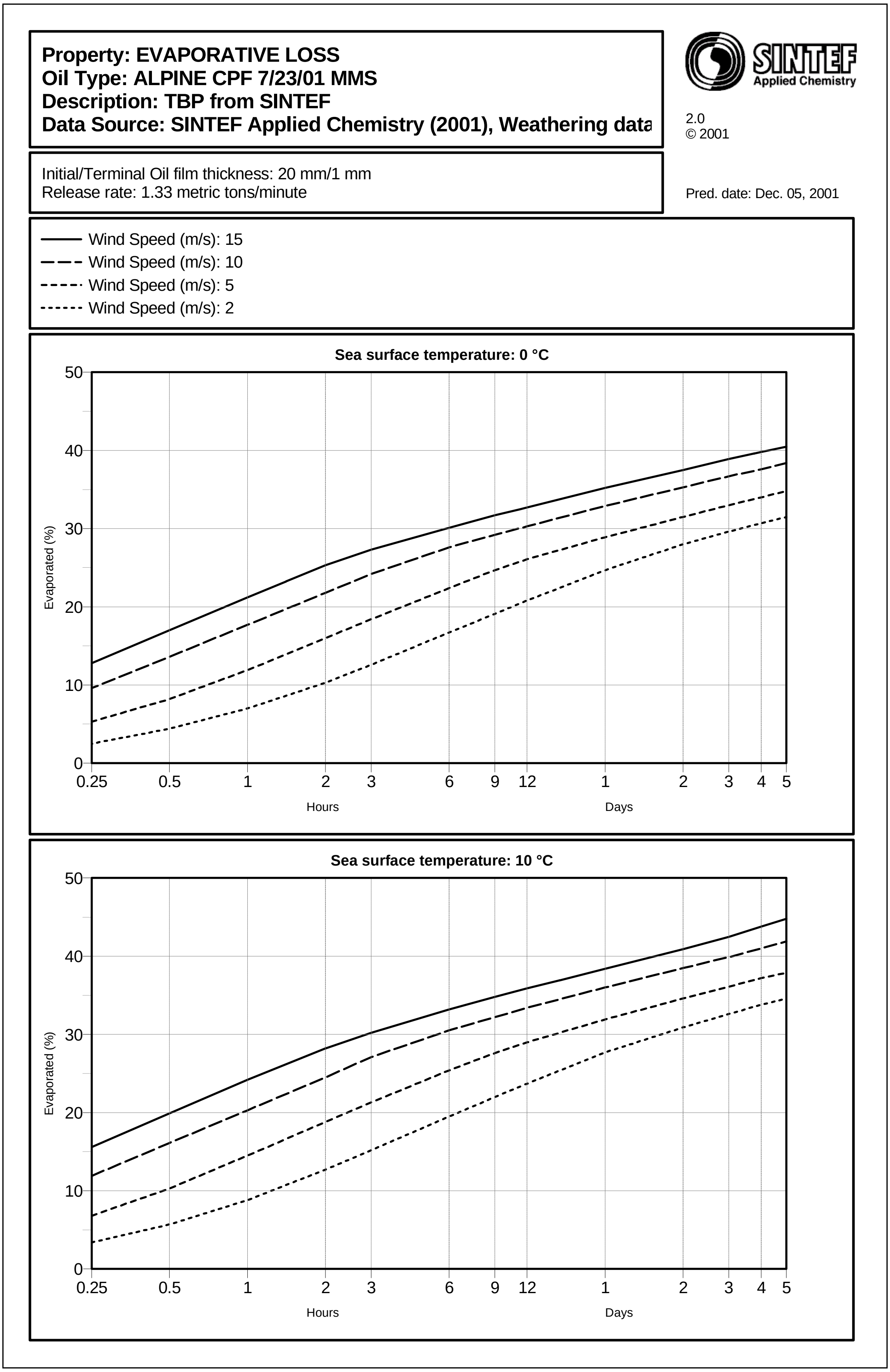
Alpine Composite will form w/o-emulsions with a maximum water content of 80 % at both winter and summer temperatures, yielding approximately five times the original spill volume. The w/o-emulsion formed after one day of weathering at sea is stable and in order to effectively dehydrate the w/o-emulsions when using the emulsion breaker Alcopol O 60 % a minimum dosage of 2000 ppm should be applied.

After one day of weathering the Alpine Composite w/o-emulsions at winter and summer temperatures will have a viscosity of over 1000 cP and the viscosity will only exceed 10 000 cP after several days of weathering on the sea surface. High viscosity should not compromise the success off a mechanical recovery operation, for at least a week after the time of the release.

The Alpine Composite will have a high degree of natural dispersion at high wind speeds. E.g. at 15 m/s wind speed the slick will be almost removed from the sea surface within a day.

The prediction charts for the weathering of the Alpine Composite oil at sea are given in Figure 2.12 to Figure 2.17.

The mass balance for the Alpine Composite at the mean summer and winter temperatures in the Alaska North Slope region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figure 2.18 to Figure 2.21. These figures illustrate the degree of natural dispersion at varying sea conditions.



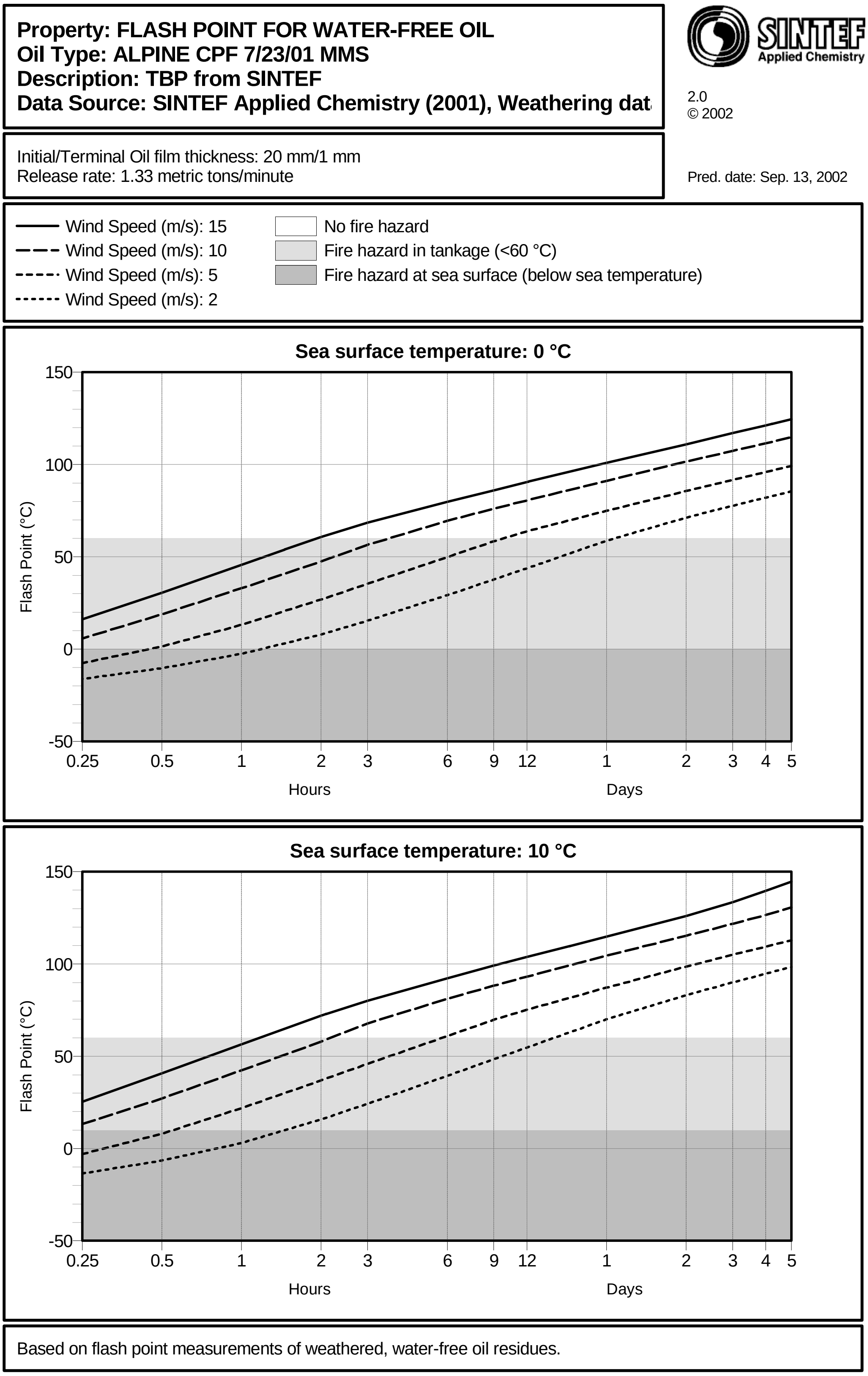
Property: EVAPORATIVE LOSS
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

2.0
© 2001

Pred. date: Dec. 05, 2001

Figure 2.12: The predicted evaporative loss for the Alpine Composite oil at summer (10℃) and winter (0℃) mean temperatures.



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

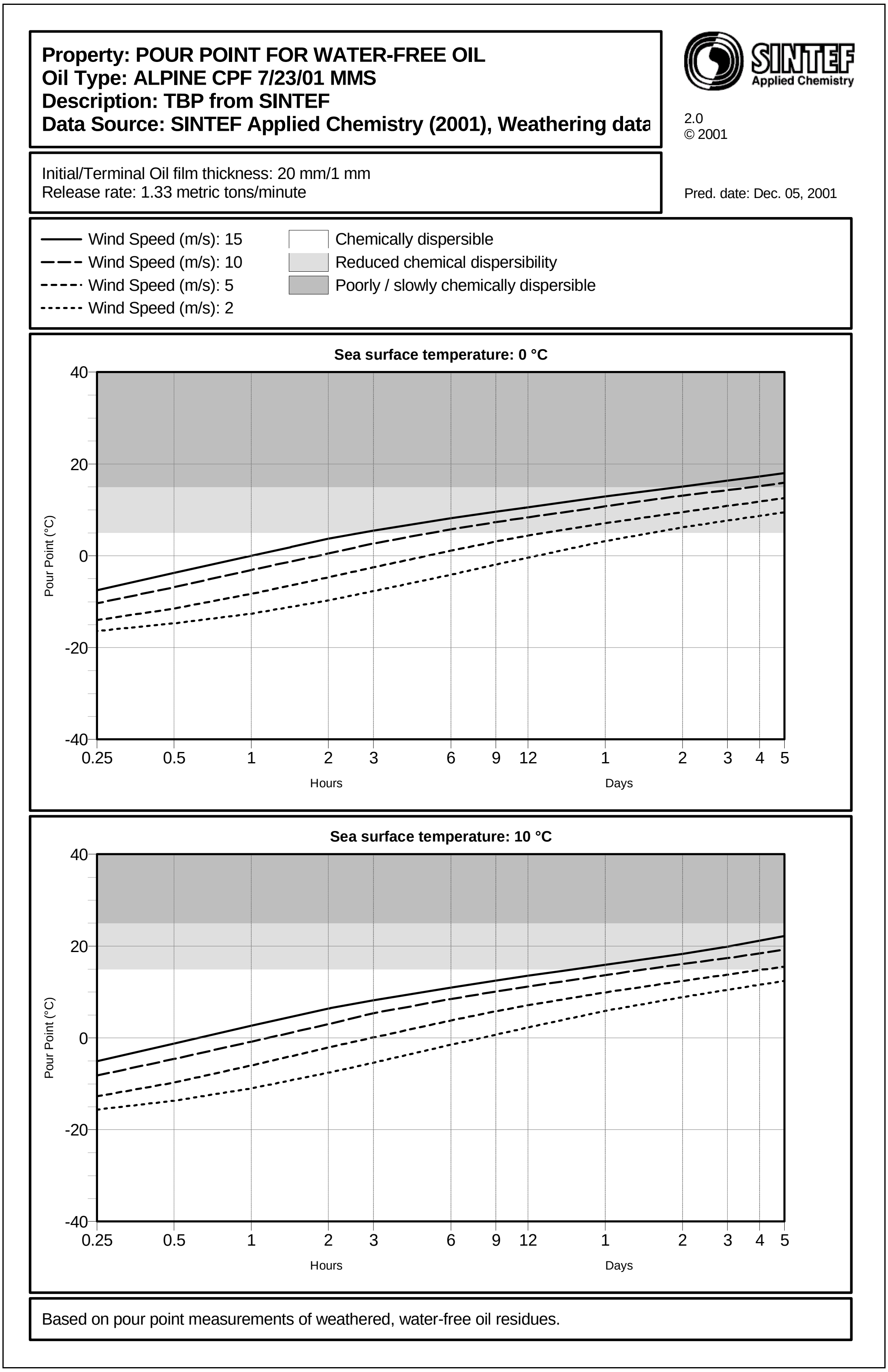
Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

2.0
© 2002

Pred. date: Sep. 13, 2002

Based on flash point measurements of weathered, water-free oil residues.

Figure 2.13: The Flash point for water-free Alpine Composite at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 05, 2001

——— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
······ Wind Speed (m/s): 2

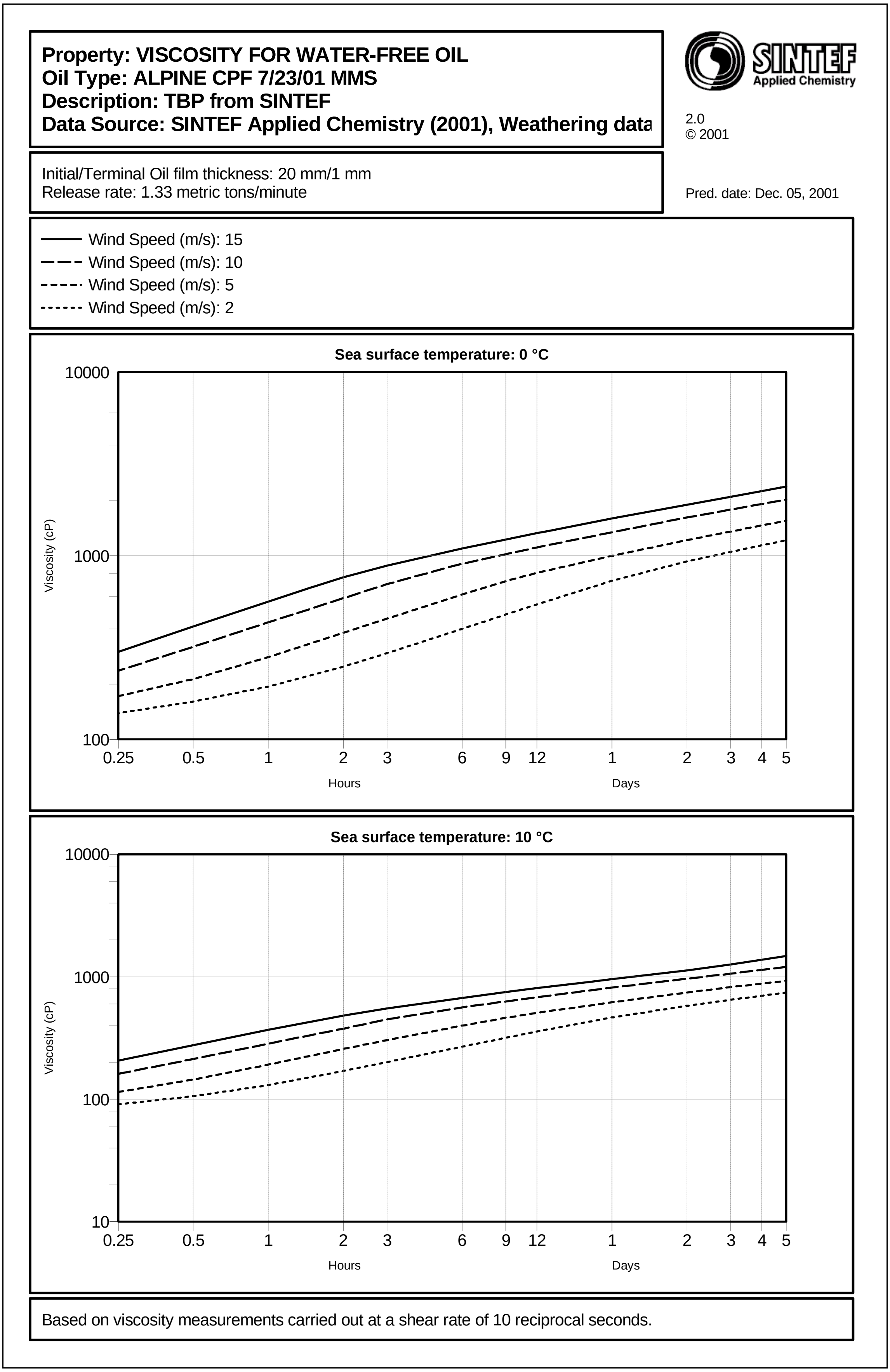
□ Chemically dispersible
░ Reduced chemical dispersibility
▒ Poorly / slowly chemically dispersible

Sea surface temperature: 0 °C

Sea surface temperature: 10 °C

Based on pour point measurements of weathered, water-free oil residues.

Figure 2.14: The predicted pour point for water-free Alpine Composite at different wind speeds at the summer (10°C) and winter (0°C) mean temperatures.



Property: VISCOSITY FOR WATER-FREE OIL
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

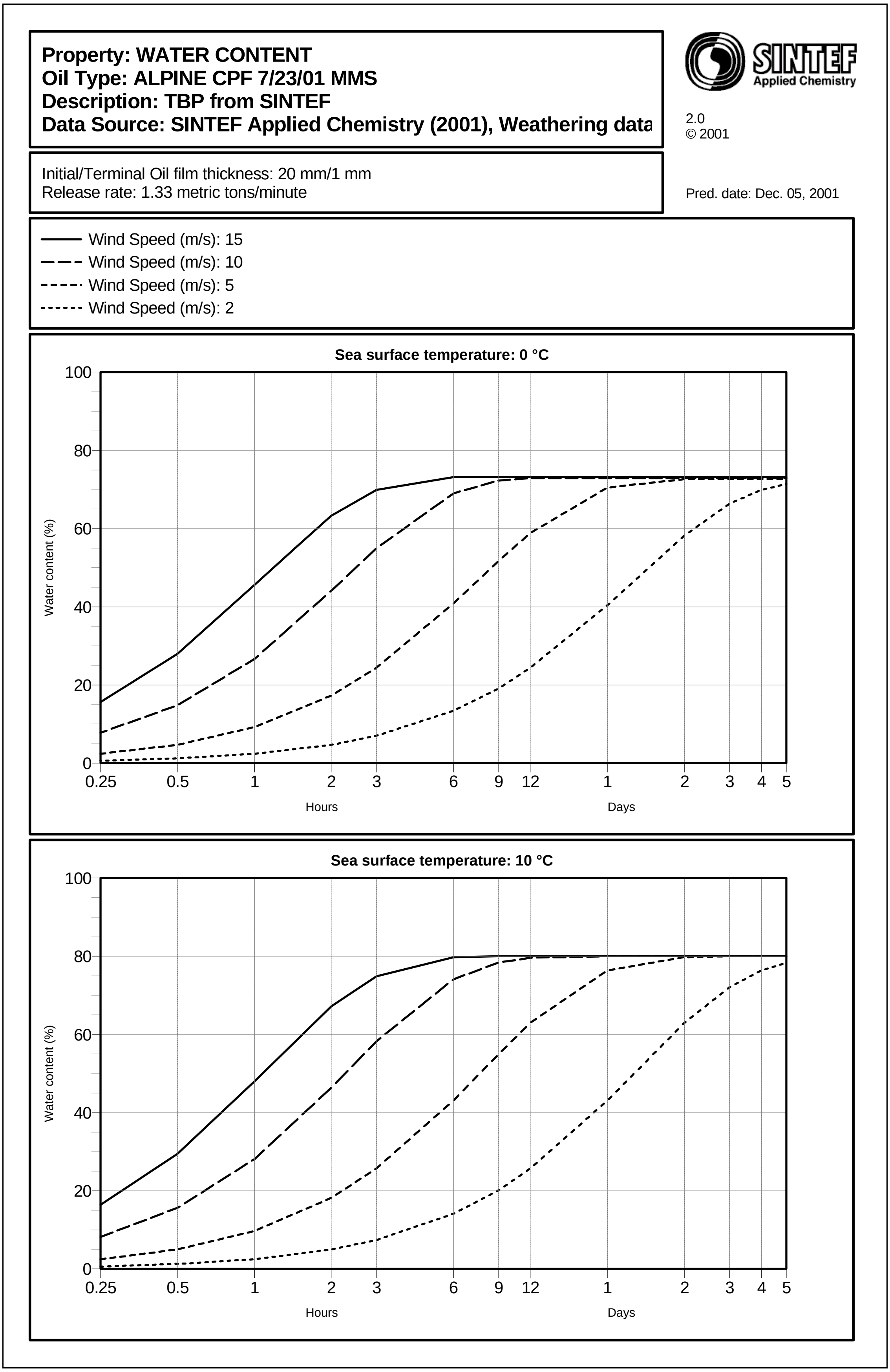
SINTEF Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 05, 2001

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.15: The predicted viscosity for water-free Alpine Composite for different wind speeds at the summer (10 °C) and winter (0 °C) mean temperatures.



Property: WATER CONTENT
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 05, 2001

Figure 2.16: The predicted water content in the Alpine Composite w/o-emulsions for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures.

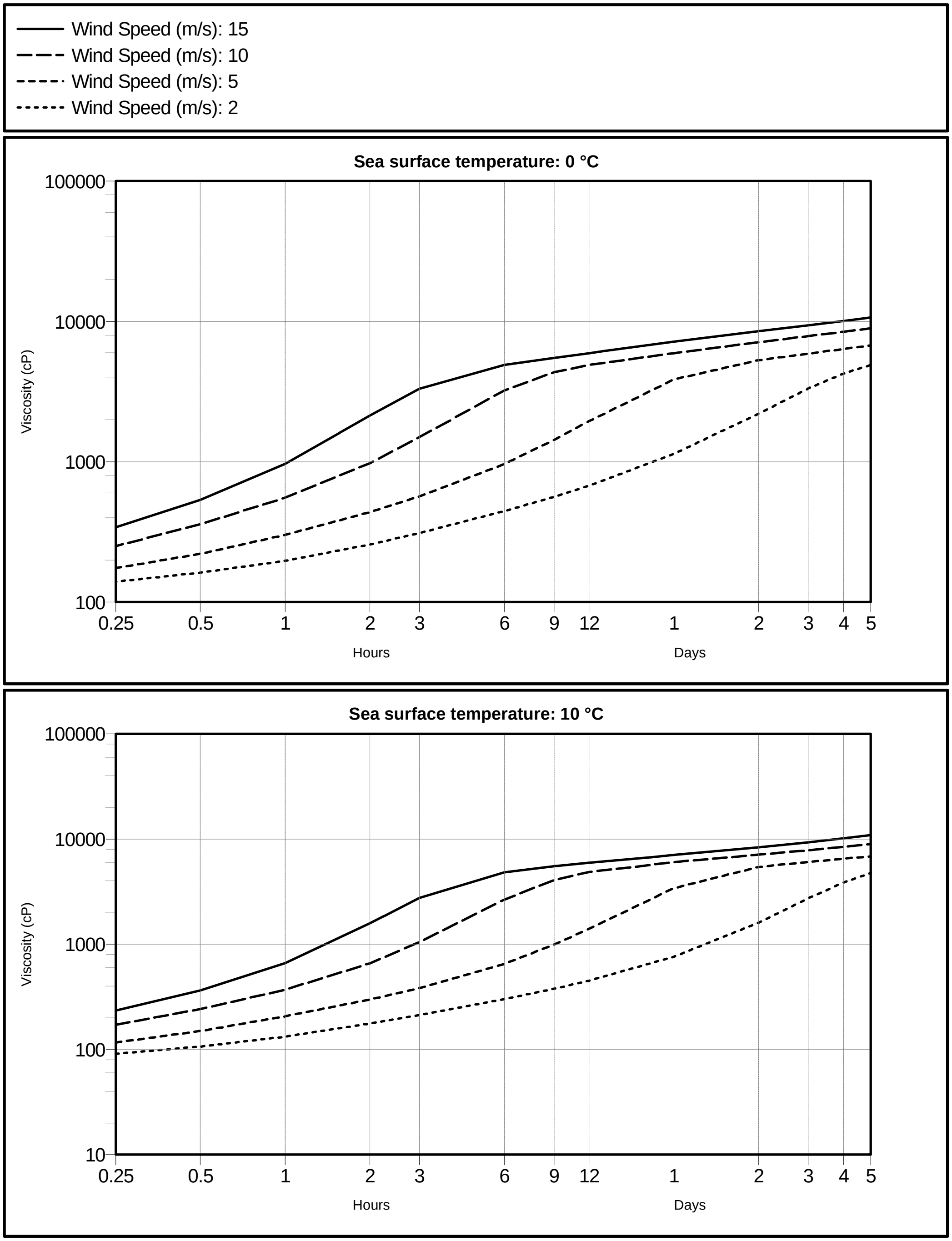
Property: VISCOSITY OF EMULSION
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

SINTEF Applied Chemistry

2.0
© 2001

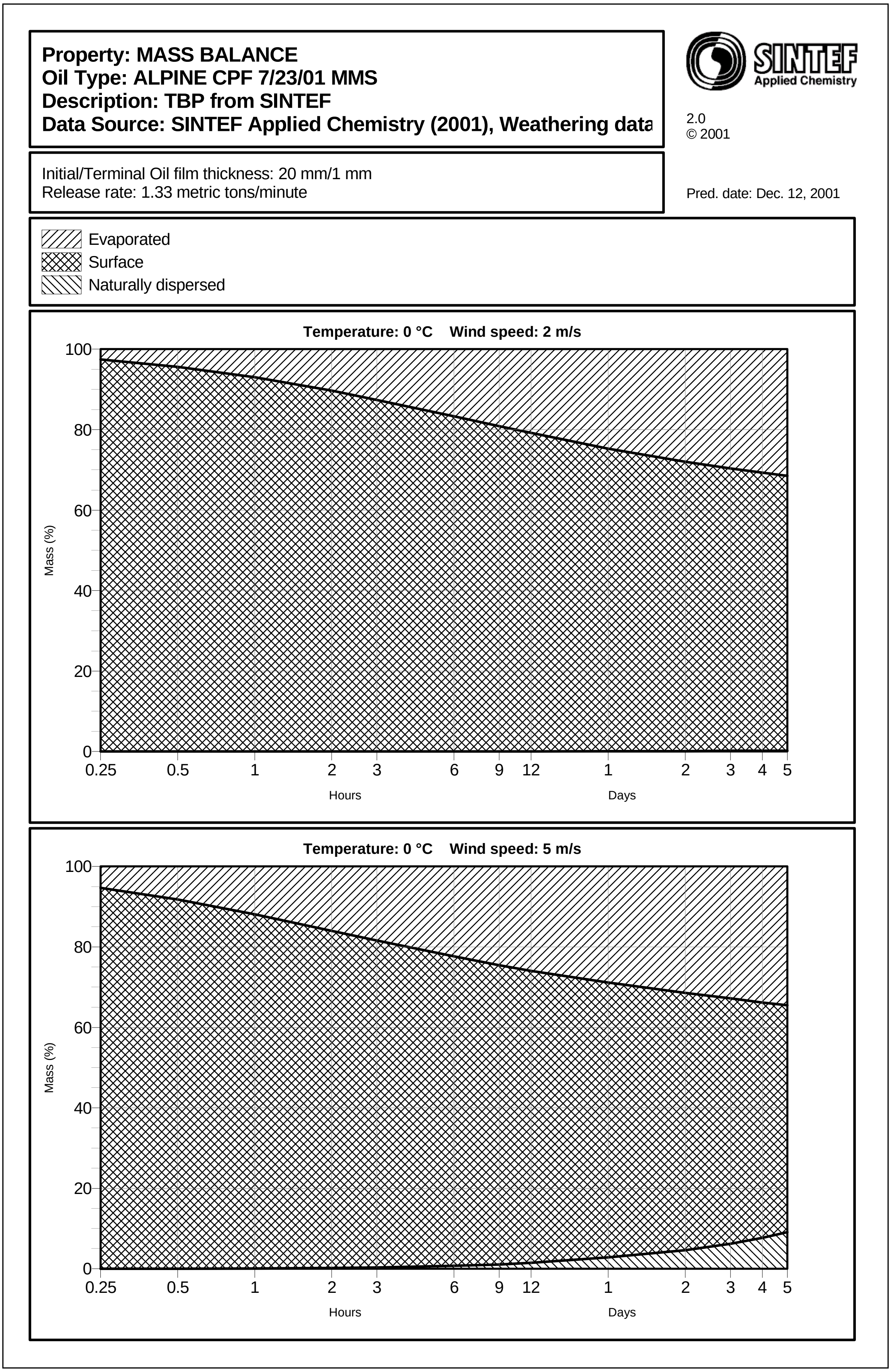
Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 05, 2001



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.17: The predicted viscosity of the Alpine Composite w/o-emulsions for different wind speeds at the summer (10°C) and winter (0°C) mean temperatures.



Property: MASS BALANCE
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

2.0
© 2001

Pred. date: Dec. 12, 2001

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Figure 2.18: The mass balance for Alpine Composite at the mean winter temperature (0 ℃) in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.

Property: MASS BALANCE
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 12, 2001

▨ Evaporated
▩ Surface
▧ Naturally dispersed

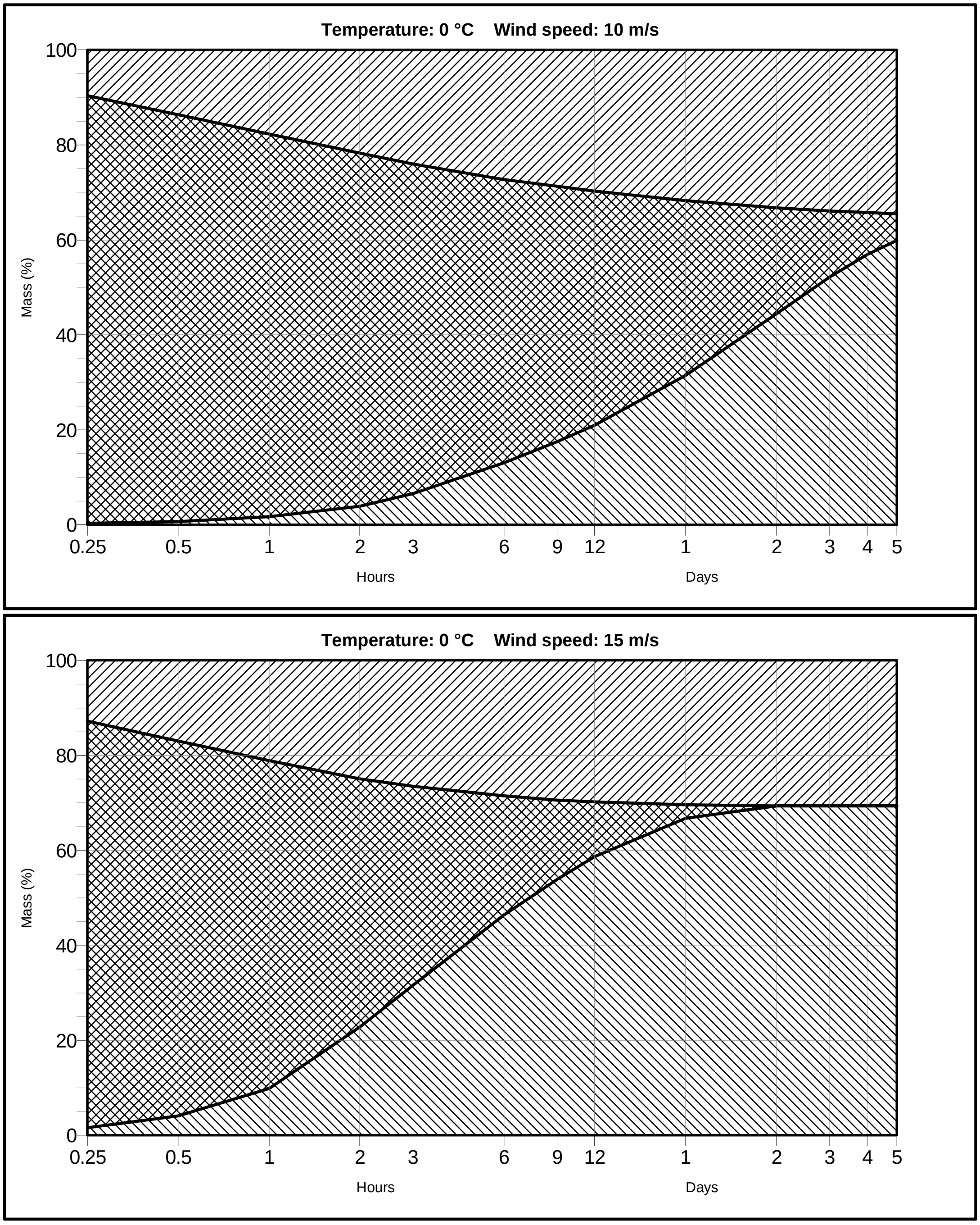


Figure 2.19: The mass balance for Alpine Composite at the mean winter temperature (0°C) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.

Property: MASS BALANCE
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

SINTEF Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 12, 2001

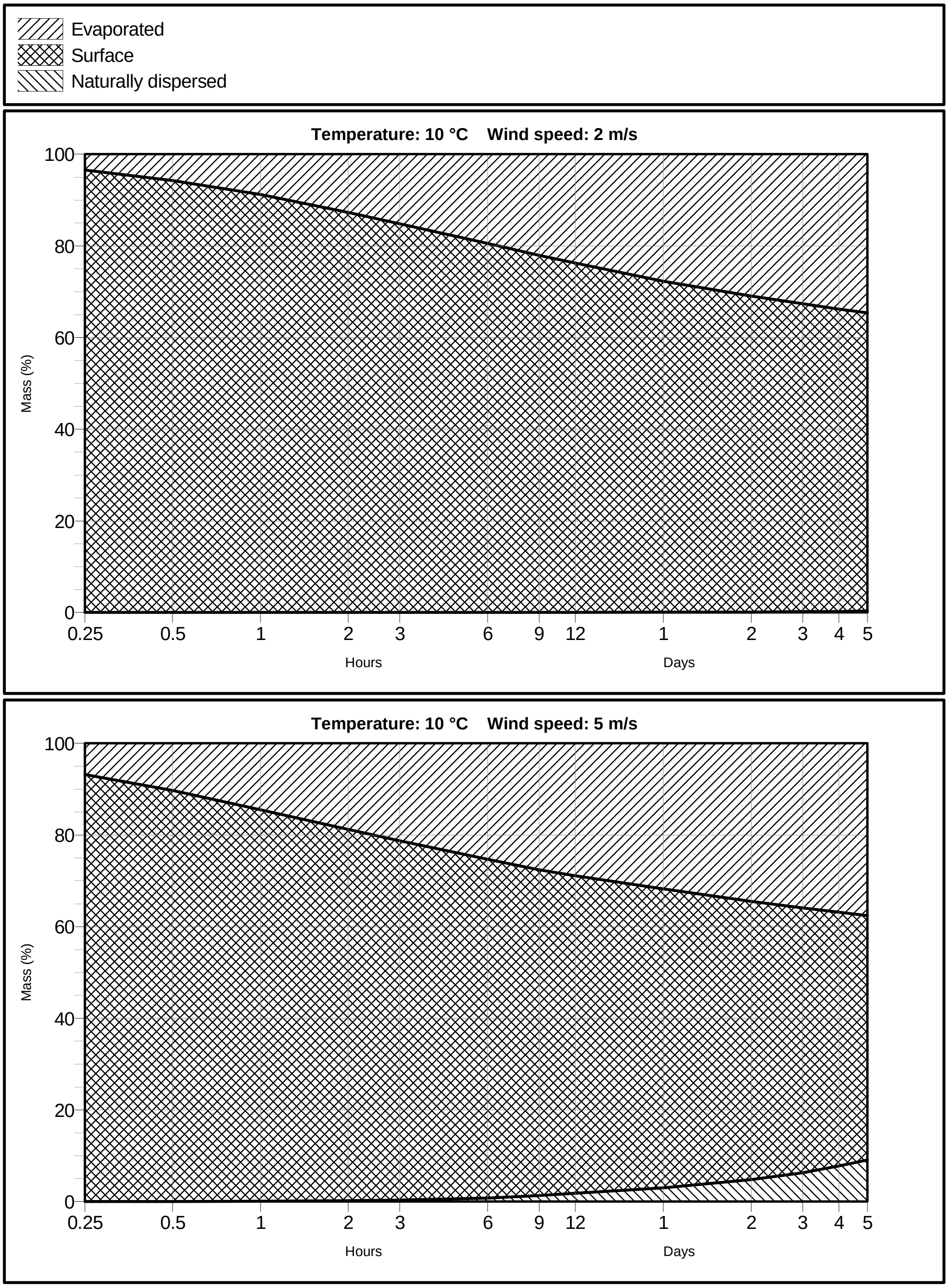
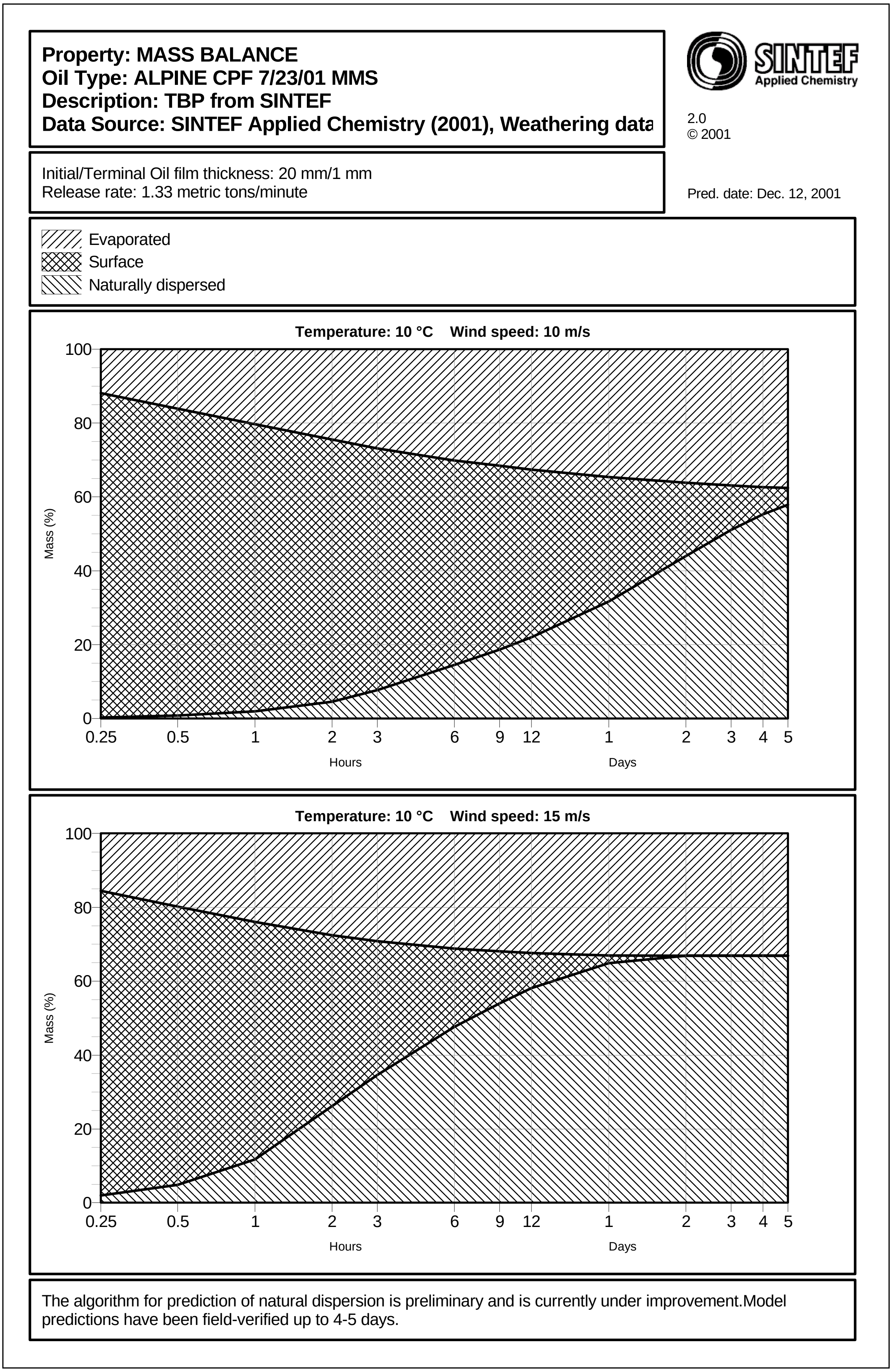


Figure 2.20: The mass balance for Alpine Composite at the mean summer temperature (10 °C) in the Alaskan North Slope region at wind speeds of 2 and 5 m/s.



Property: MASS BALANCE
Oil Type: ALPINE CPF 7/23/01 MMS
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Dec. 12, 2001

- ▨ Evaporated
- ▨ Surface
- ▨ Naturally dispersed

The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Figure 2.21: The mass balance for Alpine Composite at the mean summer temperature (10 °C) in the Alaskan North Slope region at wind speeds of 10 and 15 m/s.

2.5.3 Summary of the Milne Point Unit Oil's weathering properties at sea

Detailed information of the Milne Point Unit oil sample

Area/block:	Alaskan North Slope
Jerry cans marked:	MPJ-01 CRUDE OIL

Summary of the Milne Point Unit oil's weathering properties at sea

The Milne Point Unit oil sample were emulsified at arrival. The emulsion were extremely stable and could not be broken without the addition of an excess of emulsion breaker and heating. The laboratory evaporation of the oil, that forms the fundament of the weathering studies, could not be performed on the emulsified oil. Predictions could therefore not be made for the Milne Point Unit oil.

The Milne Point Unit oil is a heavy naphthenic oil with an approximate density of 0.95g/ml. The oil seems to be highly biodegraded (i.e. no paraffinic components are present in the Gas Chromatogram seen in fig C5) The emulsion is extremely stable and can only be dehydrated at high temperatures and with the addition of a high dosage of demulsifier (approximately 10%). Dehydration of the emulsion in a mechanical recovery operation could therefore prove difficult. The water content of the arrived oil was 30-40%.

From previous studies at SINTEF, testing with a weir skimmer has showed poor recovery efficiency at viscosities above 20.000. A 30% emulsion of the "fresh" Milne Point Unit oil has a viscosity of approximately 8000 cP at 10°C. A high degree of evaporation is not expected for the Milne Point Unit oil, but the viscosity will increase with weathering on the sea surface (both evaporation and further emulsification), and high viscosities could cause problems in a mechanical recovery operation for the Milne Point Unit oil, particularly at winter conditions.

SINTEF recommend a non emulsified Milne Point oil is supplied if possible, and the weathering properties are further investigated.

2.5.4 Prediction charts and summary of the North Star Oil's weathering properties at sea

Detailed information of the North Star oil sample

Sample no :	1.08
Client:	BP Alaska
Installation:	North Star
Date:	5.6-02
Bottle no.:	n/a
Well:	NS-08
Test:	test1
Time:	21:25
Sample	Nature: Atmospheric oil
Sampling point:	Separator Oil Line
Sample bottle:	5gallon can
Job no.:	NAM 1076

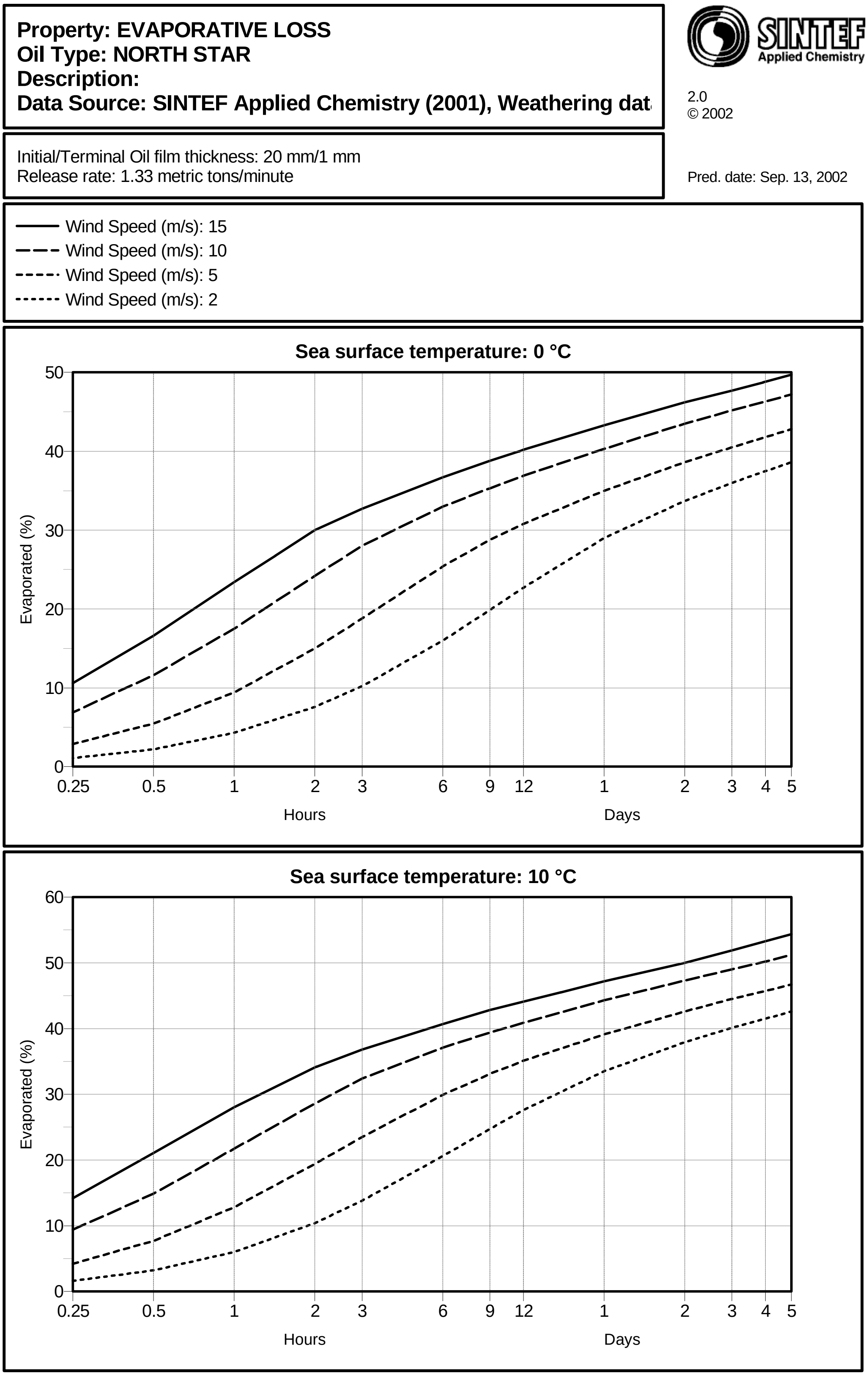
Summary of the North Star oil's weathering properties at sea

The North Star oil is a light paraffinic crude oil, with a density of 0.8155 g/mL. The North Star oil contains a relatively large amount of lower molecular weight compounds and approximately 30 % of its original volume will evaporate 24 hours after the spill at both summer and winter temperatures. The wax content of the North Star oil is 5.9 wt%. The pour point for the North Star oil is very low for a paraffinic crude at –39°C for the fresh crude.

A viscosity of 1000 cP is considered to be a lower limit for efficient mechanical oil recovery. This is due to leakage under the oil booms at lower viscosities (Norvik *et.al*. 1992). The North Star oil will have viscosities below this limit initially and in a span of time highly dependent on wind and temperature (e.g. 2 hours for 0°C and 15m/s wind speed, and 2 days for 10°C and 2 m/s wind speed). During mechanical combat operations loss of oil could be expected within this time-frame.

No laboratory study is performed to assess the window of opportunity for the use of chemical dispersants. The natural dispersion, however, will be of significance at high wind speeds. At both summer and winter temperatures and 15 m/s wind speed the oil slick is expected to vanish from the sea surface within a day due to natural dispersion. At lower wind speeds the oil could be persistent on the sea surface for several days.

The prediction charts for the weathering of the North Star oil at sea are given in *Figure 2.22* to *Figure 2.27*. The mass balance for the North Star oil at the mean summer and winter temperatures in the Alaska North Slope region at different wind speeds (2, 5, 10 and 15 m/s) are given in *Figure 2.28* to *Figure 2.31.*



Property: EVAPORATIVE LOSS
Oil Type: NORTH STAR
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

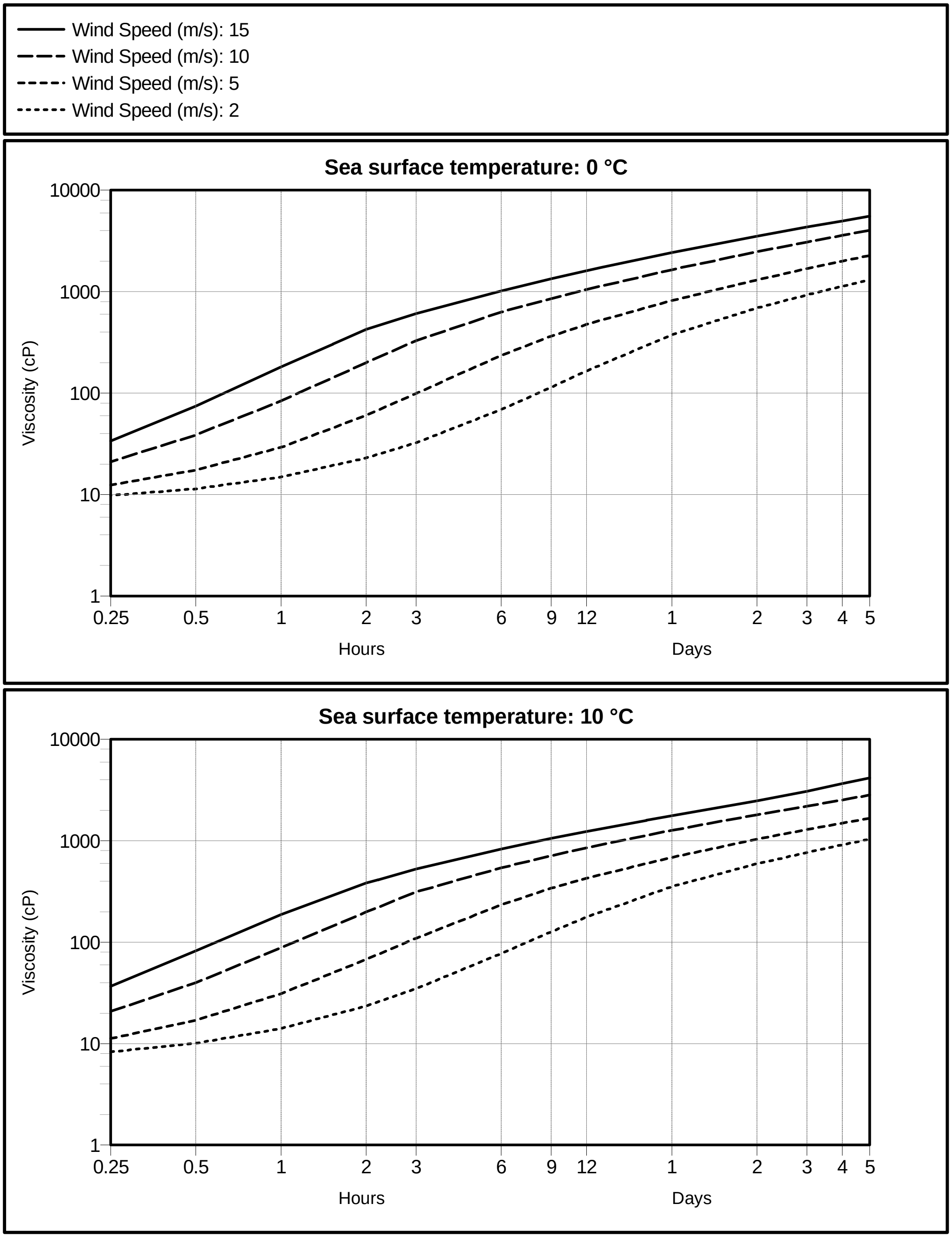
Figure 2.22: The predicted evaporative loss for the North Star oil at the mean summer (10 ℃) and winter (0 ℃) temperatures for the Alaska North Slope region.

Property: VISCOSITY FOR WATER-FREE OIL
Oil Type: NORTH STAR
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.23: The predicted viscosity for water-free North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

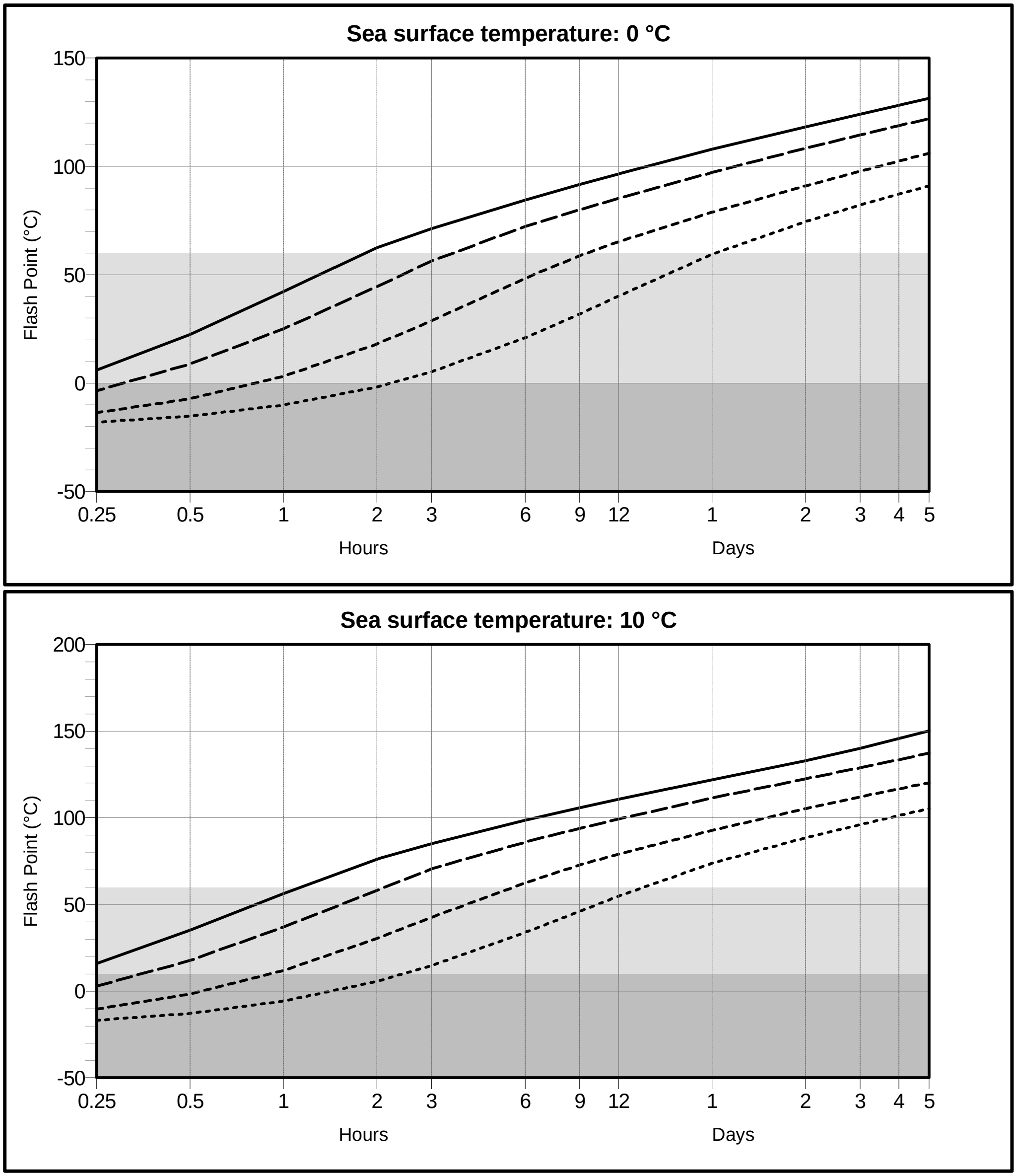
Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: NORTH STAR
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

——— Wind Speed (m/s): 15	☐ No fire hazard
— — — Wind Speed (m/s): 10	░ Fire hazard in tankage (<60 °C)
- - - - Wind Speed (m/s): 5	▒ Fire hazard at sea surface (below sea temperature)
······ Wind Speed (m/s): 2	



Based on flash point measurements of weathered, water-free oil residues.

Figure 2.24: The Flash point for water-free North Star oil at the mean summer (10 °C) and winter (0 °C) temperatures for the Alaska North Slope region.

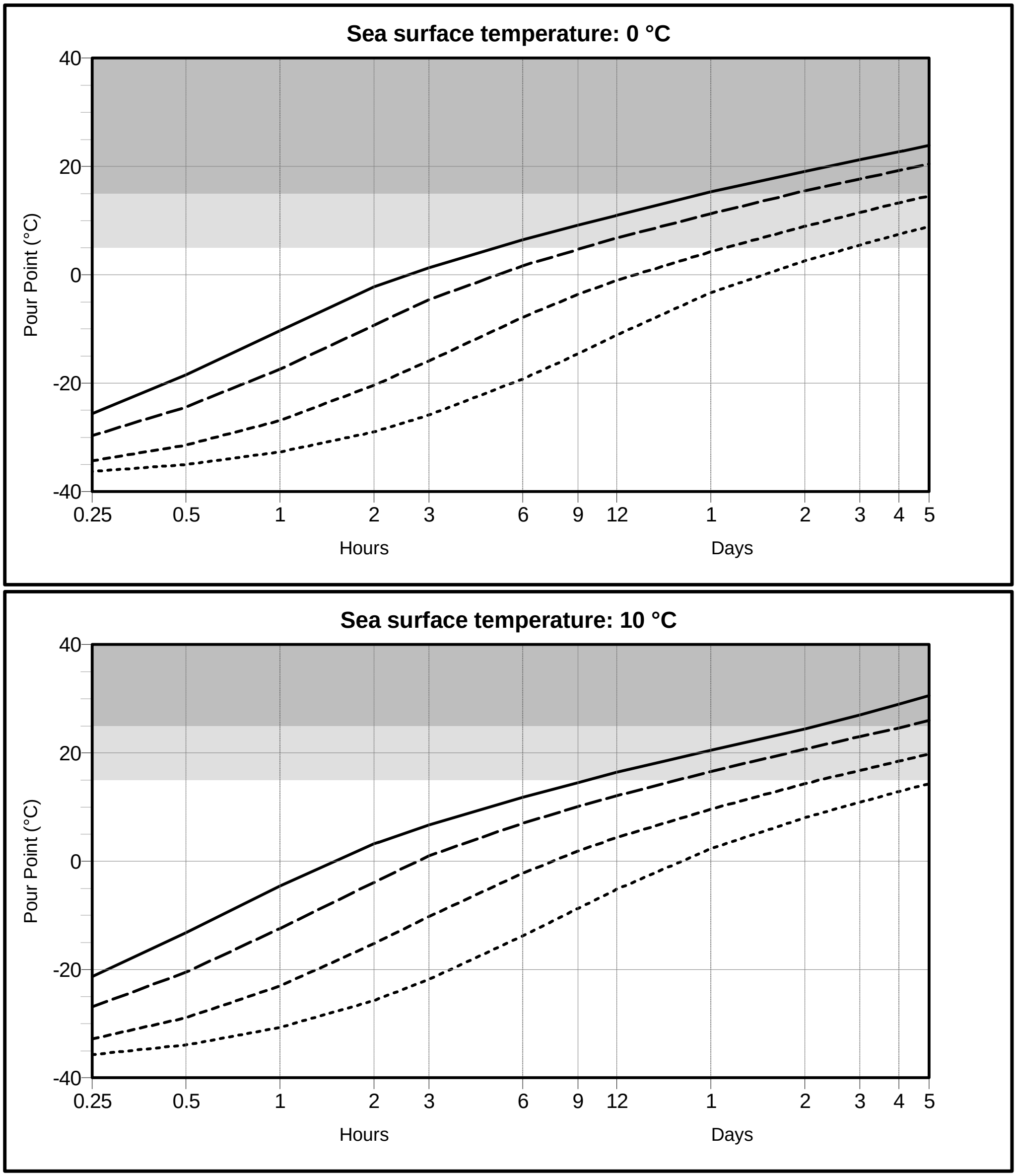
Property: POUR POINT FOR WATER-FREE OIL
Oil Type: NORTH STAR
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

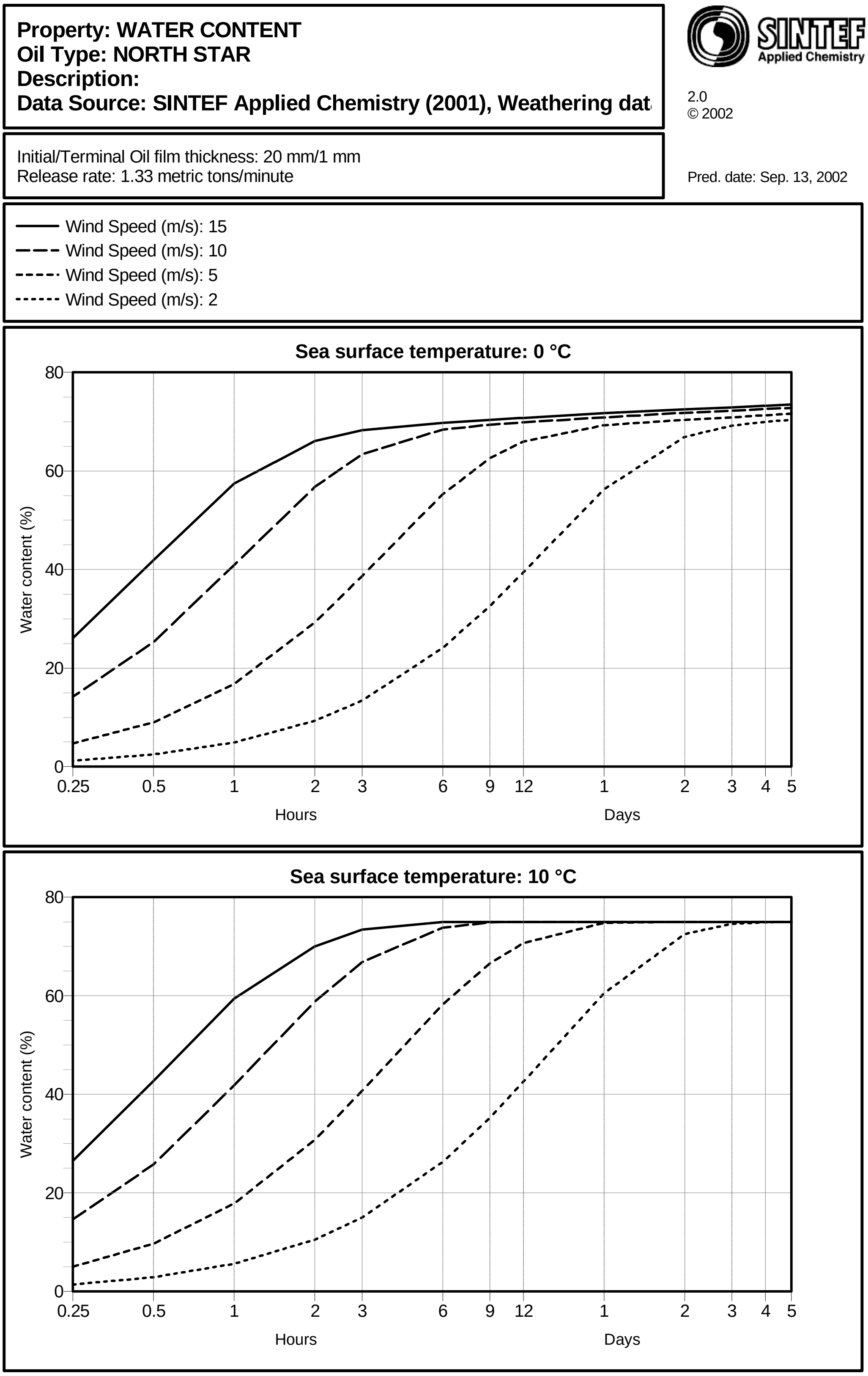
Pred. date: Sep. 13, 2002

—— Wind Speed (m/s): 15	☐ Chemically dispersible
– – – Wind Speed (m/s): 10	░ Reduced chemical dispersibility
- - - - Wind Speed (m/s): 5	▒ Poorly / slowly chemically dispersible
...... Wind Speed (m/s): 2	



Based on pour point measurements of weathered, water-free oil residues.

Figure 2.25: The predicted pour point for water-free North Star oil at the mean summer (10 °C) and winter (0 °C) temperatures for the Alaska North Slope region.



Property: WATER CONTENT
Oil Type: NORTH STAR
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

Figure 2.26: The predicted water uptake for North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.

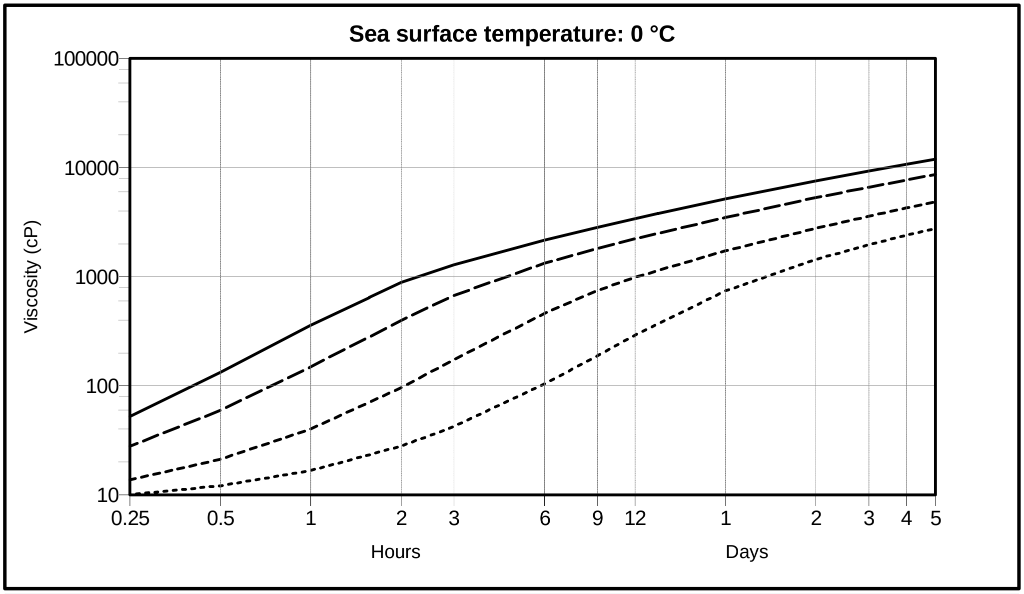
Property: VISCOSITY OF EMULSION
Oil Type: NORTH STAR
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

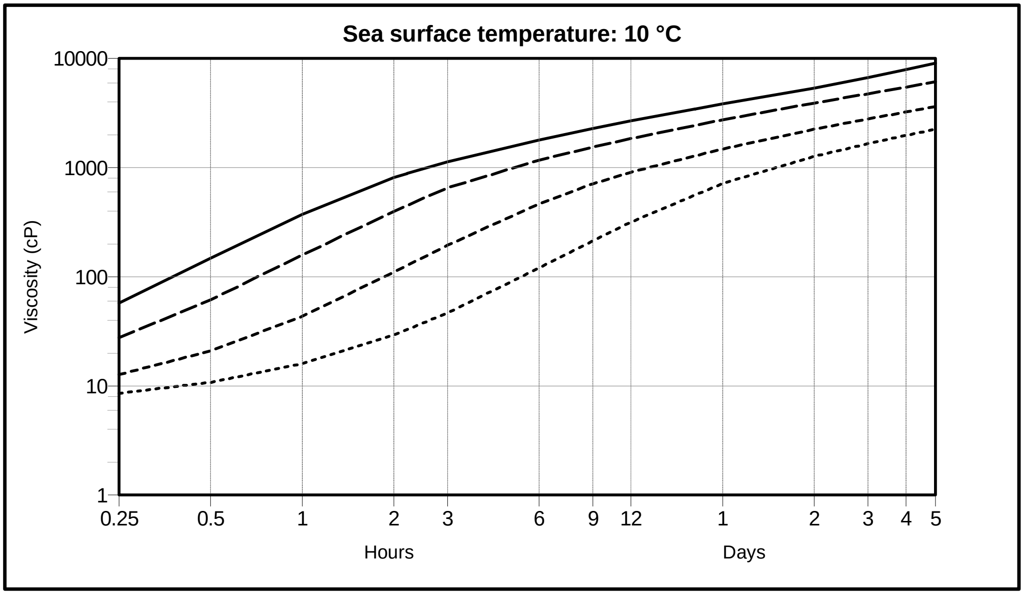
Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

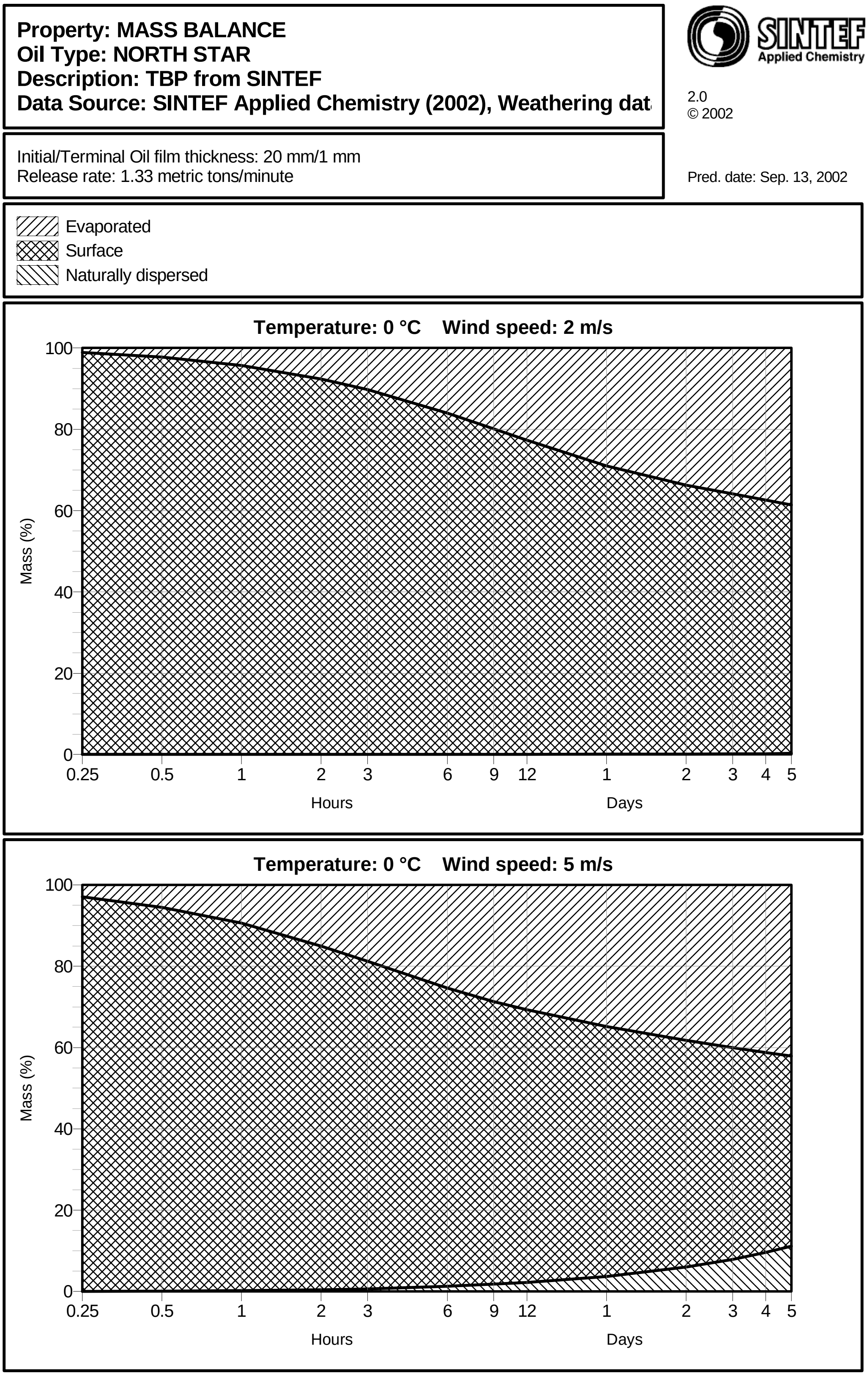
- ——— Wind Speed (m/s): 15
- — — Wind Speed (m/s): 10
- - - - - Wind Speed (m/s): 5
- ------ Wind Speed (m/s): 2





Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.27: The predicted emulsion viscosity for North Star oil at the mean summer (10°C) and winter (0°C) temperatures for the Alaska North Slope region.



Property: MASS BALANCE
Oil Type: NORTH STAR
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2002), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

- ▨ Evaporated
- ▩ Surface
- ▧ Naturally dispersed

Figure 2.28: The mass balance for the North Star oil at the mean winter temperature (0°C) for the Alaska North Slope region at wind speeds of 2 and 5 m/s.

Property: MASS BALANCE
Oil Type: NORTH STAR
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2002), Weathering dat

SINTEF Applied Chemistry
2.0

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

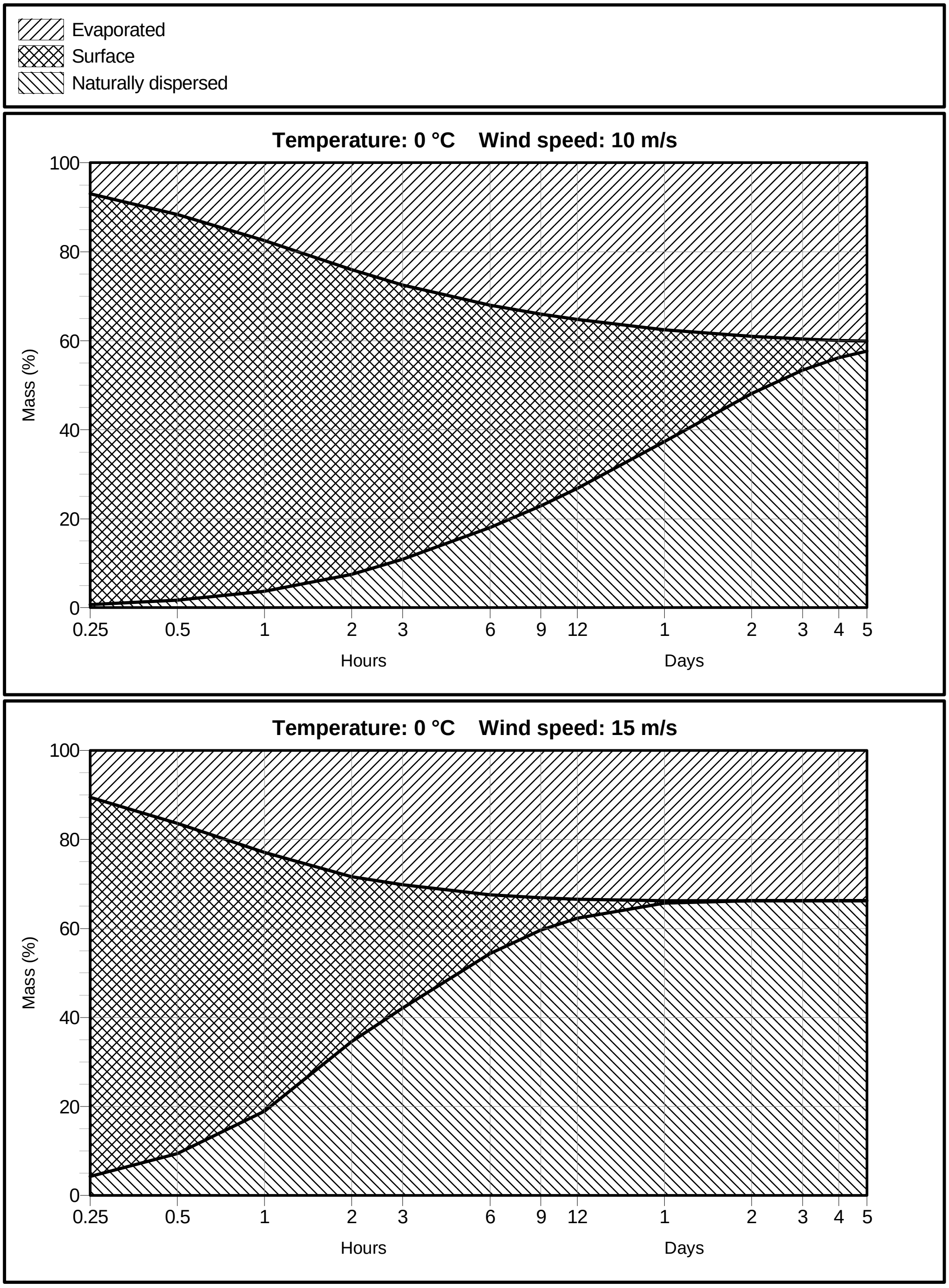


Figure 2.29: The mass balance for the North Star oil at the mean winter temperature (0°C) for the Alaska North Slope region at wind speeds of 10 and 15 m/s.

Property: MASS BALANCE
Oil Type: NORTH STAR
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2002), Weathering dat

SINTEF
Applied Chemistry

2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002

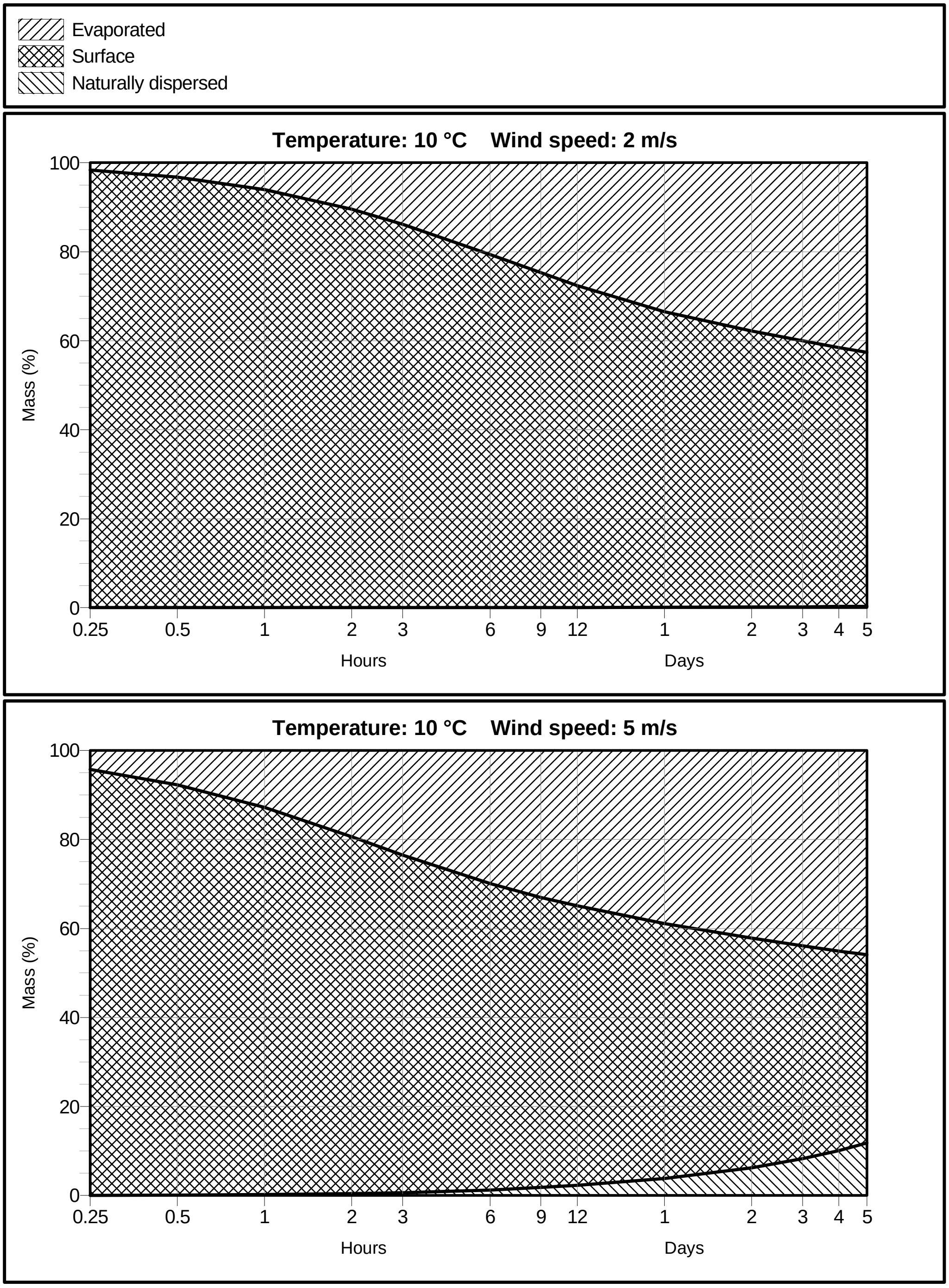


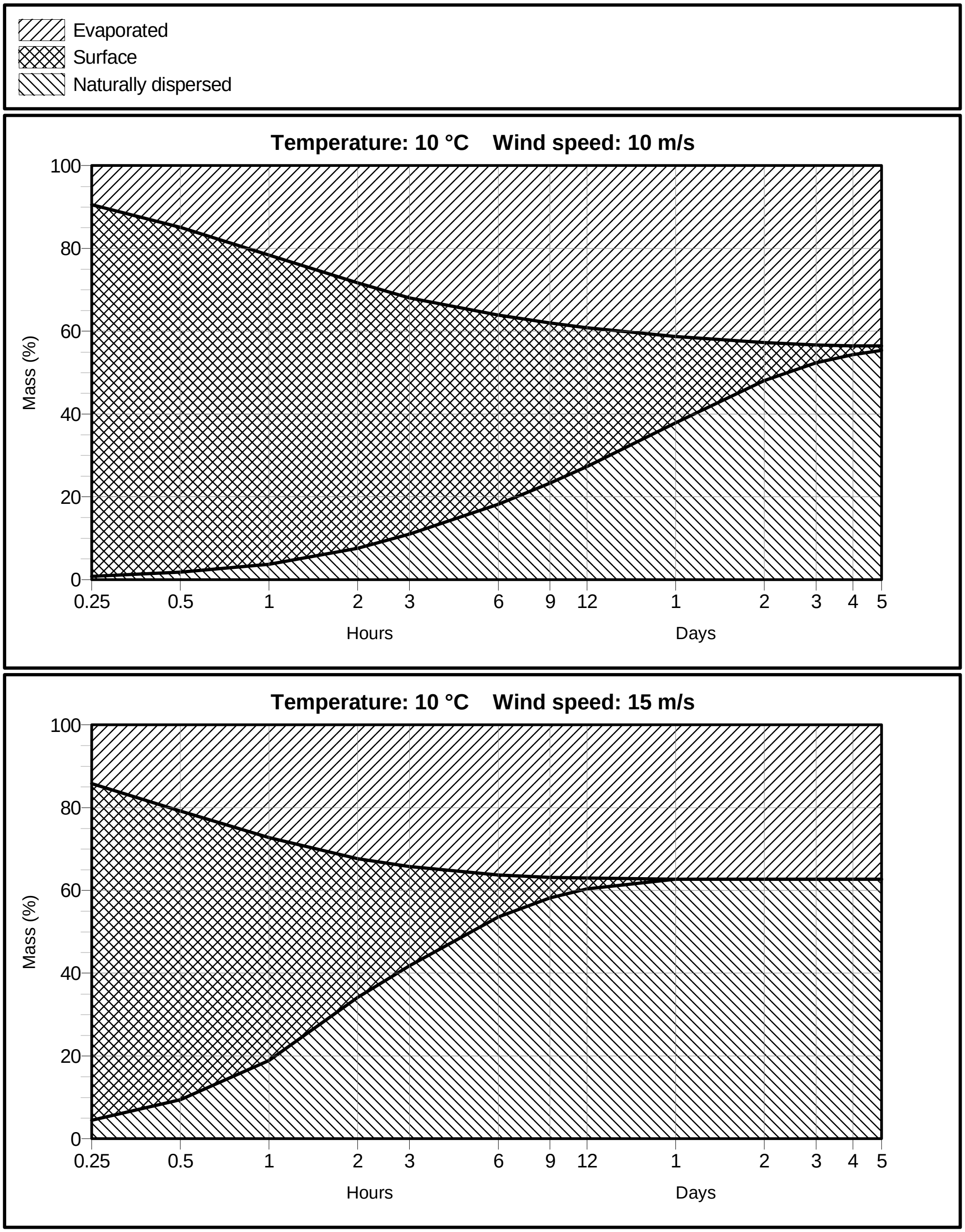
Figure 2.30: The mass balance for the North Star oil at the mean summer temperature (10 °C) for the Alaska North Slope region at wind speeds of 2 and 5 m/s.

Property: MASS BALANCE
Oil Type: NORTH STAR
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2002), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 13, 2002



The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Figure 2.31: The mass balance for the North Star oil at the mean summer temperature (10 °C) for the Alaska North Slope region at wind speeds of 10 and 15 m/s.

2.6 Prediction charts for Gulf of Mexico oils

2.6.1 Prediction charts and summary of the Neptune Field Composite's weathering properties at sea

Detailed information of the Neptune Field Composite sample

Area/block:	VK 826
MMS Structure name:	A
Sample date:	14. November 2000
Sample number:	DGM 5870
Common field name:	Neptune
Field/unit:	VK 825
Company name:	Kerr-McGee
MMS Platform ID:	VK 826A

Composite sample from the following API well numbers:
Well A-1 through A-10, A-12st, 825-4, 825-5 and 826-12.

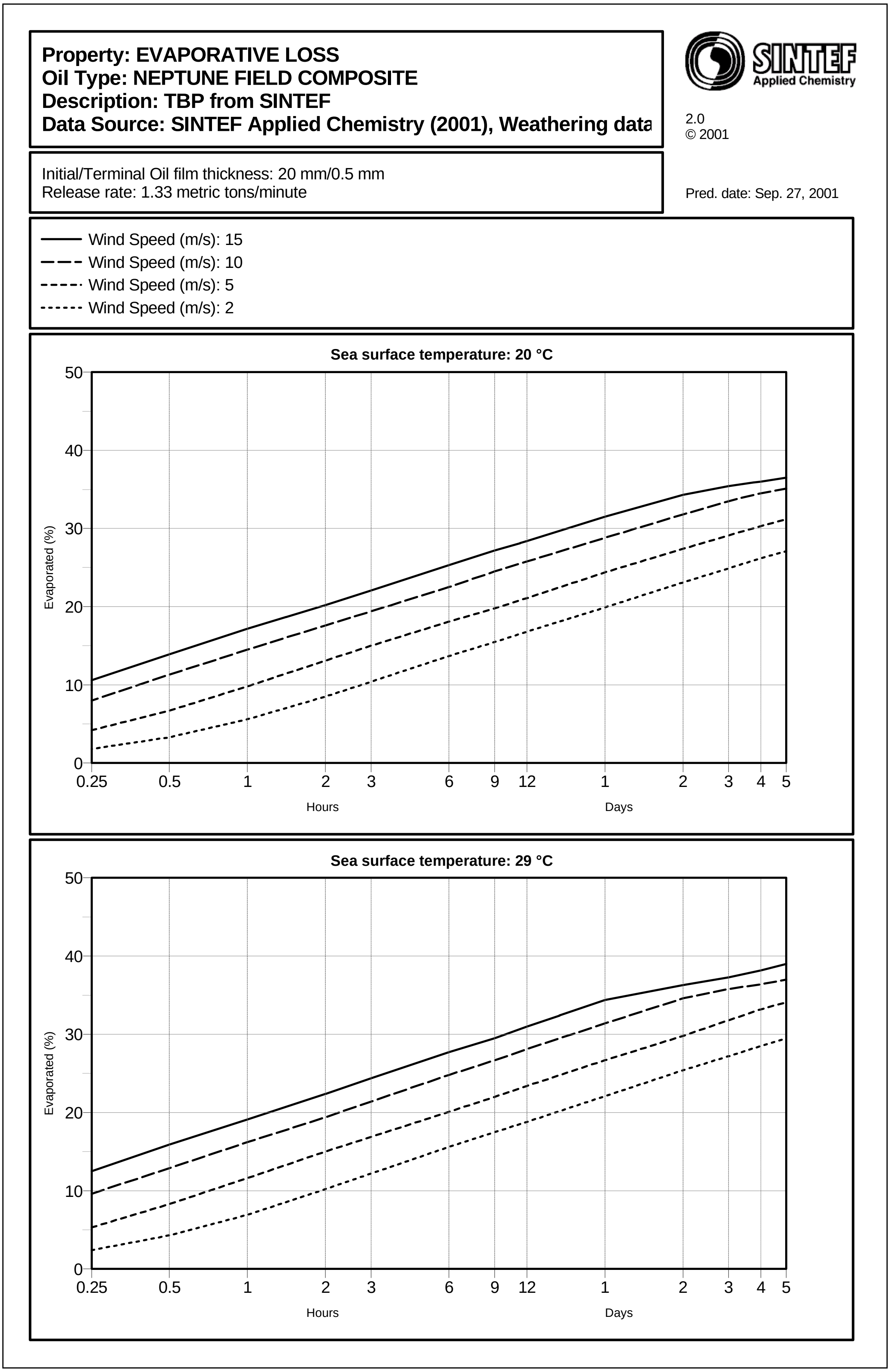
Summary of the Neptune Field Composite's weathering properties at sea

The Neptune Field Composite is a paraffinic crude oil, with a density of 0,869 g/mL. The Neptune Field Composite contains a relatively large amount of lower molecular weight compounds and over 30 % of its original volume will be evaporated 24 hours after the spill at both summer and winter temperatures. The wax content of the Neptune Field Composite is medium (~ 4 wt%). The fresh oil has a pour point of -9°C and increases with weathering to approximately 15°C at a wind speed of 10 m/s.

The experimental results showed that the Neptune Field Composite did not form stable w/o-emulsions. One normally would expect that a crude oil with a wax and asphalthene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production/process chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This suspicion is supported by the un-normal low interfacial tension value measured for the fresh crude (6 mN/m). SINTEF proposes that MMS inquire if offshore chemicals are present in this crude oil sample, and that a follow up study of an untreated oil should be discussed based on the findings.

The viscosity of the Neptune Field Composite only exceeds the lower viscosity limit for an effective mechanical response (1000 cP at shear rate $10s^{-1}$) after 5 days. The viscosity will not increase drastically with weathering since the Neptune Field Composite does not form stable w/o-emulsions on the sea surface. The initial spill volume will not increase significantly and the Neptune Field Composite will most likely spread quickly on the sea surface. In a mechanical clean up operation the Neptune Field Composite may have a significant degree of leakage from the oil spill boom due to the oils low viscosity (< 1000 cP) (Nordvik *et.al.* 1992), even after several days of weathering on the sea surface. Chemical dispersion may be a possible response operation since the viscosity and pour point of the Neptune Field Composite are low, however, this was not investigated in this study.

The prediction charts for the weathering of the Neptune Field Composite at sea are given in Figures 2.32 to 2.35. The mass balance for the Neptune Field Composite at the mean summer and winter temperatures in the GOM region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figures 2.36 to 2.40. These figures illustrate that the natural dispersion process of the Neptune Field Composite is high (at wind speeds above 10 m/s) due to the low viscosity and that the oil does not form stable w/o-emulsions (i. e. the Neptune Field Composite will have a short lifetime on the sea surface).



Property: EVAPORATIVE LOSS
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

SINTEF Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 27, 2001

Figure 2.32: The predicted evaporative loss for the Neptune Field Composite at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

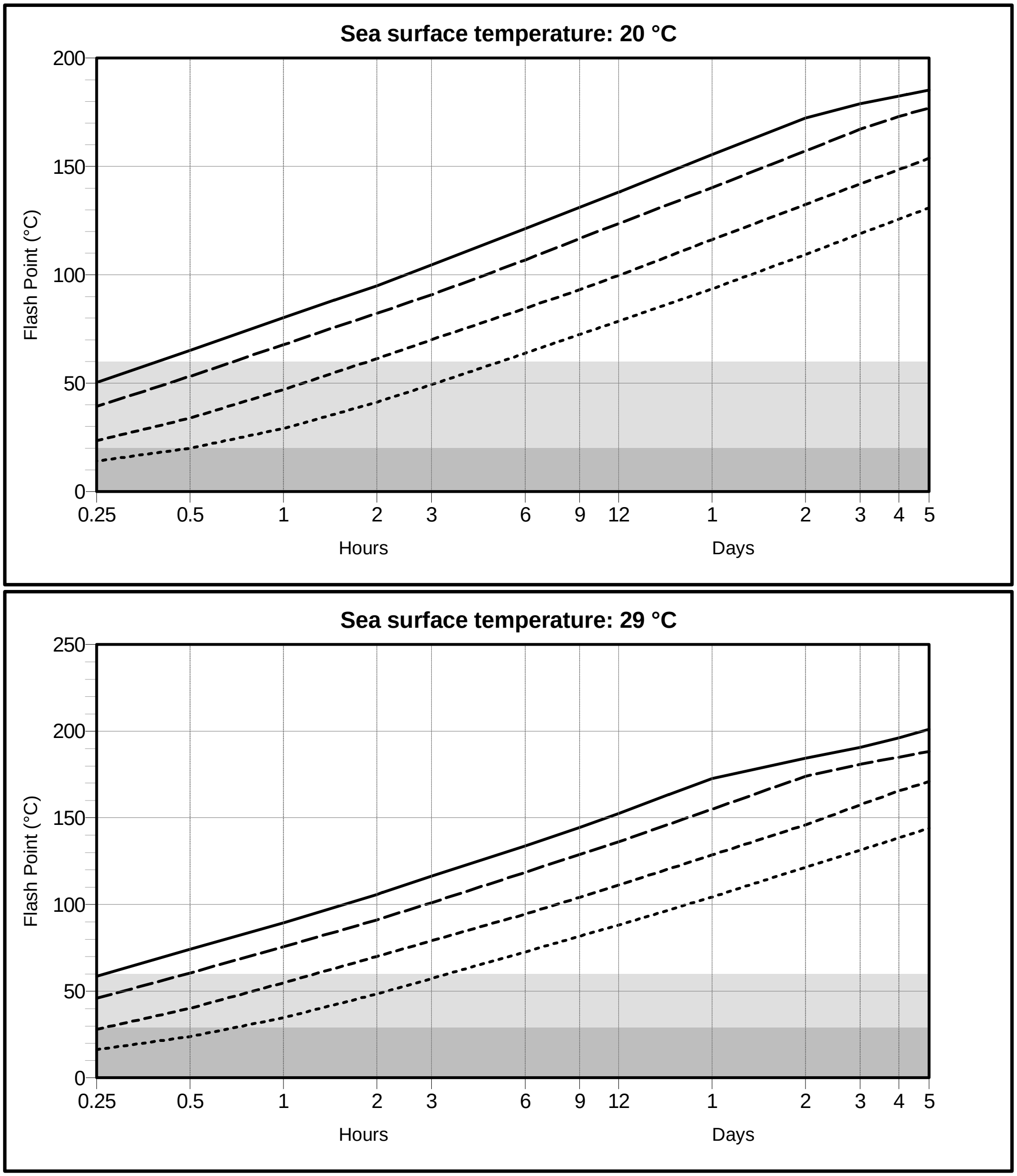
Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

SINTEF Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

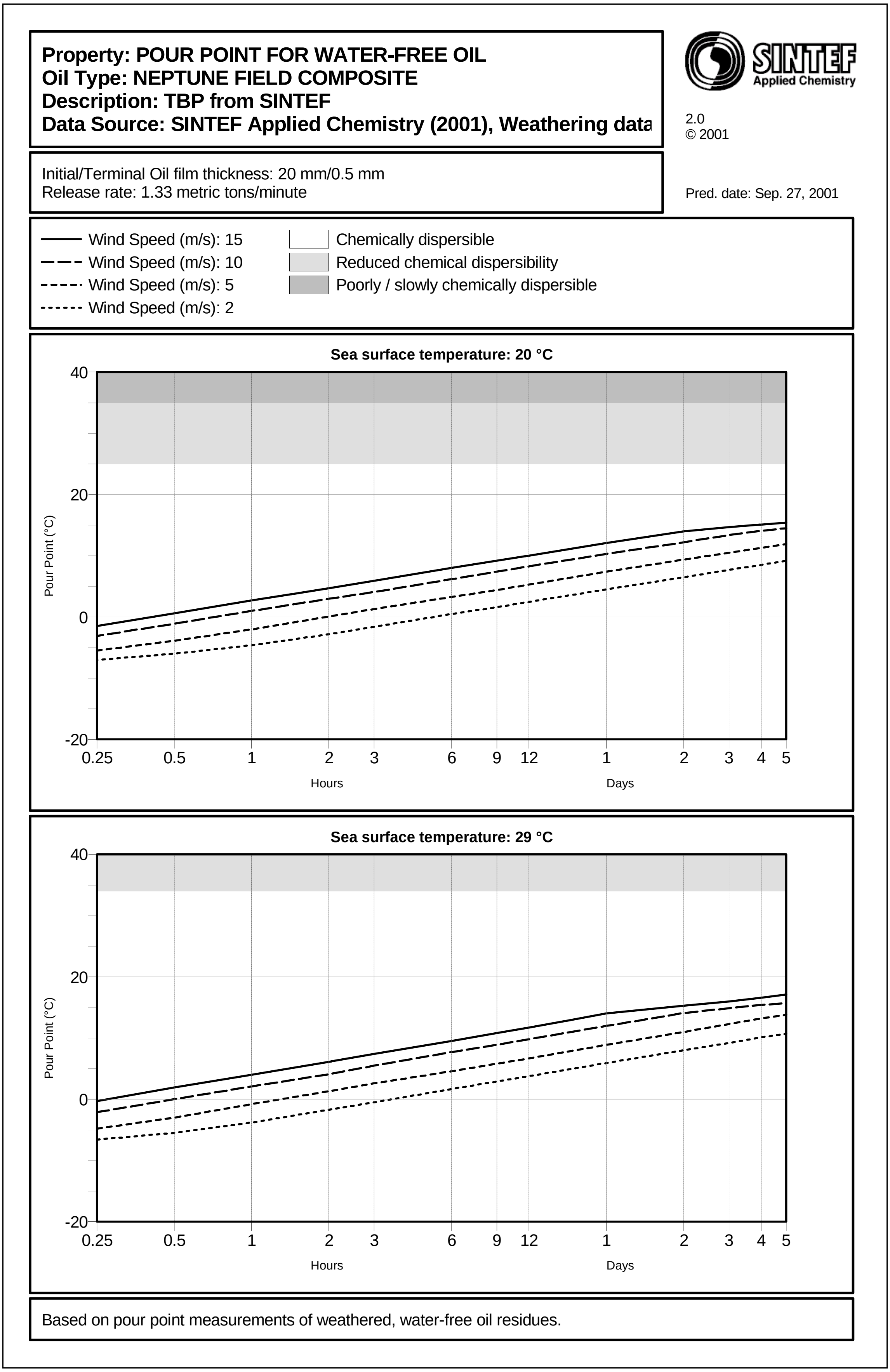
Pred. date: Sep. 13, 2002

——— Wind Speed (m/s): 15	☐ No fire hazard
— — — Wind Speed (m/s): 10	▨ Fire hazard in tankage (<60 °C)
- - - - - Wind Speed (m/s): 5	■ Fire hazard at sea surface (below sea temperature)
······ Wind Speed (m/s): 2	



Based on flash point measurements of weathered, water-free oil residues.

Figure 2.33: The Flash point for water-free Neptune Field Composite at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 27, 2001

Based on pour point measurements of weathered, water-free oil residues.

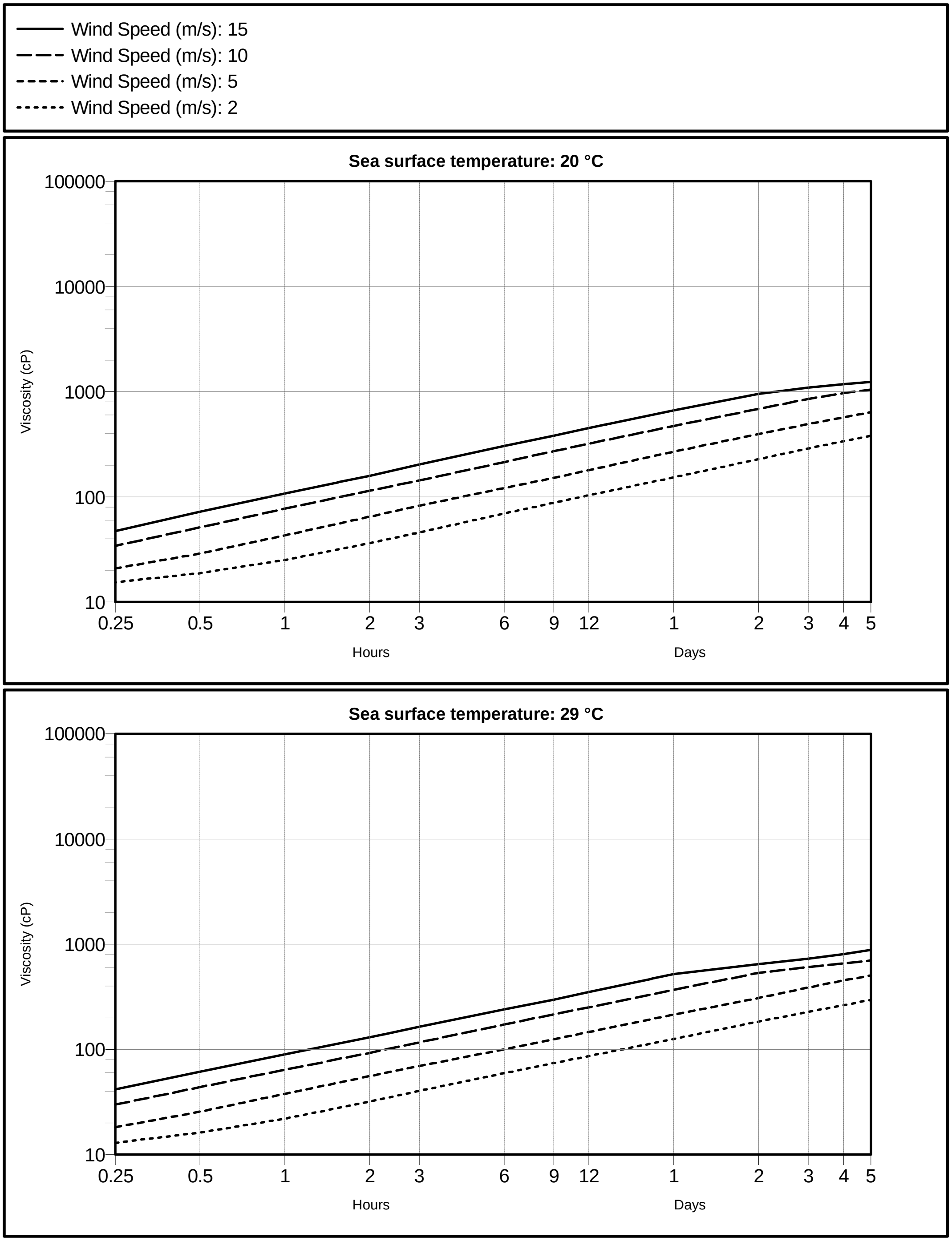
Figure 2.34: The predicted pour point for the Neptune Field Composite at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

Property: VISCOSITY FOR WATER-FREE OIL
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry
2.0
© 2001

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Sep. 27, 2001



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.35: The predicted viscosity for water-free Neptune Field Composite at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

Property: MASS BALANCE
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

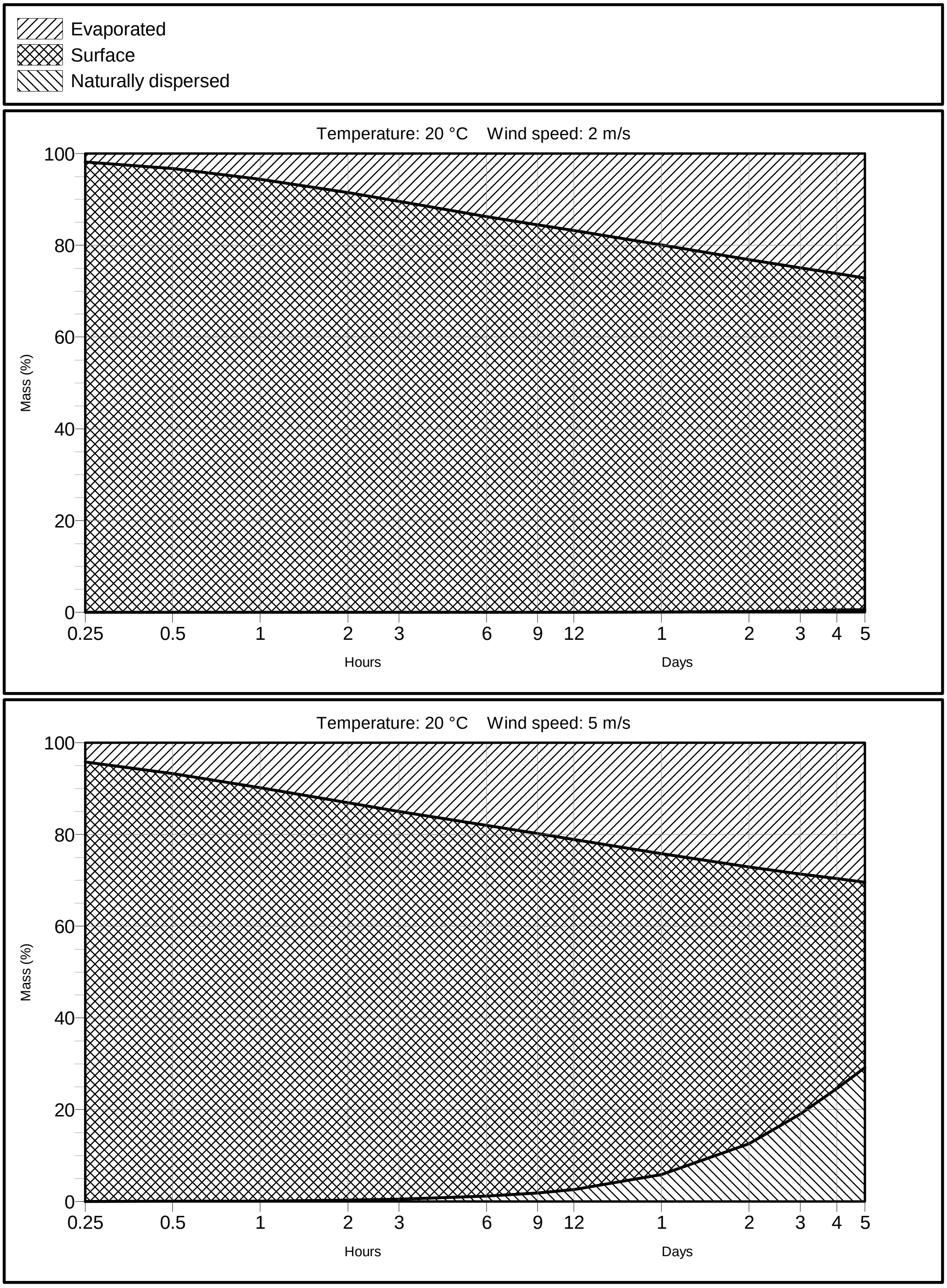
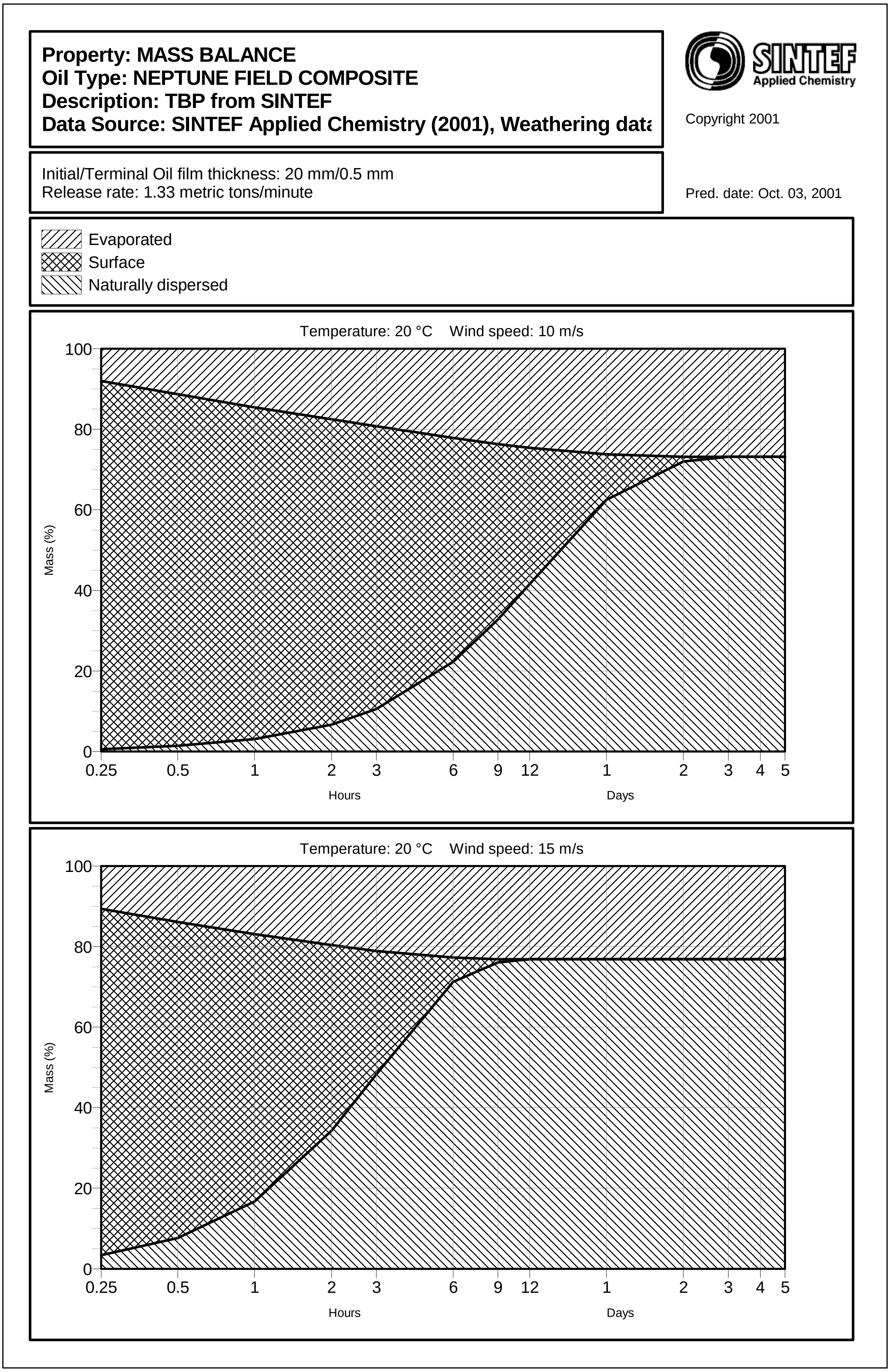


Figure 2.36: The mass balance for the Neptune Field Composite at the mean winter temperature (20°C) for the GOM region at wind speeds of 2 and 5 m/s.



Property: MASS BALANCE
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

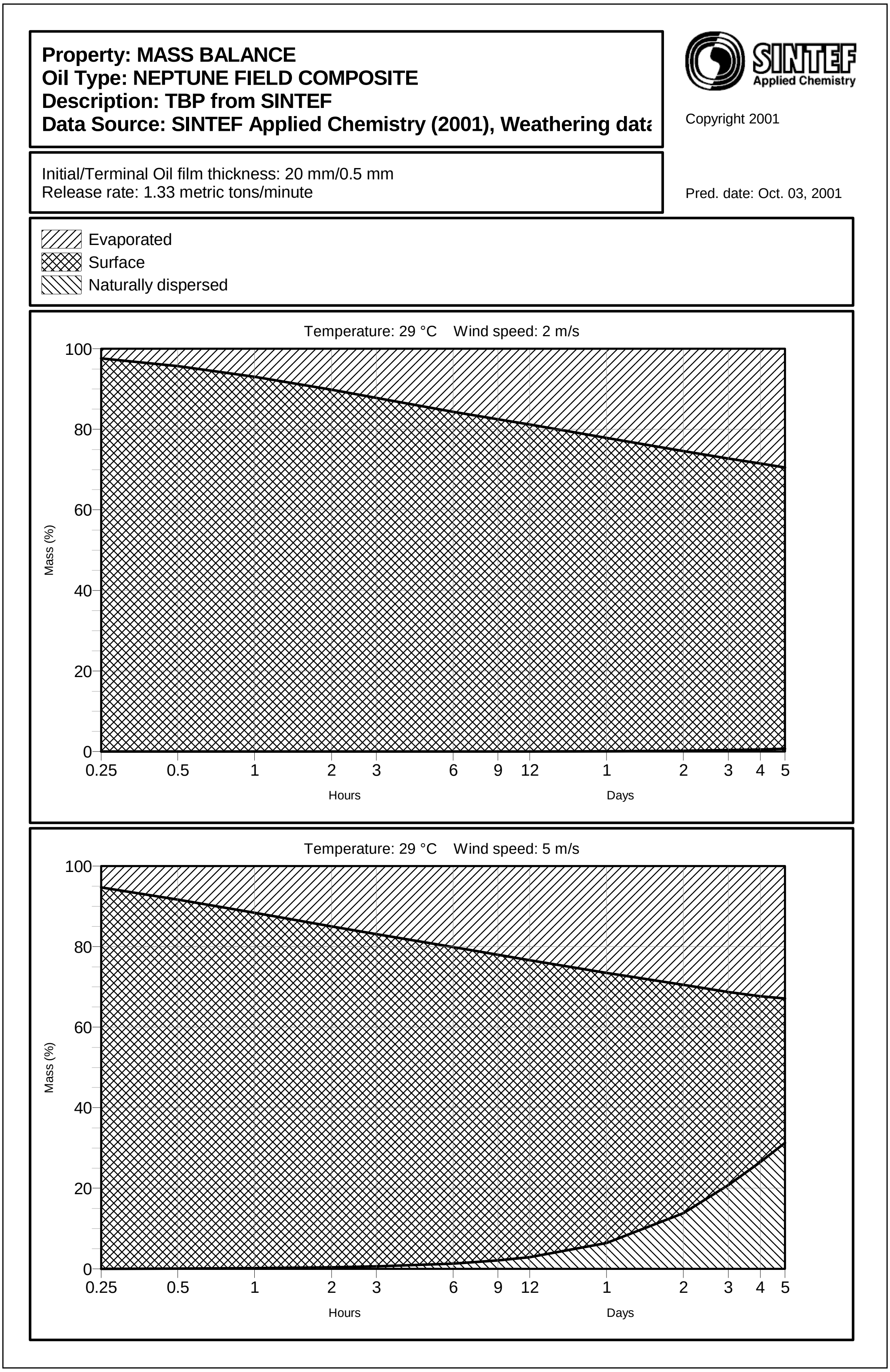
SINTEF Applied Chemistry

Copyright 2001

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

Figure 2.37: The mass balance for the Neptune Field Composite at the mean winter temperature (20°C) for the GOM region at wind speeds of 10 and 15 m/s.



Property: MASS BALANCE
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

Applied Chemistry

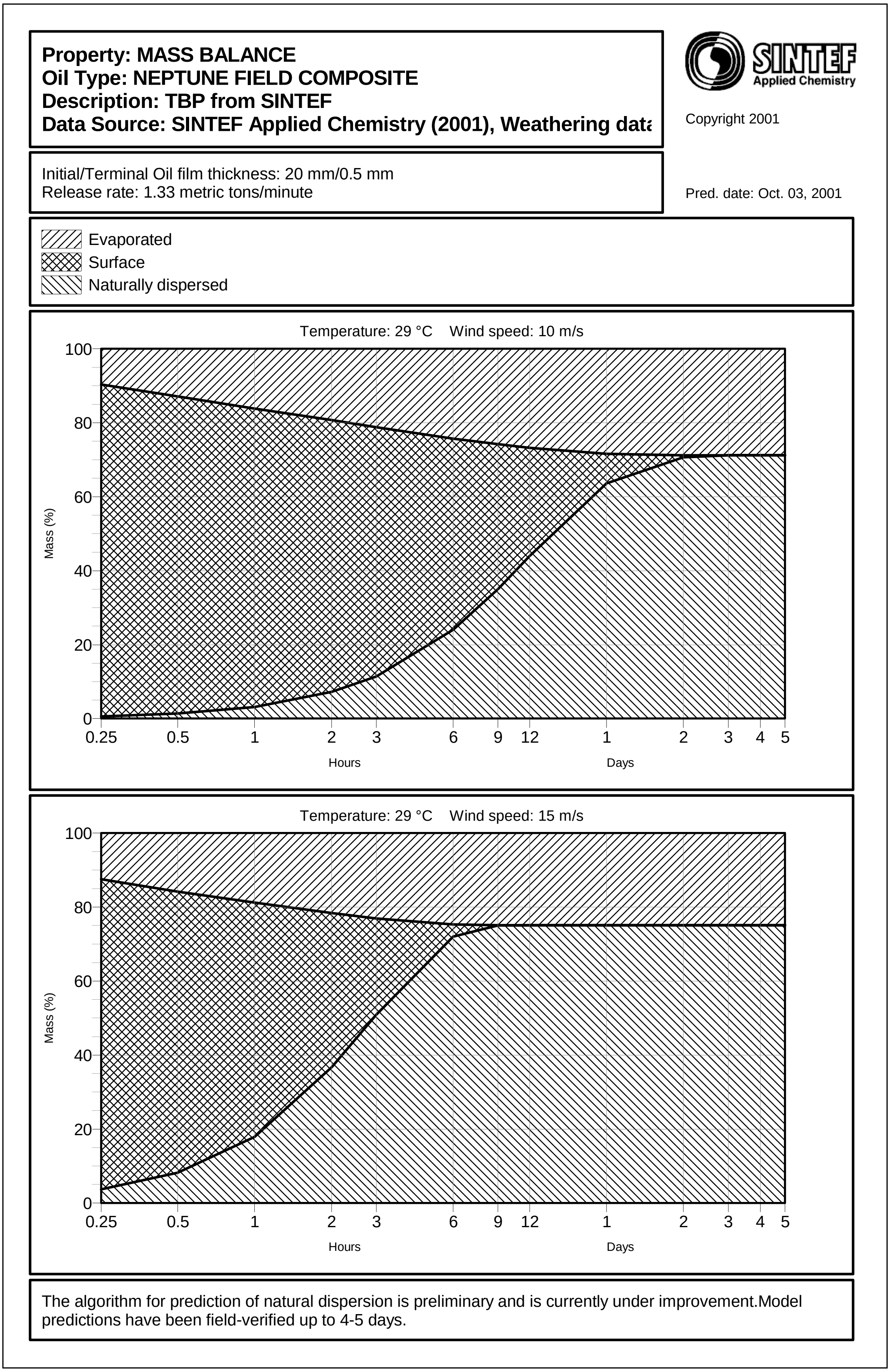
Copyright 2001

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Figure 2.38: The mass balance for the Neptune Field Composite at the mean summer temperature (29 °C) for the GOM region at wind speeds of 2 and 5 m/s.



Property: MASS BALANCE
Oil Type: NEPTUNE FIELD COMPOSITE
Description: TBP from SINTEF
Data Source: SINTEF Applied Chemistry (2001), Weathering data

SINTEF Applied Chemistry

Copyright 2001

Initial/Terminal Oil film thickness: 20 mm/0.5 mm
Release rate: 1.33 metric tons/minute

Pred. date: Oct. 03, 2001

- ▨ Evaporated
- ▩ Surface
- ▧ Naturally dispersed

The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

Figure 2.39: The mass balance for the Neptune Field Composite at the mean summer temperature (29°C) for the GOM region at wind speeds of 10 and 15 m/s.

2.6.2 Prediction charts and summary of the High Island Composite's weathering properties at sea

Detailed information of the High Island oil sample

Area/block:	High Island Block A573
MMS structure name:	A
Sample date:	December 8, 2000
Sample number:	DGM 6013
Common field name:	none
Field name:	HIA573A
Company name:	UNOCAL
Well number:	A006
API well number:	427094016200

Composite sample from the following API well numbers:
Well A-1 through A-10, A-12st, 825-4, 825-5 and 826-12.

Summary of the High Island oil's weathering properties at sea

The High Island oil were emulsified at arrival (~15%). Water was removed by leaving the emulsion at rest for approximately a month in a 10 litre flask. At this time the oil/emulsion had formed a gradient with no water in the top layers of the flask increasing to an emulsion of 80%water in the bottom of the flask. The water free upper layer of the flask was used in the further weathering study. The meso-scale flume experiment, however, was performed on the emulsion as delivered, and yield supplementary data as input to the OWM.

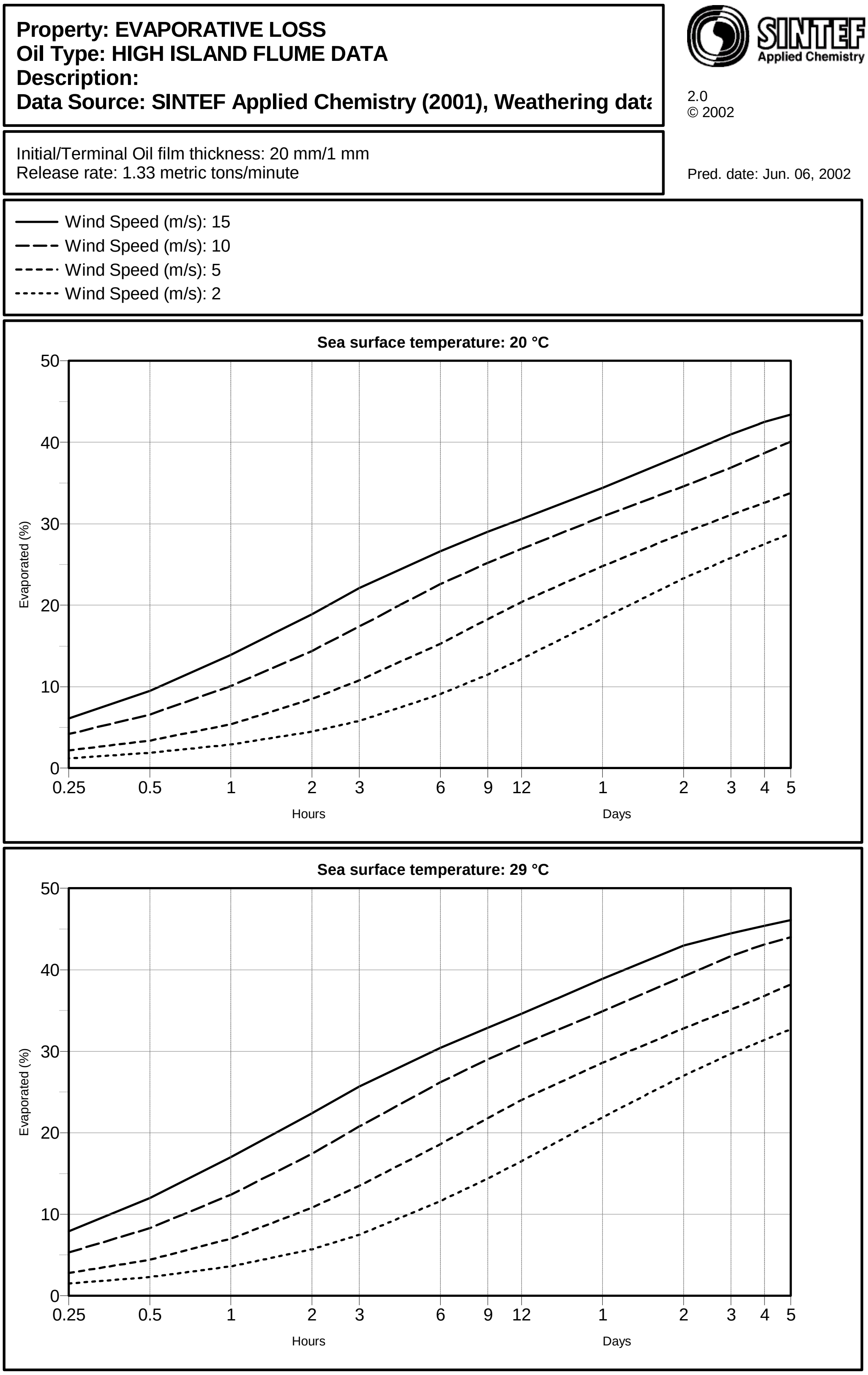
The High Island oil is a naphthenic crude oil, with a density of approximately 0.85 g/mL. The High Island oil contains medium amount of lower molecular weight compounds and over 20 % of its original volume will evaporate 24 hours after the spill at both summer and winter temperatures. The wax content of the High Island oil is low (1.6 wt%). and the pour point for the High Island oil is also low (–16°C for the fresh crude).

Results from the meso scale flume shows that High Island oil form unstable emulsions with low viscosity. Maximum water content is high at 70%, but observations from the meso scale flume shows that emulsions dehydrate almost completely within an hour when left at rest (e.g. in a tank).

A viscosity of 1000 cP is considered to be lower limit for efficient mechanical oil recovery. This is due to leakage under the oil booms at lower viscosities (Nordvik *et.al.* 1992). The High Island oil will have viscosities below this limit for at least four days of weathering at the sea surface, and problems with leakage under the boom could be expected during recovery.

No laboratory study is performed to assess the window of opportunity for the use of chemical dispersants. However, dispersibility testing in the meso scale flume shows fairly good dispersibility after 3 days of weathering in the flume basin. Natural dispersion is high at high wind speeds and the slick will have an estimated lifetime of 12 hours and 3 days respectively for 15 m/s and 10 m/s wind speed. For lower win speeds the slick will be persistent on the sea surface, and the lifetime will exceed 5 days.

The prediction charts for the weathering of the High Island oil at sea are given in Figures 2.40 to 2.44. The mass balance for the High Island oil at the mean summer and winter temperatures in the GOM region at different wind speeds (2, 5, 10 and 15 m/s) are given in Figures 2.45 to 2.48.



Property: EVAPORATIVE LOSS
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Jun. 06, 2002

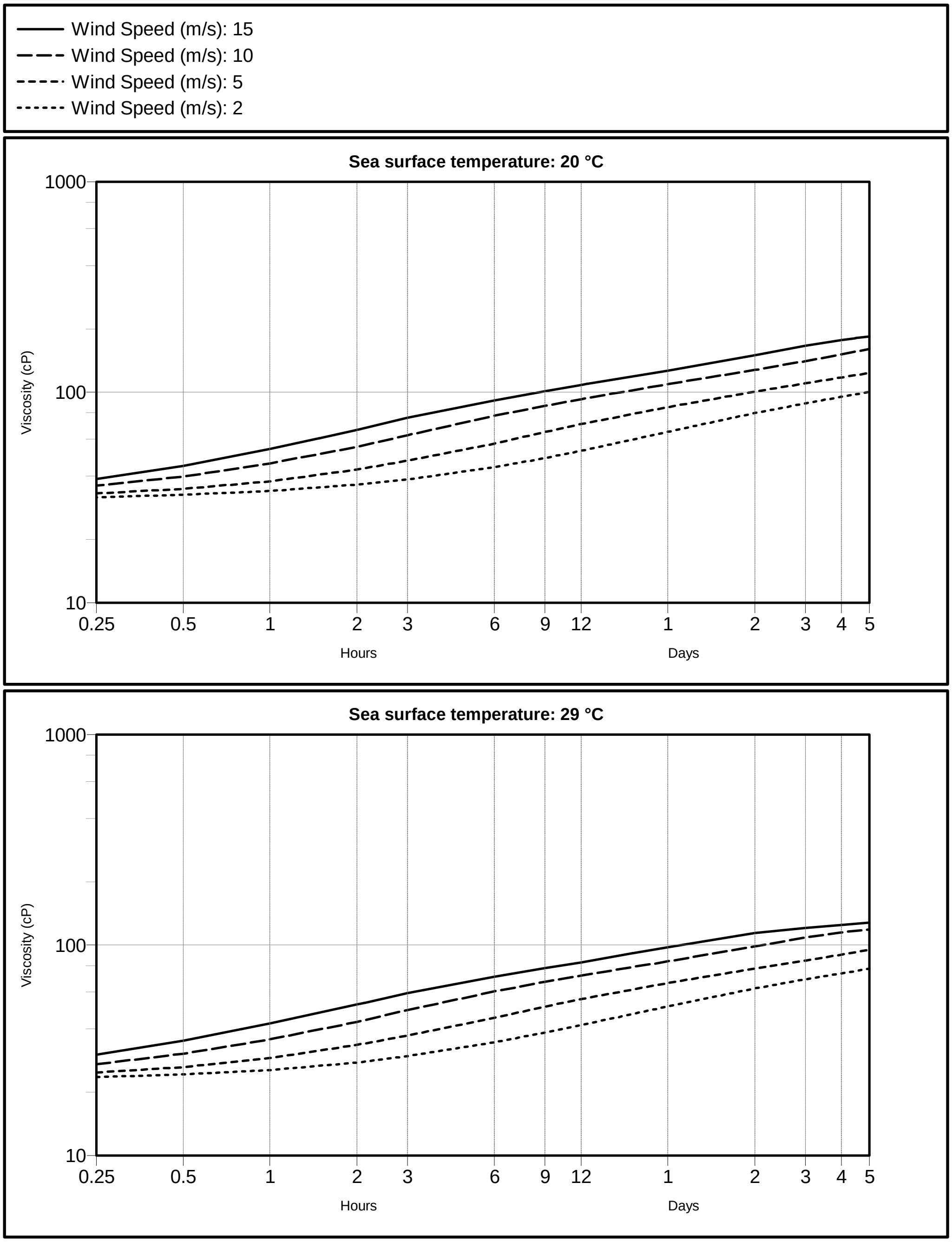
Figure 2.40: The predicted evaporative loss for the High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

Property: VISCOSITY FOR WATER-FREE OIL
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Jun. 06, 2002



Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.41: The predicted viscosity for water-free High Island oil at the mean summer (29℃) and winter (20℃) temperatures for the GOM region.

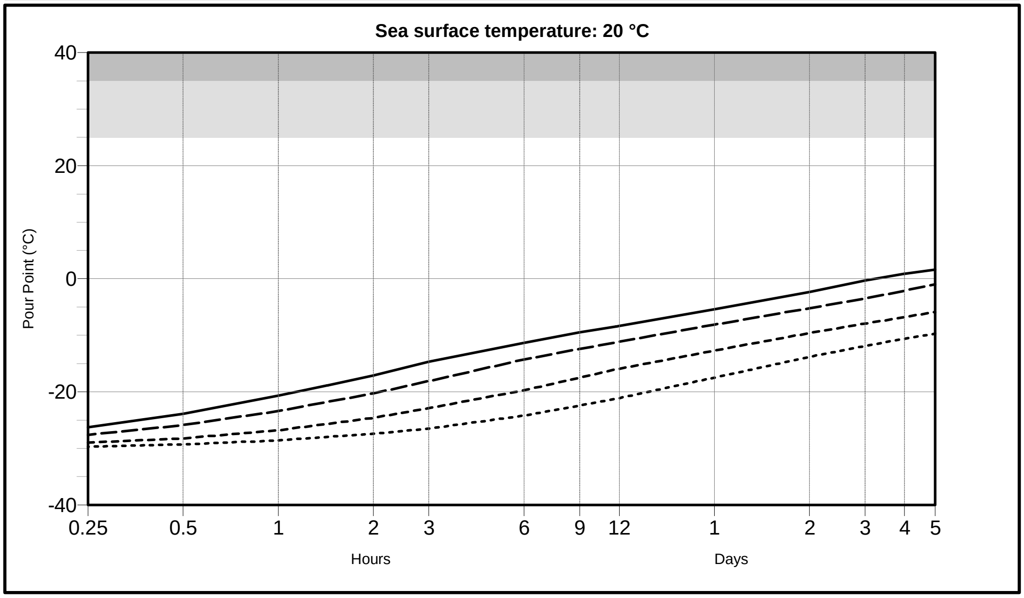
Property: POUR POINT FOR WATER-FREE OIL
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

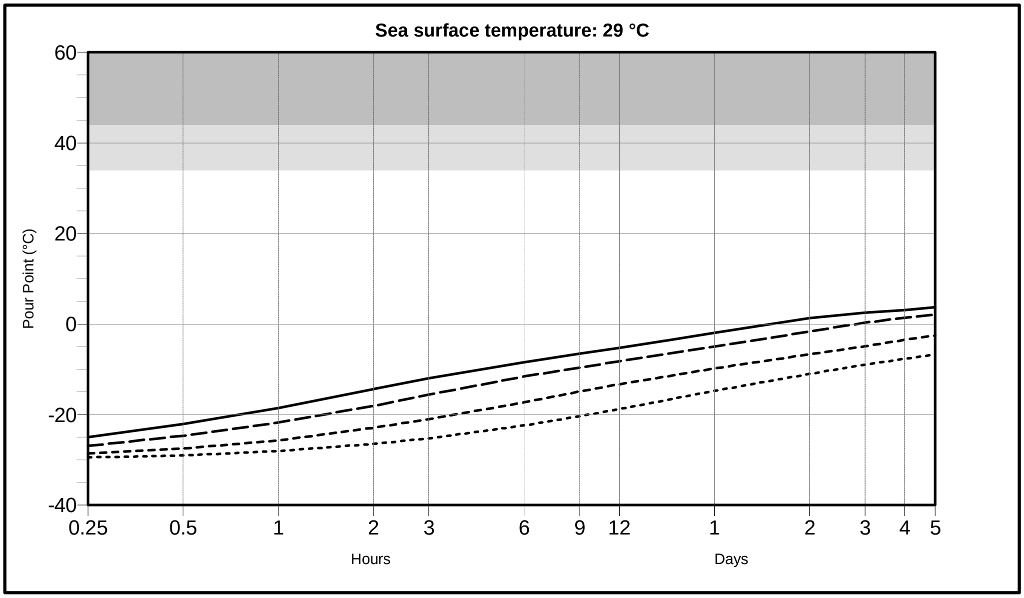
SINTEF Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Jun. 06, 2002

—— Wind Speed (m/s): 15	☐ Chemically dispersible
— — Wind Speed (m/s): 10	▨ Reduced chemical dispersibility
- - - - Wind Speed (m/s): 5	▩ Poorly / slowly chemically dispersible
······ Wind Speed (m/s): 2	





Based on pour point measurements of weathered, water-free oil residues.

Figure 2.42: The predicted pour point for water-free High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

Property: WATER CONTENT
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Nov. 10, 2002

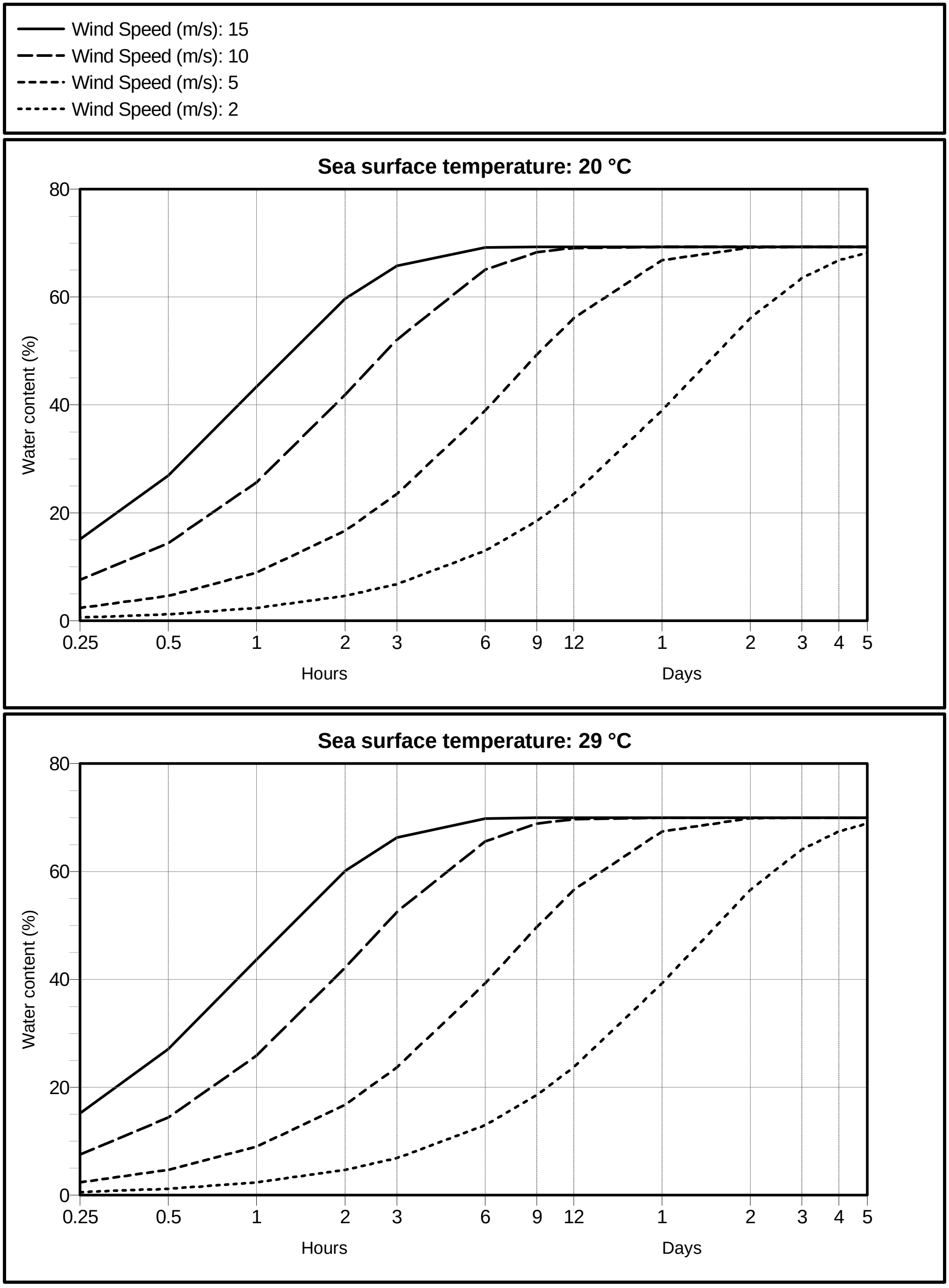
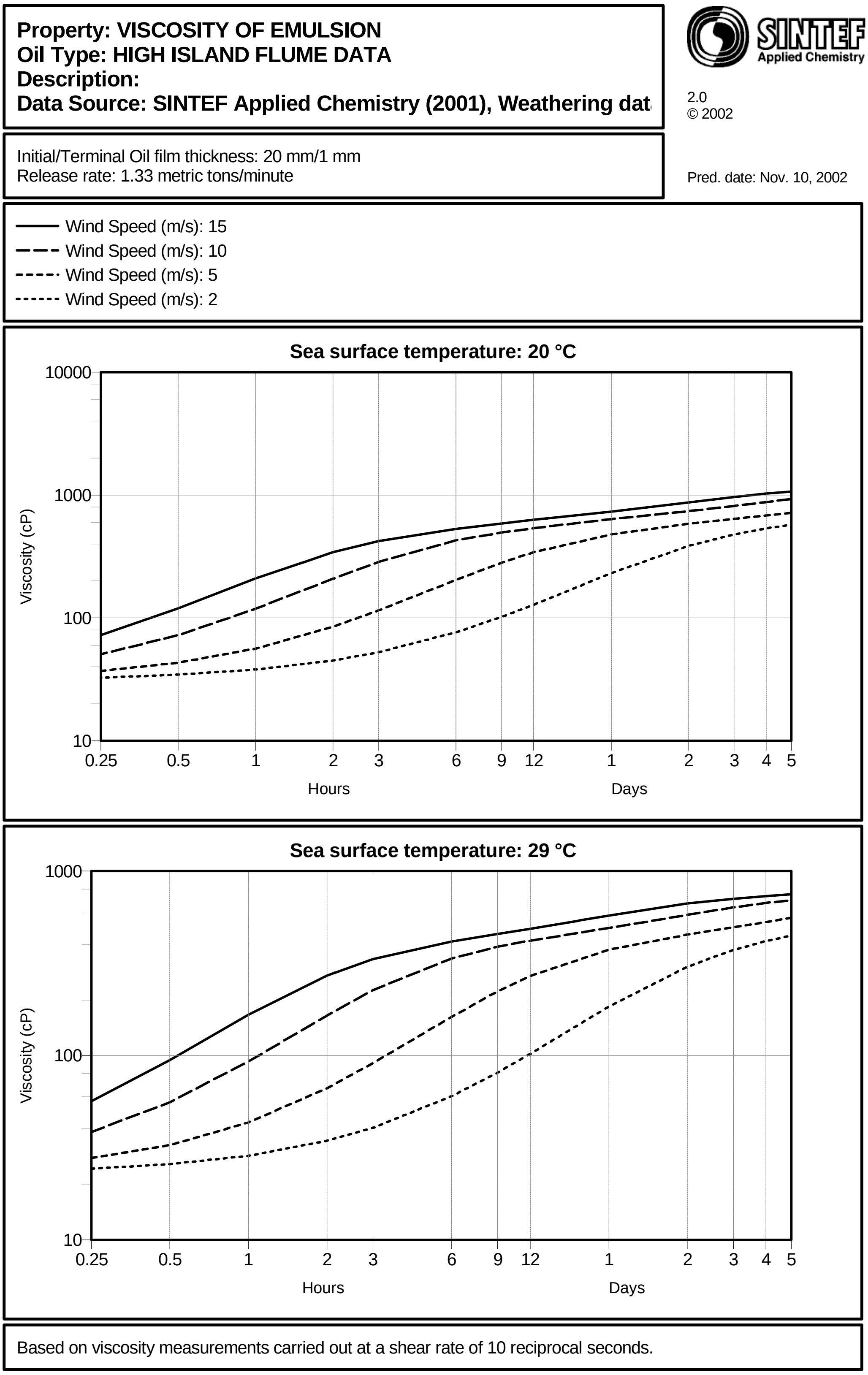


Figure 2.43: The predicted water uptake for High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.



Property: VISCOSITY OF EMULSION
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Nov. 10, 2002

——— Wind Speed (m/s): 15
– – – Wind Speed (m/s): 10
- - - - Wind Speed (m/s): 5
······ Wind Speed (m/s): 2

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 2.44: The predicted emulsion viscosity for High Island oil at the mean summer (29°C) and winter (20°C) temperatures for the GOM region.

Property: MASS BALANCE
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

SINTEF Applied Chemistry

2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Nov. 10, 2002

▨ Evaporated
▩ Surface
▧ Naturally dispersed

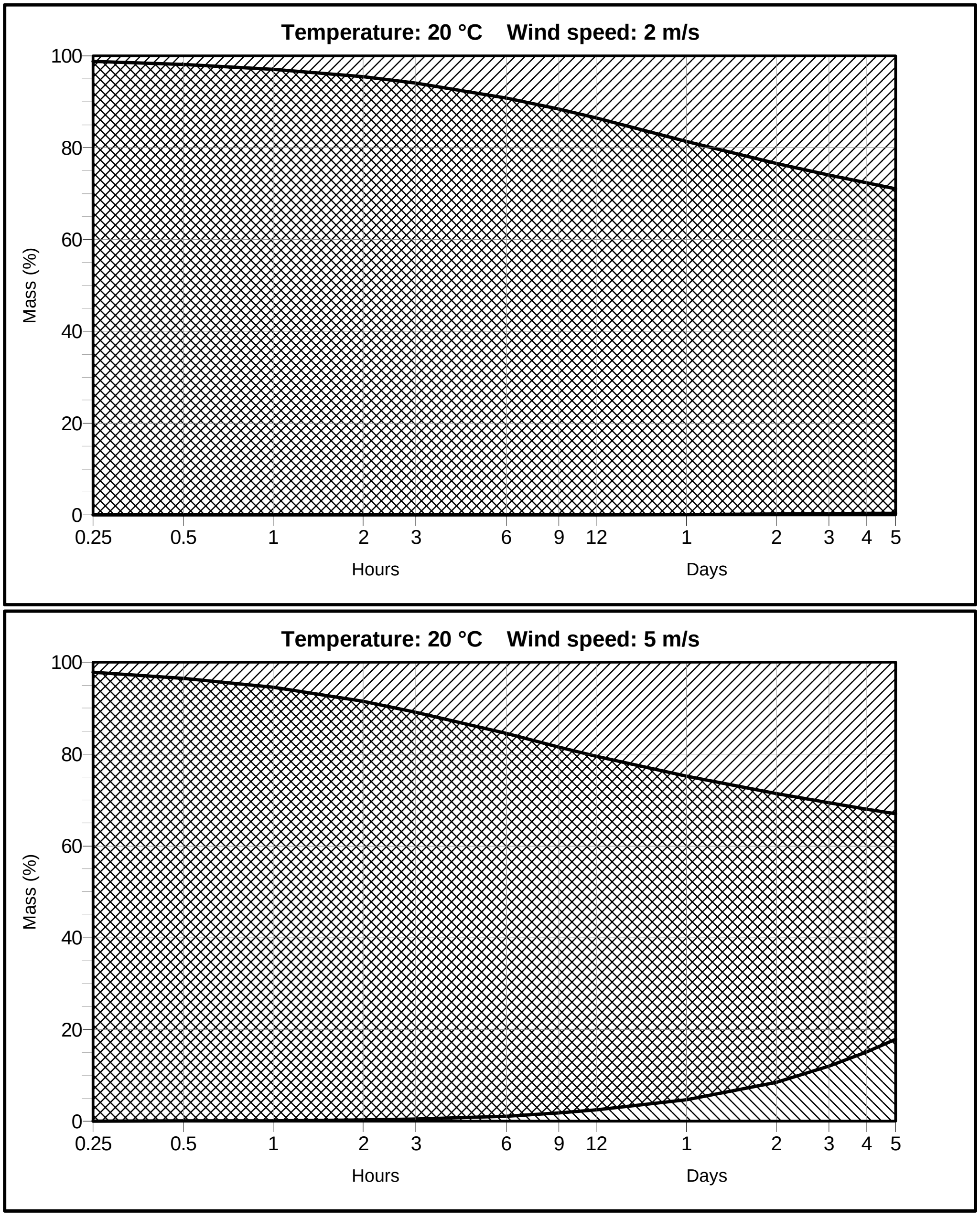


Figure 2.45: The mass balance for the High Island oil at the mean winter temperature (20°C) for the GOM region at wind speeds of 2 and 5 m/s.

Property: MASS BALANCE
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

SINTEF Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Nov. 10, 2002

▨ Evaporated
▦ Surface
▧ Naturally dispersed

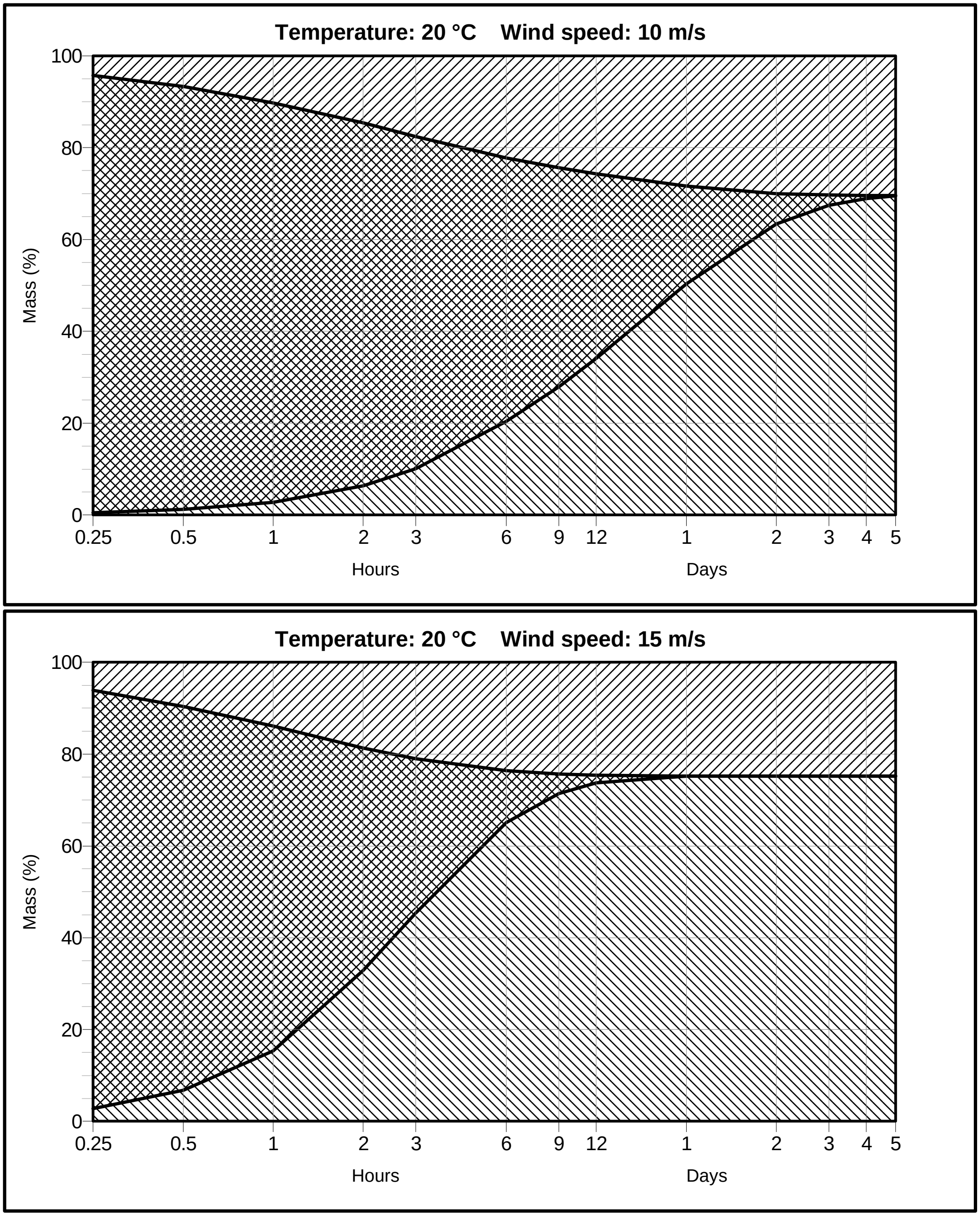
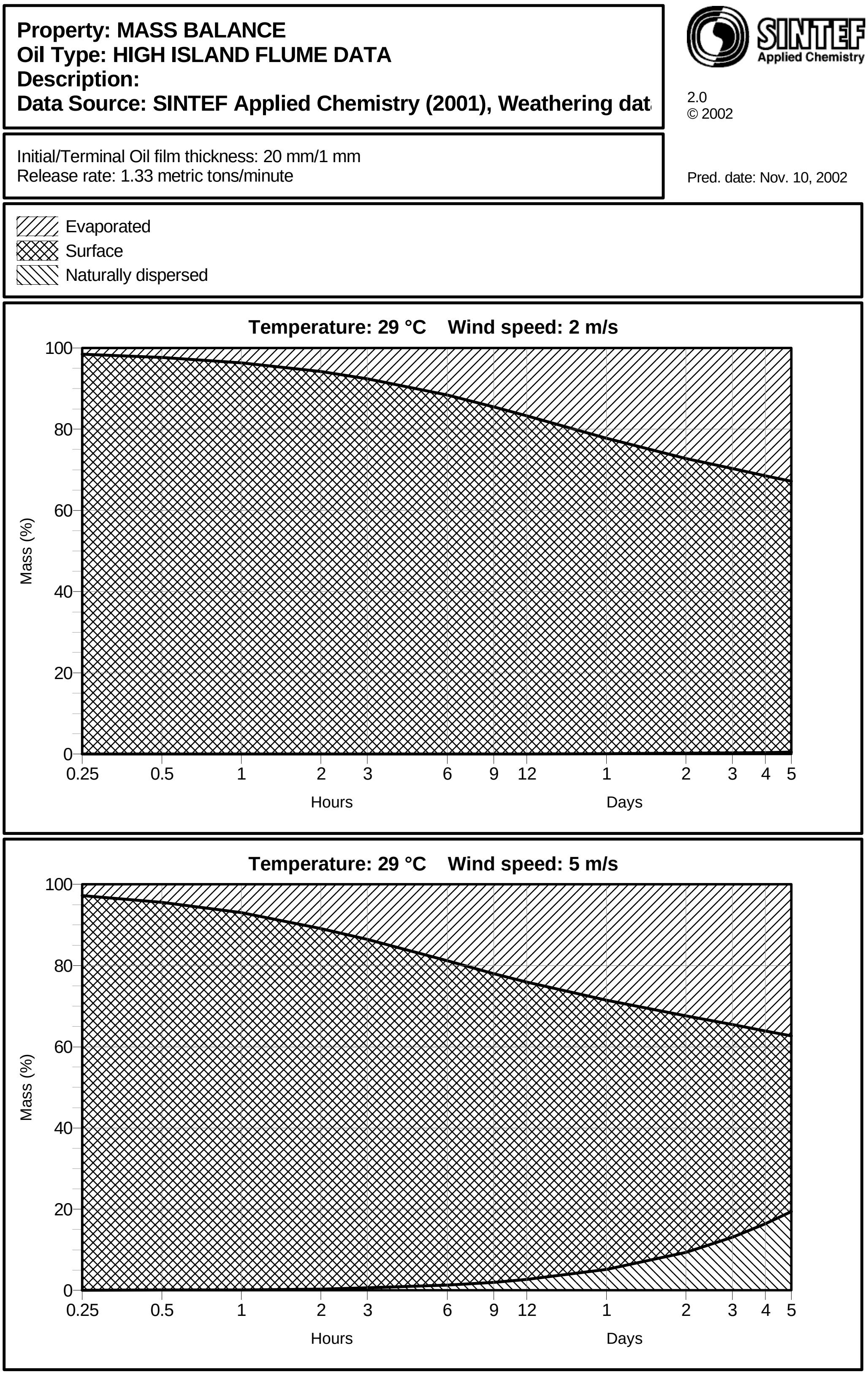


Figure 2.46: The mass balance for the High Island oil at the mean winter temperature (20°C) for the GOM region at wind speeds of 10 and 15 m/s.



Property: MASS BALANCE
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Nov. 10, 2002

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Figure 2.47: The mass balance for the High Island oil at the mean summer temperature (29°C) for the GOM region at wind speeds of 2 and 5 m/s.

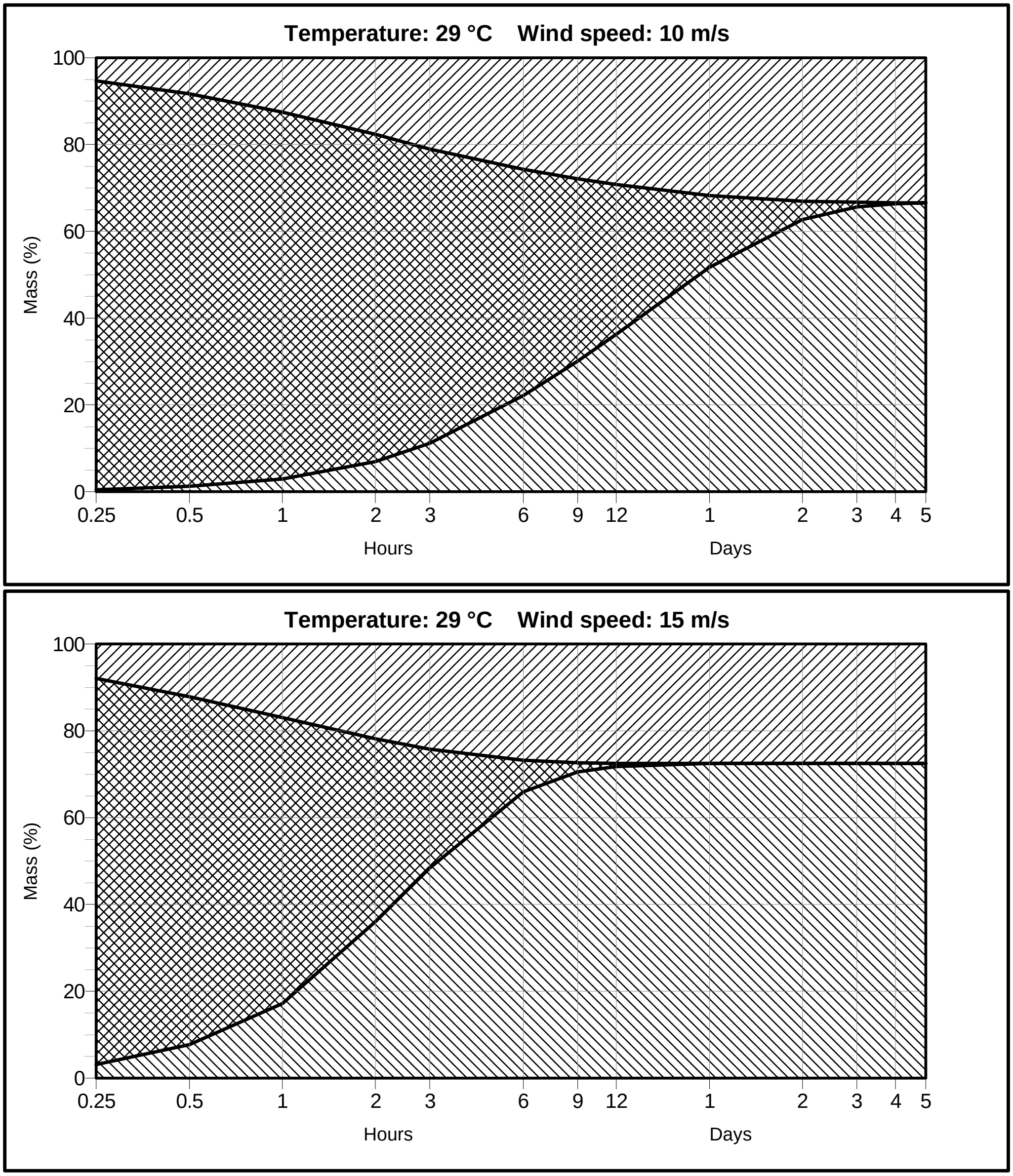
Property: MASS BALANCE
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering dat

SINTEF Applied Chemistry
2.0
© 2002

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

Pred. date: Nov. 10, 2002

▨ Evaporated
▩ Surface
▧ Naturally dispersed



The algorithm for prediction of natural dispersion is preliminary and is currently under improvement.Model predictions have been field-verified up to 4-5 days.

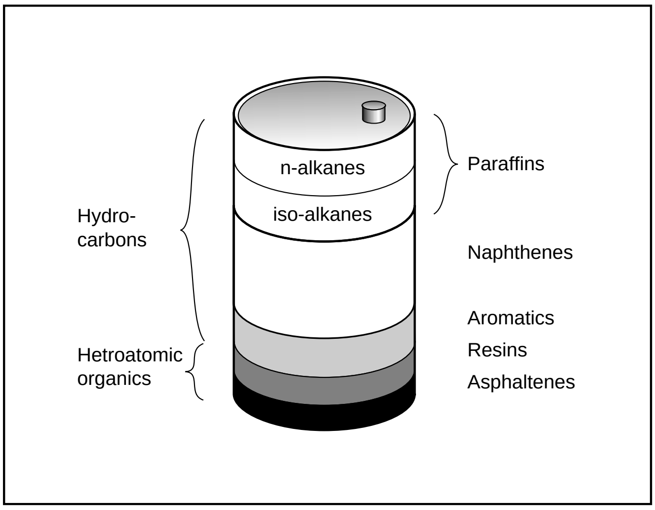
Figure 2.48: The mass balance for the High Island oil at the mean summer temperature (29°C) for the GOM region at wind speeds of 10 and 15 m/s.

.

Appendix A: The behavior of crude oils on the sea surface

A1 The chemical composition of crude oils

Crude oil is a complex mixture of thousands of chemical components. The relative compositions vary, giving rise to crude oils with different chemical and physical properties. The components found in crude oil are classified into two main chemical groups, these are hydrocarbons and heteroatomic organics, see Figure A1.



6621/handboker/grafisk/fig-eng/crudeoil2.eps

Figure A1: The chemical composition of crude oil.

A1.1 Hydrocarbons

The majority of compounds in crude oil are hydrocarbons. Hydrocarbons are compounds that contain carbon (C) and hydrogen (H) and include both saturated and unsaturated molecules in linear, branched and cyclic configurations. Volatile gases, such as methane (CH_4) as well as complex molecules containing more than one hundred carbon atoms ($C_{>100}$) are included in this group.

Hydrocarbons are further classified into aliphatic and aromatic compounds. The two main groups of aliphates are paraffins and naphthalenes.

Paraffins

Paraffins include *n*-alkanes and *iso*-alkanes aliphatic compounds. The common term for paraffinic molecules, which consist of more than twenty carbon atoms ($C_{>20}$), is wax. At elevated temperatures the wax will be present in solution, however, at lower temperatures the wax can precipitate. The wax content of crude oils can vary from 0,5 to 50 wt%, however the majority have a wax content of 2 to 15 wt%.

Naphthenes

Naphthenes are saturated cyclic hydrocarbons with one or more rings. Each ring can have one or more paraffinic side chains.

Aromatics
Aromatics are a specific type of unsaturated cyclic hydrocarbons. Benzene, toluene and xylenes are examples of mono-ring aromatics, naphthalenes are di-ring aromatics and polynuclear aromatic hydrocarbons (PAH) contain three or more aromatic rings.

A1.2 Hetroatomic organics

Hetroatomic organics can, in addition to carbon and hydrogen, contain small amounts of sulphur (S), nitrogen (N), oxygen (O) and trace amounts of vanadium (V) and nickel (Ni). Resins and asphaltenes are important subgroups of organic non-hydrocarbons.

Carboxylic acids, sulphoxides and phenol compounds are relatively polar compounds classified as resins. Asphaltenes consist of high molecular weight polycyclic aromatic compounds.

A2 Physical properties of crude oils

The physical properties of specific oils are a result of their chemical compositions. The most important physical properties in oil spill scenarios are discussed below.

A2.1 Density

The density of crude oil normally lies between 0,78 to 0,95 g/mL at 15,5°C. Paraffinic oils have lower density values, while oils that contain large amounts of high molecular weight aromatic, naphthenes and asphalthenic compounds usually have higher density values.

A2.2 Viscosity

The viscosity of crude oil expresses its resistance to flow and is of special interest when pumping mechanically collected oil. The viscosity of crude oils can vary from 3 to 2000 cP at 13°C. In comparison water has a viscosity of 1 cP and syrup a viscosity of 120 000 cP at 20°C.

The viscosity is temperature dependent. For liquids the viscosity decreases with increasing temperatures. Figure A2 shows the variations in viscosity as a function of temperature for various crude oils and oil products. Viscous crude oils or crude oils that contain wax can exhibit non-Newtonian behaviour (viscosity varies with shear rate), especially close to or below their pour point.

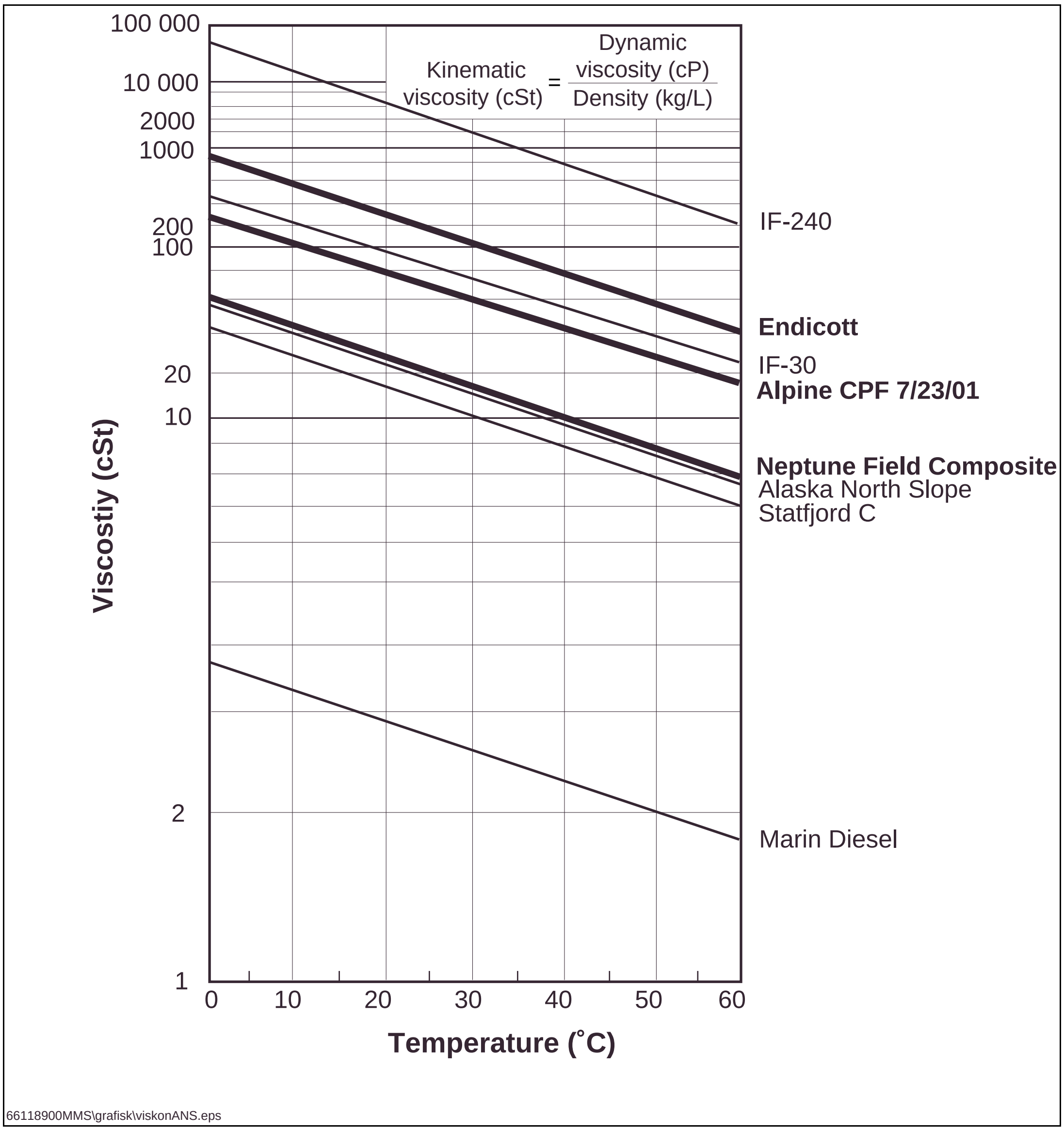


Figure A2: The variation in viscosity as a function of temperature for several crude oils and oil products. The figure is not valid below the oil's pour points.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain. The difference in viscosity for crude oils is approximately 3 to 2000 cP for fresh crude oils and several hundred/thousand cP for their residues.

Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil, this is illustrated in Figure A3.

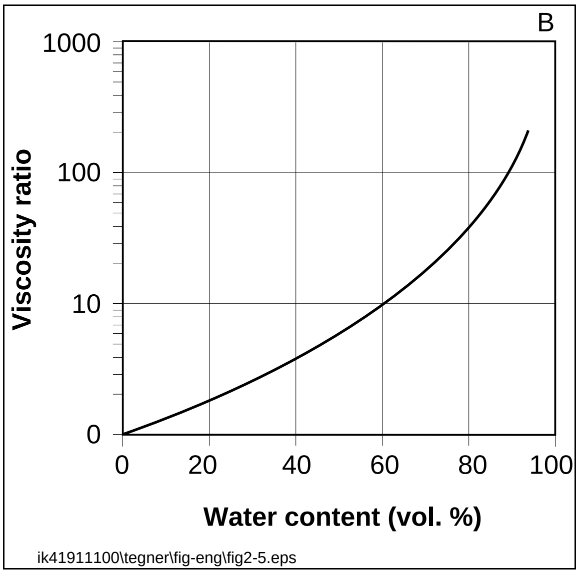


Figure A3: An example of the viscosity ratio as a function of increasing water content (Mackay et al., 1980).

Due to the shear thinning rheological properties, the viscosity of w/o-emulsions will decrease with increasing shear rate. A w/o-emulsion can therefore flow under turbulent conditions on the sea surface, but can become more viscous under calmer sea conditions or if washed on shore. Viscosity measurements must therefore be made under controlled conditions in the laboratory.

A2.3 Pour point

The temperature when an oil ceases to flow when cooled without disturbance under standardised conditions in the laboratory (ASTM-D97) is defined as the oils pour point. In oil spill clean up situations the pour point provides important information when determining the efficiency of various skimmers, pumping rates and the use of dispersion agents.

The pour point is related to the chemical composition of the parent crude oil, particularly its wax content. The ASTM Pour Point test is performed under static conditions. Field experience shows that under dynamic conditions on the sea surface, effects of oil solidification will occur 10-15°C below the laboratory generated pour points.

The pour point of an oil with a high wax content will increase dramatically with weathering as the lower weight molecules that contribute in keeping the wax in solution are lost. The pour point of oils with high wax contents can reach 30°C, while low viscous naphthenic (highly biodegraded) oils can have pour points as low as –40°C.

A2.4 Distillation curve

Distillation curves for crude oils give important information about the relative amount of lighter compounds in the oil and is therefore fundamental for determining the degree of evaporative loss after it is spilled on the sea surface. The curve is obtained by plotting the vapour temperature as a function of the amount of distillate. Figure A4 shows segments of the distillation curves for selected crude oils.

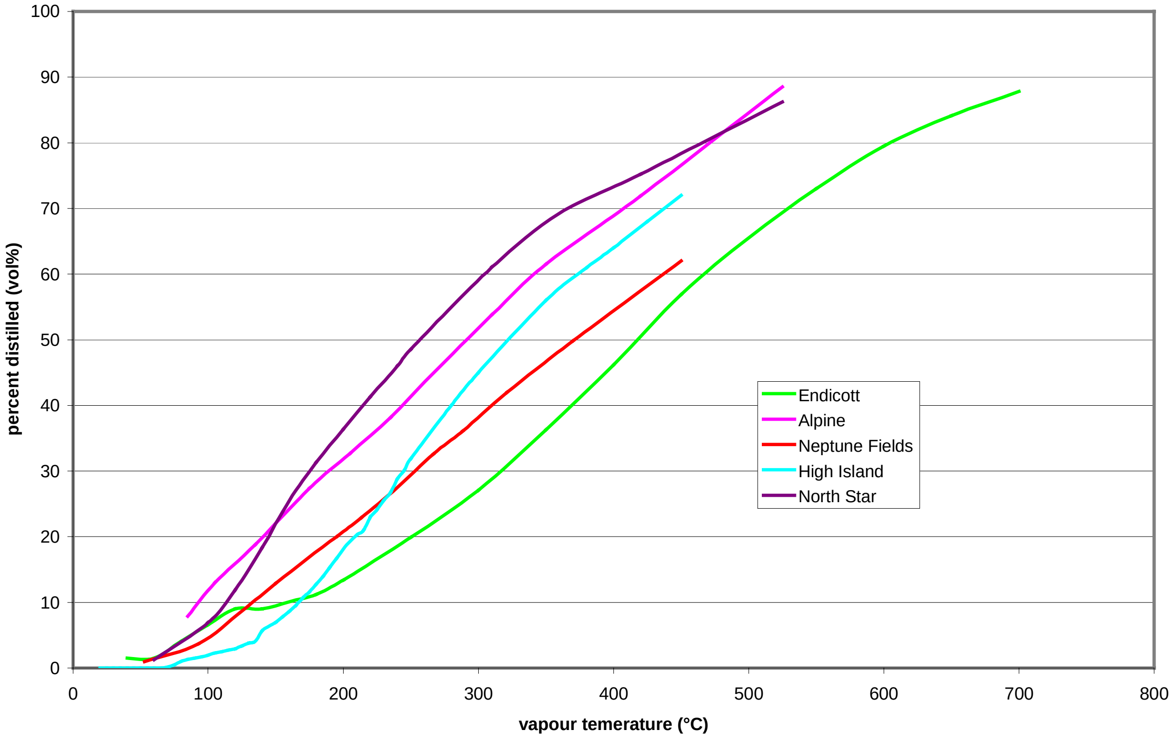


Figure A4: Distillation curves for the crude oils tested during the project.

A2.5 Flash point

The flash point is the lowest temperature at which the gas or vapour generated by heating an oil can be ignited by a flame. The flash point depends on the proportion of low molecular weight components. Fresh crude oils normally have a low flash point (from –40°C to 30°C).

From a safety point of view flash points are of most significance at or slightly above the maximum temperature that may be encountered in storage or transport. The flash point is an approximate indicator of the relative fire and explosion hazard of an oil.

A rule of thumb says that moving in an oil spill where the flash point of the oil is close to or lower than the sea temperature implies a fire and explosion hazard. Natural weathering processes like evaporation and emulsification formation contribute in reducing the potential hazard by increasing the flash point. There is therefore a relatively short fire and/or explosion danger in the initial stages of an oil spill.

In the laboratory, the flash point is measured in a closed system where there is equilibrium between the components in the oil and gas. In the field, however, the weather situation will influence the flammability of the air above the slick. For instance the gas concentration will be high just above the oil film in calm weather and high temperatures, whereas the concentration will be low in cold and windy weather due to dilution and transport and a lower degree of evaporation.

A3 The behavior of crude oil spilt at sea

When a crude oil is spilt at sea a number of natural processes take place, which change the volume and the chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, release of oil components into the water column, spreading, sedimentation, oxidation and biodegradation. A common term for all of these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. Figure A5 illustrates the various weathering processes and Figure A6 shows their relative importance with time.

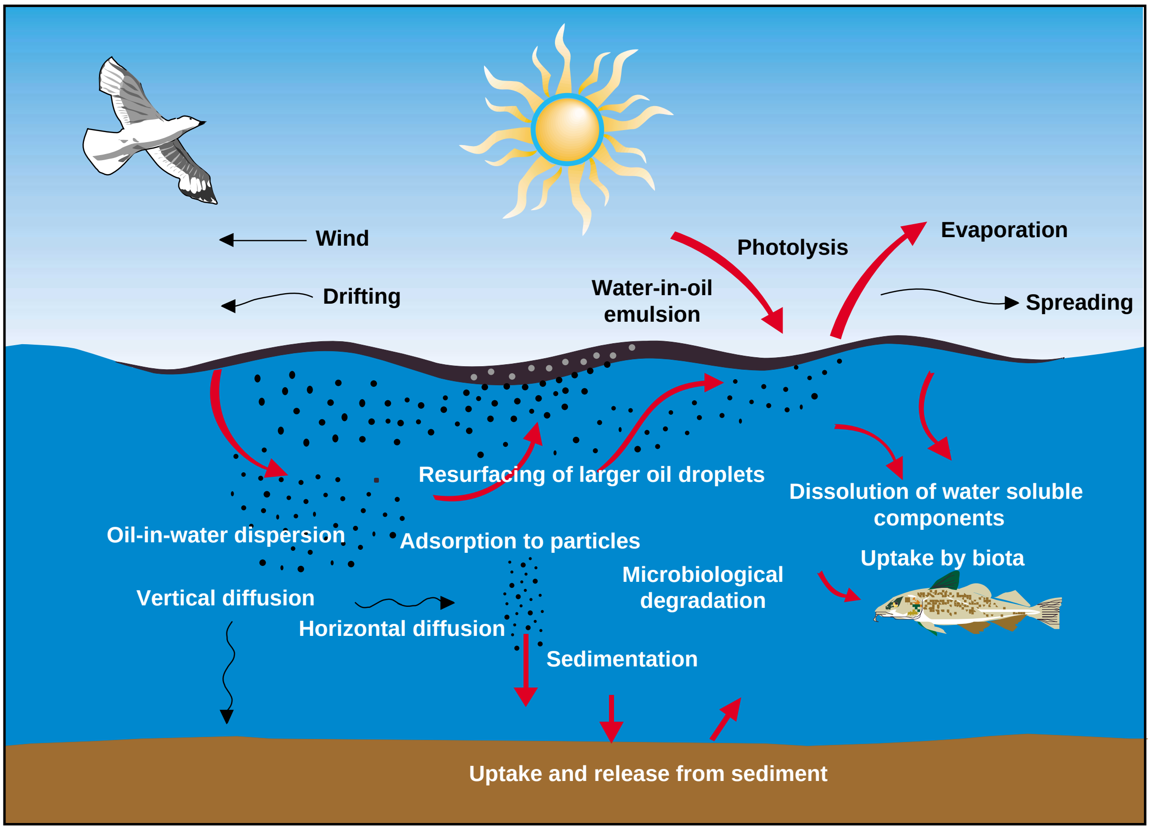
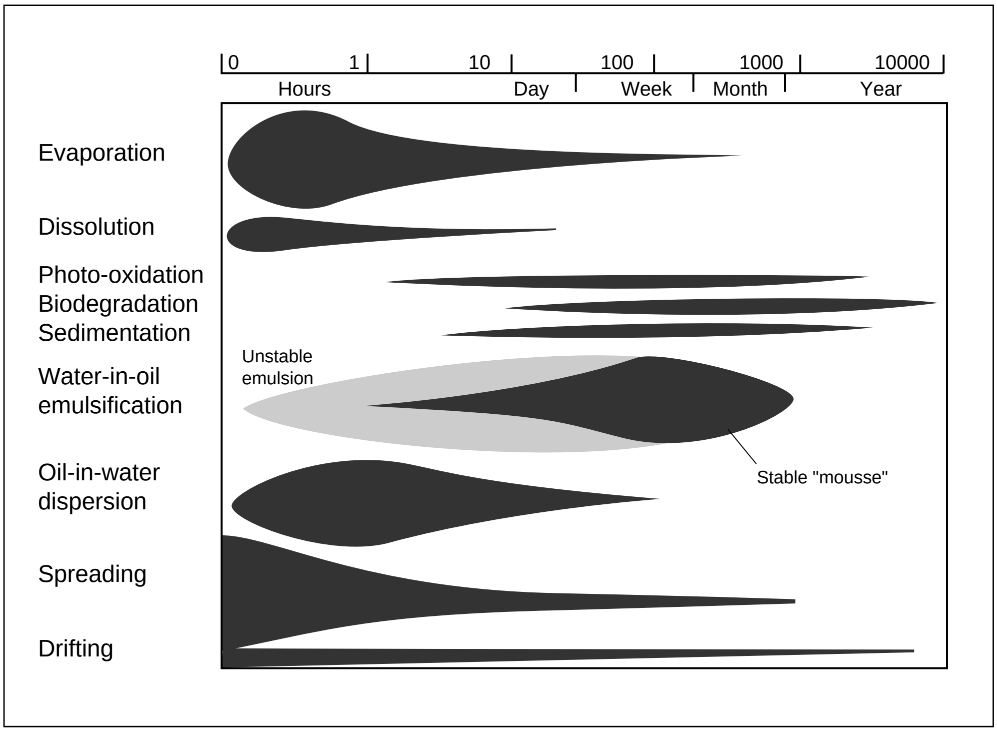


Figure A5: The weathering processes that take place when an oil is spilt on the sea surface.



6621\handboker\grafiske\fig-eng\emulsion.eps

Figure A6: Weathering processes' relative importance with time.

The weathering of oil depends on the oil type (chemical and physical properties), the weather conditions (wind, waves, temperature and sunlight) and the properties of the seawater (salinity, temperature, bacteria flora etc.).

A3.1 Evaporation

Evaporation is one of the natural processes that helps in removing spilt oil from the sea surface. The evaporation process starts immediately after the oil is spilled and the evaporation rate decreases exponentially throughout the duration of the oil spill.

The amount evaporated depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature and the oil film thickness.

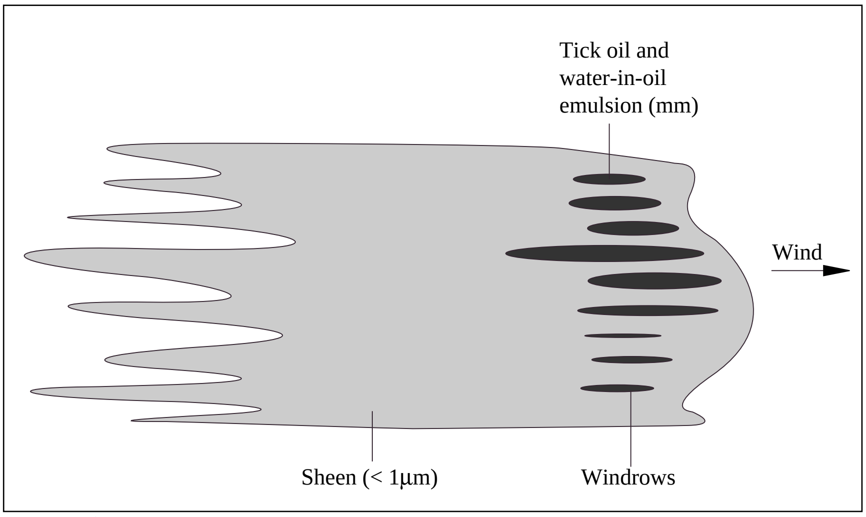
The rate of evaporation will vary for different oil types. Light refinery products (e.g. gasoline and kerosene) may completely evaporate after a few hours/days on the sea surface. Condensates and lighter crude oils can loose 50 % or more of their original volume during the first days after an oil spill.

The most significant difference caused by evaporation is the loss of volatile and semi-volatile compounds increases the relative amounts of higher molecular weight compounds. The chemical and physical properties of the remaining oil change, for example the density, viscosity, pour point and the relative wax and asphaltene contents will increase with increased evaporation.

A3.2 Spreading

Oil spilt at sea will spread on the sea surface. Spreading is often the dominating process in the initial stages of an oil spill, however see Figure A6, its importance decreases as the viscosity and density of the remaining oil increases. The spreading process is also retarded if the oil's pour point is 10-15°C below the sea temperature.

Oceanographic conditions (e. g. wind, waves and current) will affect the spreading process. The oil slick will be broken into windrows aligned in the wind direction, see Figure A7. The oil film thickness of the oil slick will vary, often differing with a factor of several thousand. Past experience has shown that 90 vol% of the oil spilt will consist of patches of w/o-emulsion with a film thickness of 1 to 5 mm that often constitute for less than 10 % of the total oil slick area. The remaining 10 vol% will cover 90 % of the spill area in the form of a sheen (<1 µm oil thickness).



ik41961100/tegner/fig-eng/sheen.eps

Figure A7: The spreading of oil spilt on the sea surface and the distribution within the oil slick.

A3.3 Drift of an oil slick

Prevailing surface currents cause the oil slick to drift, see Figure A8. Surface currents are controlled by currents in the water column but will also be influenced by wind speed and direction. This influence will be about 3% off the wind speed and direction compared to the drift contribution from currents.

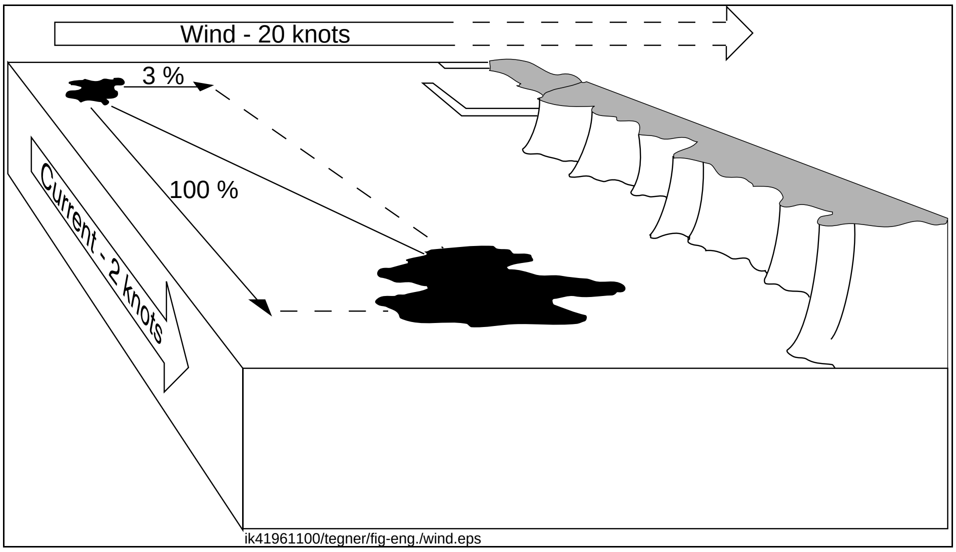


Figure A8: An illustration showing how wind and current can influence the drift of an oil slick.

A3.4 Water-in-oil (w/o) emulsion

The formation of w/o-emulsions is one of the major weathering processes that contributes in keeping oil on the sea surface. A w/o-emulsion has a higher viscosity than the parent crude oil and the emulsification process will therefore retard/delay the evaporation and the natural dispersion process.

The minimum criteria for the formation of w/o-emulsions is the presence of breaking waves (i. e. a wind speed of 5 m/s), however, a slow water uptake can also take place during calmer weather.

Surface active components present in crude oil will promote the formation of w/o-emulsions and contribute in stabilising the emulsion. These components contain both hydrophilic and hydrophobic groups.

The maximum water uptake will vary for different crude oils. Tests performed at SINTEF have shown that the maximum water uptake is fairly independent of the prevailing weather conditions as long as the lower energy barrier for the formation of w/o-emulsions is exceeded, however, the rate of emulsification depends highly on the weather conditions. Previous tests of asphalthenic oils performed at SINTEF show that the water uptake is in inverse ratio with the viscosity.

The rate of formation of the w/o-emulsion varies for different oil types since it is dependent on the chemical composition if the oil. A large amount of wax will for instance increase the rate of formation. Another important factor that influences the rate of formation is the prevailing weather conditions. Figure A9 shows an example of how the wind speed influences the rate of formation.

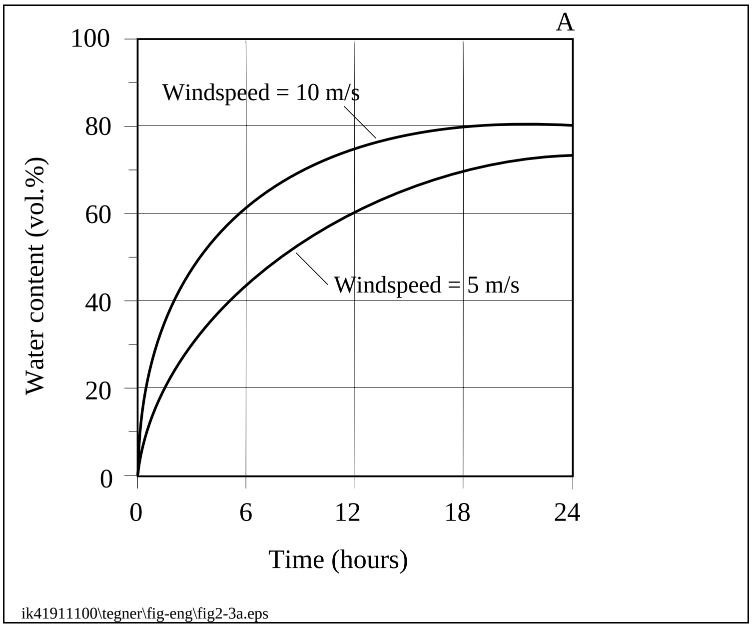


Figure A9: An example of how the prevailing weather conditions influence the rate of the w/o-emulsion formation for a typical crude oil.

The stability of the w/o-emulsion depends on the water droplet size in the emulsion. Not all of the water droplets in the emulsion are stabile. The largest droplets may coalesce and settle out of the w/o-emulsion. Larger water droplets may be reduced in size by the flexing, stretching and compressing motion of a slick due to wave action. After a period of time the emulsion may only contain small water droplets with a diameter of 1 to 10 µm. Figure A10 illustrates the effect of rotation time on the water droplet size in a w/o-emulsion formed in the laboratory.

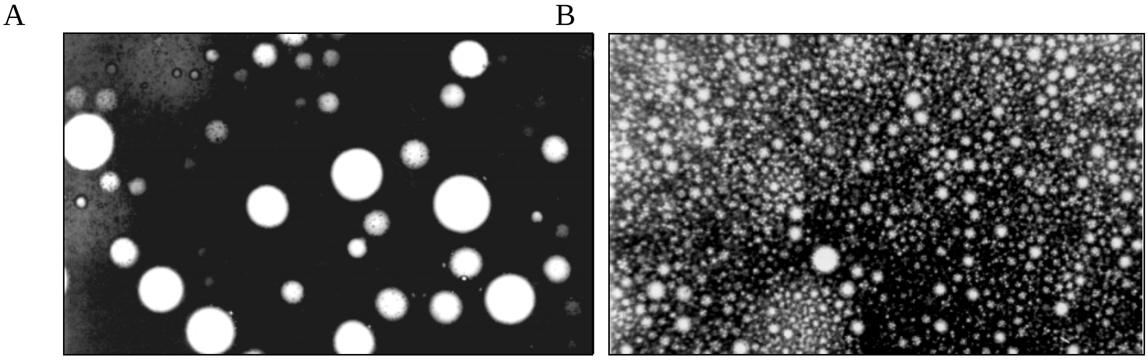
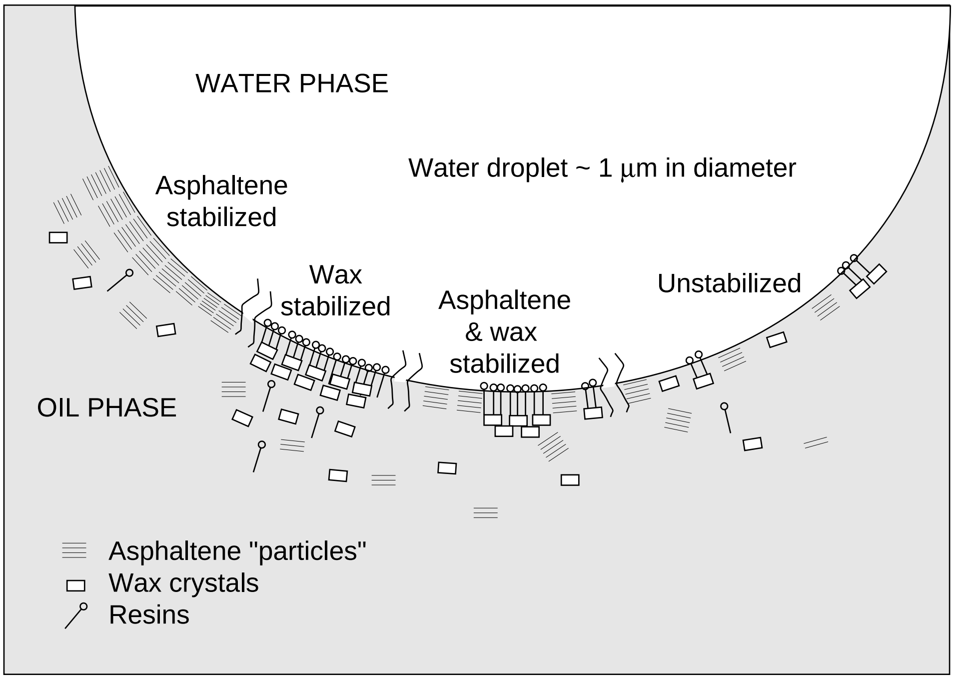


Figure A10: A picture taken with a microscope of the water droplet size in a w/o-emulsion after (A) 1 hour and (B) 24 hours in a rotating cylinder.

Another factor that influences the w/o-emulsion’s stability is the amount of surface-active components present in the parent oil. Resins and asphaltenes have hydrophobic and hydrophilic properties and will concentrate at the interface between the water and oil thereby forming a layer that stabilises the water droplets. The hydrophobic properties can lead to the concentration of wax along the water droplets, which further stabilises the interfacial “skin” layer. The interfacial layer between the oil and water forms a physical barrier hindering coalescence and will stabilise the w/o-emulsion by hindering the fusion of water droplets. The stabilisation of the water droplets by asphaltenes and by asphaltenes and wax are shown in Figure A11.



ik41961100:tegner\fig_eng\interfac.eps

Figure A11: Stabilization of the interfacial layer between the water and oil in a w/o-emulsion by wax and asphaltenes.

Oils that contain a large amount of wax and little asphaltenes can form w/o-emulsions that may appear to be stabile. These w/o-emulsions appear to be stabled by the continuos phase's rheological strength (viscosity and elasticity). This strength is due to the wax structure formed by precipitated wax. Wax stabilised emulsions are characterised by large water droplets and are fairly stabile when stored, however, they may break when stress is applied and/or when the emulsion is heated to e. g. 40-50°C.

A3.5 Oil-in-water (o/w) dispersion

Natural o/w dispersion will take place if there is sufficient energy on the sea surface, i. e. if there are breaking waves present. The waves will break the slick into droplets typically with a diameter between 1 to1000 µm which are mixed into the water masses. The largest oil droplets will resurface forming a sheen (see 0) behind the oil slick.

In addition to weather conditions the dispersion rate depends highly on the oil type and can be one of the main processes that determine the lifetime of an oil slick on the sea surface. The natural o/w dispersion will gradually decrease since evaporation of the lighter components will increase the viscosity of the remaining oil.

The purpose of applying chemical dispersion agents is to increase the natural o/w dispersion rate. When effective chemical dispersion is achieved small oil droplets are formed with a diameter of 5 to 50 µm. The dispersion agent reduces the interfacial tension between the water and oil and promotes dispersion.

A3.6 Water solubility

The water solubility of saturated hydrocarbons ($<C_4$) is very low, while lower molecular weight aromatic compounds are water-soluble. Within the various types of hydrocarbons the water solubility decreases from aromatics to naphthenes and from *iso*-paraffins to *n*-paraffins. In each series the water solubility decreases with increasing molecular weight.

Evaporation and the release of oil components in to the water masses are competitive processes since most of the water-soluble components are also volatile. The evaporation process is approximately 10 to 100 times faster than the dissolution into the water column. The concentration of soluble oil components in the water column during an oil spill is quite low (<1 mg/L). The dissolution of oil components into the water column does not contribute in removing the oil from the sea surface. However the water-soluble fraction (WSF) is of great interest since it has a high bioavailability and therefore the potential to cause acute toxic effects on marine organisms.

A3.7 Photo-oxidation

Under the influence of sunlight some of the oil components will slowly be oxidised to resins and eventually asphaltenes. This contributes to the stability of w/o-emulsions and therefore has a large influence on the oils persistence on the sea surface. The photo-oxidised components will stabilise the w/o-emulsions. After a long period of weathering at sea, tar-balls can be formed. Tar-balls are broken down very slowly both at sea and on beaches.

A3.8 Biodegradation

Theoretically, seawater contains micro-organisms that can break down all types of oil components. The various micro-organisms prefer specific oil components as an energy source.

Several factors influence the biodegradation rate, among these are temperature, the supply of nutritive substances that contain nitrogen and phosphor, the oxygen supply, oil type and the degree of weathering. Bacteria can only degrade oil that is in contact with seawater and is dependent of the water/oil interface area. The interface area increases as the oil is spread over the sea surface as a thin layer or by chemical or natural dispersion of oil in the water masses. An area increase due to chemical and/or natural dispersion will increase the degradation rate in the water mass to 10 to 100 times the rate at the water/oil interface.

A3.9 Sedimentation

Crude oil and oil residues rarely sink into the water masses since there are few oils that have a density higher than water, even after extreme weathering. Oil can, however, sink if sticking to particular material present in the water masses. The increased density will make oil-soiled particles sink more readily.

A3.10 Submersion

Highly weathered oils can temporarily submerge from the sea surface. This can greatly influence the effectiveness of combating oil pollution in the marine environment. The oil density and viscosity in addition to the weather conditions influence submersion. W/o-emulsions have a higher density value than the parent oil and can therefore submerge more easily.

Appendix B: Experimental Design of the Bench-Scale and Meso-scale Laboratory Testing

B1 Oil Samples received for the study

SINTEF received two fresh oil samples from the Alaskan North Slope (Endicott and Milne Point Unit) on the 14th of November 2000, two fresh oil samples from the Gulf of Mexico (Neptune Field Composite and High Island Composite) on the 30th of January 2001 and an oil sample from the North Slope (Alpine Central Production Facility) on the 15th of August 2001. At 11th of June 2002, the last Alaskan North Slope oil arrived (North Star Oil). These oil samples were supplied by MMS.

Alaskan North Slope samples

B1.1 Detailed information of the Endicott crude oil sample

Area/block:	Alaskan North Slope
Common field name:	Endicott
Well number:	133 G-12-00

B1.2 Detailed information of the Milne Point Unit oil sample

Area/block:	Alaskan North Slope
Jerry cans marked:	MPJ-01 CRUDE OIL

B1.3 Detailed information of the Alpine Central Production Facility oil sample (Alpine Composite)

Area/block:	Alpine Oilfield
Sample date:	July 23, 2001

Composite sample of all of the producing wells at Alpine.

B1.4 Detailed information of the North Star oil sample

Sample no :	1.08
Client:	BP Alaska
Installation:	North Star
Date:	5.6-02
Bottle no.:	n/a
Well:	NS-08
Test:	test1
Time:	21:25
Sample	Nature: Atmospheric oil
Sampling point:	Separator Oil Line
Sample bottle:	5gallon can
Job no.:	NAM 1076

Gulf of Mexico Oils

B1.5 Detailed information of the Neptune Field Composite sample

Area/block: VK 826
MMS Structure name: A
Sample date: November 14, 2000
Common field name: Neptune
Field/unit: VK 825
Company name: Kerr-McGee
MMS Platform ID: VK 826A
Composite sample from the following API well numbers:
Well A-1 through A-10, A-12st, 825-4, 825-5 and 826-12

B1.6 Detailed information of the High Island Composite

Area/block: High Island Block A573
MMS structure name: A
Sample date: December 8, 2000
Common field name: none
Field name: HIA573A
Company name: UNOCAL
Well number: A006
API well number: 427094016200

B2 Test temperatures

The temperatures chosen for the bench-scale laboratory testing are:

Endicott: 10°C
Milne Point Unit: 10°C
Alpine Composite: 10°C
North Star 10°C

The Neptune Field Composite: 23°C
High Island Composite: 23°C

B3 Bench-scale laboratory testing

In order to isolate and map the various weathering processes that take place when an oil is spilled on the sea surface, the weathering of the oils is carried out using a systematic, stepwise procedure developed at SINTEF (Daling *et al.*, 1990). The weathering process is illustrated in Figure B1.

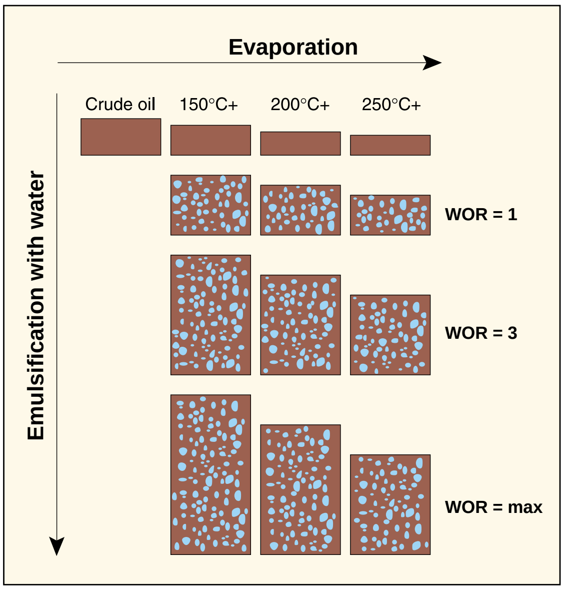


Figure B1: Flow chart for the bench-scale laboratory weathering of a crude oil.

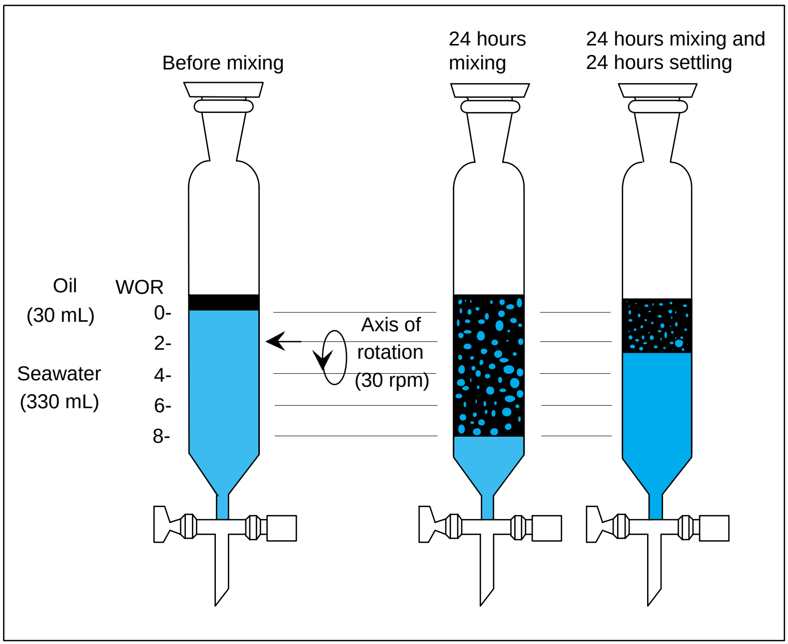
B3.1 Evaporation

Evaporation of the lighter components from the fresh crude oil is carried out according to a modified ASTM-D86/82 distillation procedure (Stiver and Mackay, 1984). The fresh crude oil is distilled, in a simple one step distillation, to a vapor temperature of 150, 200 and 250°C. This will give oil residues with an evaporation loss typically corresponding to 0,5-1 hour, 0,5-1 day and 2-5 days of weathering of an oil slick on the sea surface. These residues are referred to as 150°C+, 200°C+ and 250°C+ respectively.

B3.2 Water-in-oil (w/o) emulsification

The procedures used in the w/o-emulsification studies are described in detail by Hokstad *et al.*, 1993.

The w/o-emulsification of the fresh crude oil is carried out based on the rotating cylinder method developed by Mackay and Zagorski, 1982. Oil (30 mL) and seawater (300 mL) are rotated (30 rpm) in a separating funnel (0,5 L), see Figure B2. The emulsification kinetics are mapped by measuring the water content at fixed rotation times. The maximum water content is determined after 24 hours of rotation.



6621/handbøker/grafisk/fig-eng/3skilletrakter.eps

Figure B2: Principle of the rotating cylinder method.

To test the effectiveness of the emulsion breaker Alcopol O 60 %, two dosages (500 ppm and 2000 ppm relative to the oil volume) were added drop wise to the w/o-emulsion. After a contact period of 5 minutes and a rotation time of 5 minutes (30 rpm), the treated emulsion stood for 24 hours before the amount of water drained from the emulsion was determined.

The distilled residues were emulsified with 50 vol% and 75 vol% water in addition to the maximum water content w/o-emulsion. Four parallel runs were performed to map the w/o-emulsion kinetics and two of the parallel runs were performed with the addition of Alcopol O 60%. Several physical and chemical properties of the twelve weathered samples (see Figure B1) were determined. A detailed description of the various analyses is given in B3.3.

B3.3 Physical and chemical analysis

The viscosity, density, pour point, flash point and interfacial tension of the water free residues and w/o emulsions were determined. The analytical procedures used are given in Table B1.

Table B1: Summary of the analytical methods used in the determination of the physical properties.

Physical property	Analytical method	Instrument
Viscosity	McDonagh et al., 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour Point	ASTM method D97	-
Interfacial tension	De Nouy Ring method	Kruss tensiometer
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR

The wax content and "hard" asphaltene content will be determined using the analytical procedures given in Table B2.

Table B2: Summary of the analytical methods used in the determination of the chemical properties.

Chemical property	Analytical method
Wax content	Bridiè *et al.*, 1980
“hard” asphaltene	IP 234/84

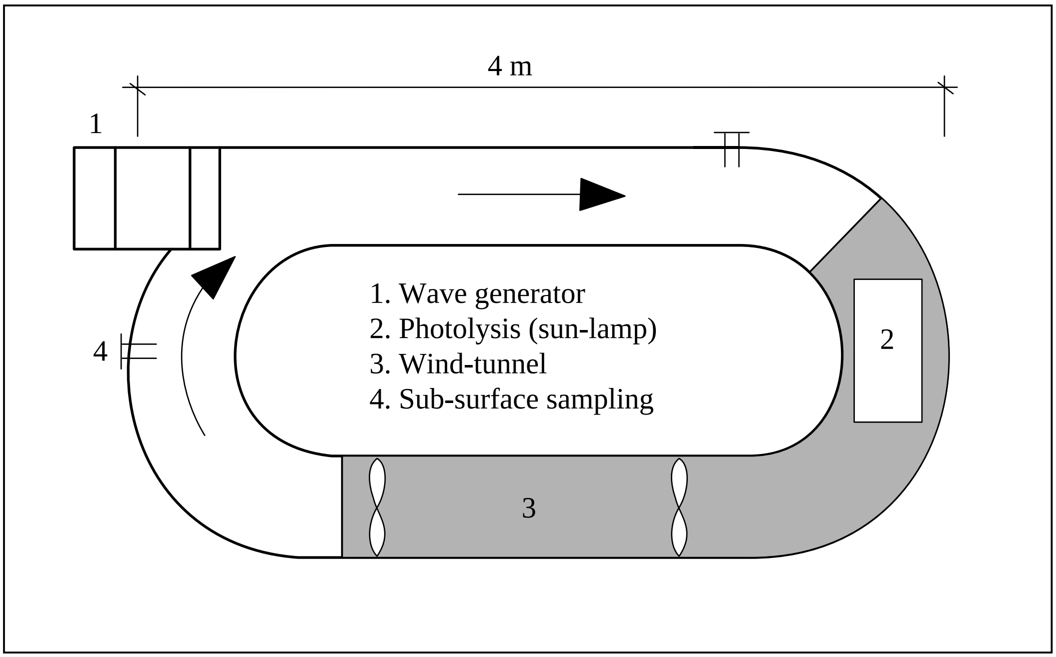
B4 Meso-scale laboratory testing

In the bench scale testing the oils are distilled and emulsified in separate processes. In an oil spill situation at sea these processes will occur simultaneously and affect each other. It is therefore important that the oils are weathered under realistic conditions when studying how the oils behaviour when spilled on the sea surface.

A meso-scale flume basin (Singsaas *et al.*, 1993) located at SINTEF is routinely used to study the weathering processes simultaneously under controlled conditions. The experimental data obtained from the meso-scale testing provides a link between the bench scale testing and field trials and is important input in the OWM. In this study a meso-scale flume basin experiment is therefore performed as a supplement to the limited bench scale study to be conducted on the heavily emulsified High Island oil sample.

B4.1 Description of the meso-scale flume

Approximately 1,7 m^3 seawater circulates in the 10 meter long flume. The flume is located in a conditioning room (20°C – 50°C). To fans (3) placed in a covered wind-tunnel allow various wind speeds. The evaporation- and emulsification rate is calibrated to simulate a wind speed of 5-10 m/s. A schematic drawing of the flume is given in Figure B3.



Boss\ik41961100/tegner/fig-eng/mesoflu_e.eps

Figure B3: A schematic drawing of the meso-scale flume.

B4.2 Oil weathering in the meso-scale flume

The emulsified oil sample (10 L) is carefully released on the water surface. The oil is weathered for a total of 72 hours. Surface oil residue, w/o-emulsion and subsurface water samples are taken after 0 min., 15 min., 30 min., 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 6 hours 12 hours, 1 day, 2 days and 3 days of weathering. The following physical properties are determined:

- water content
- viscosity
- density
- evaporation loss

B4.3 In-situ chemical dispersion

After 72 hours of weathering in the flume the dispersion agent Corexit9500 is sprayed onto the w/o-emulsion, see Table B3, where

DOR is the dispersion agent to oil ratio
DER is the dispersion to w/o-emulsion ratio

Table B3: The application time and amount of the dispersion agent Corexit 9500.

Weathering [h]	Amount of Dasic NS applied [mL]	Cumulative DOR [%]	Cumulative DER [%]
72	56	0.9	0.3

Water samples are taken 3 min., 10 min., 30 min. and 2 hours after the dispersion agent is applied in order to determine the effect of the dispersion agent in addition to observations of the surface film and w/o-emulsion.

Appendix C: Experimental results from the bench-scale and meso-scale laboratory testing

C1 Bench-scale laboratory testing

In this chapter the experimental results obtained for Endicott, the Neptune Field Composite, Alpine Composite and the North Star oils in the bench-scale laboratory testing are presented and compared.

The Milne Point Unit and the High Island oil samples were emulsified on arrival. A standard bench scale weathering study of these two oil samples could therefore not be performed. Both samples have water contents well above the safety limit for the laboratory distillation of crude oils enabling the artificial weathering of the oil samples.

The High Island Oil was emulsified on arrival at SINTEF. Three phases were formed after allowing the w/o-emulsion to settle for several weeks. A dark brown oil phase (water content less than 1%), a light brown phase (water content approximately 10%) and a water phase. The upper water free layer were “artificially” evaporated (described in B3.1), and used for obtaining data on the physical and chemical properties of the water free residues of the oil upon weathering. A meso scale experiment were performed to obtain data on the properties of the emulsions formed in a weathering situation.

The Milne Point Unit sample was an extremely stable emulsion and water could only be separated from the sample after an excess of emulsion breaker (approximately 10% of Alcopol O 60 %) was added to the sample, and the mixture were heated. The water content of the sample did not increase using the rotating cylinder method. A meso-scale laboratory study was not regarded appropriate for obtaining more information about this sample.

C1.1 Chemical composition

C1.1.1 Gas chromatographic analysis

Fresh samples of Endicott, the Alpine Composite, the Neptune Field Composite, the North Star and their evaporated residues (150°C+, 200°C+ and 250°C+) were analysed by a gas chromatograph with a flame ionisation detector (GC-FID). The gas chromatograms are given in Figure C1-C6.

The components with the lowest boiling points are seen first in the chromatogram. Some of the more complex components, e.g. resins, NSO-components and naphthenes are difficult to separate using this analysis technique and are seen as a broad, poorly defined envelope. This is described as Unresolved Complex Material (UCM). The *n*-alkanes are seen as systematic, narrow peaks protruding the UCM envelope. Heavier compounds ($>C_{40}$) cannot be analysed by this technique.

From the gas chromatograms given in Figures C1-C6 it can be seen that Endicott, the Alpine Composite, the Neptune Field Composite and the North Star have paraffinic peaks protruding the UCM envelope. Endicott contains fewer lower molecular weight components and has a larger UCM envelope than both the Alpine Composite and the Neptune Field Composite that is therefore the heaviest of the three oils.

The Milne Point Unit’s chromatogram (Figure C5) differs from the others in the total lack of *n*-alkane peaks. This indicates a high degree of biodegradation.

Gas chromatography is an important tool in identifying oil spills due to the diversity of the n-C_{17} and pristane and n-C_{18} and phytane ratios for different oil types. The ratios for Endicott, the Alpine Composite, the Neptune Field Composite and the North Star oil are given in Table C1.

Table C1: nC_{17}/Pristane and nC_{18}/Phytane ratios, calculated from peak height, for Endicott, the Alpine Composite, the Neptune Field Composite and the North Star.

Crude oil	n-C_{17}/pristane	n-C_{18}/phytane
Endicott	2.0	2.8
Neptune Field Composite	2.3	3.4
Alpine Composite	1.7	3.1
North Star	2.4	3.3
High Island Composite	1.4	1.7

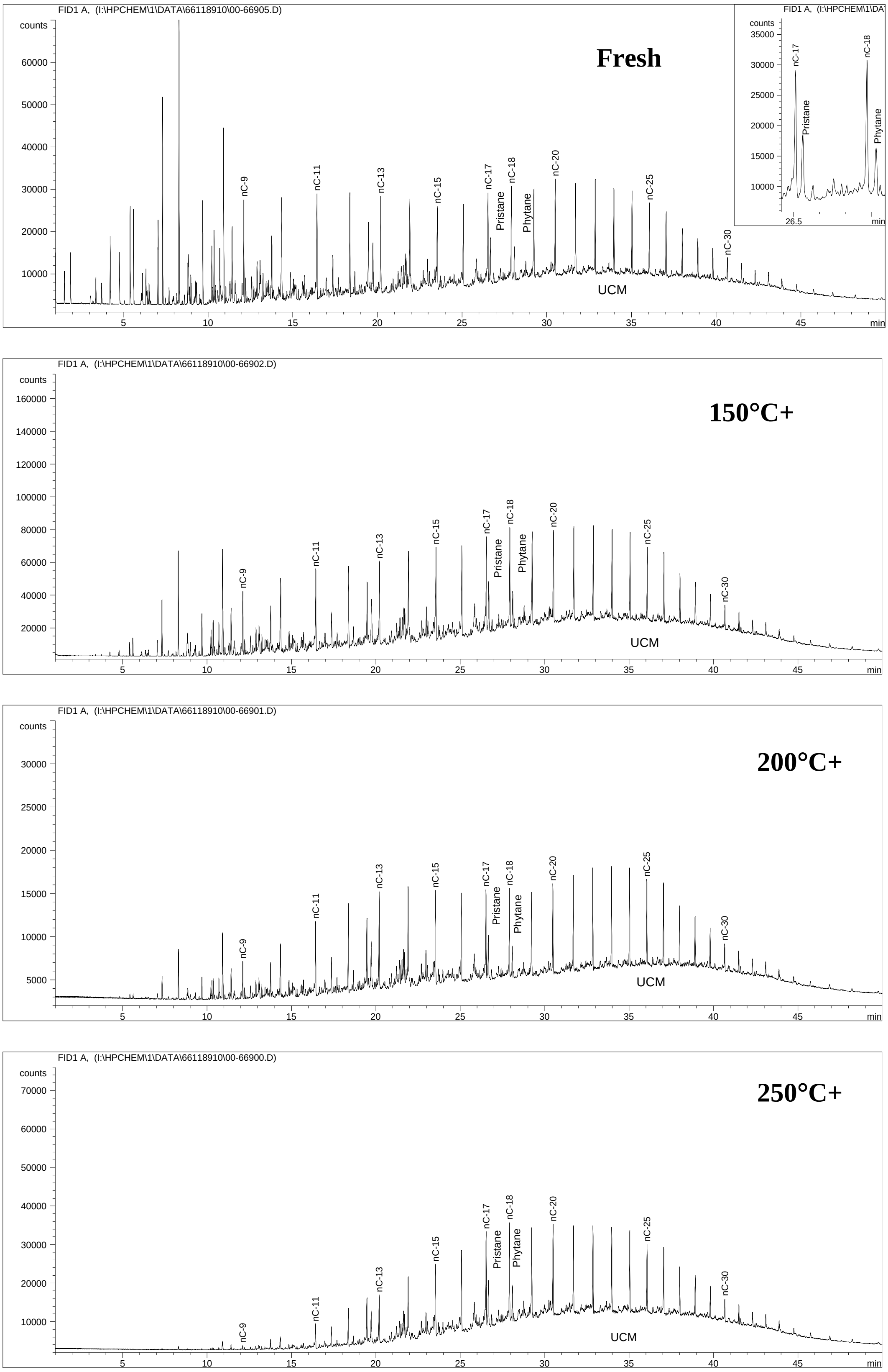


Figure C1: Gas chromatogram for fresh Endicott and it's evaporated residues.

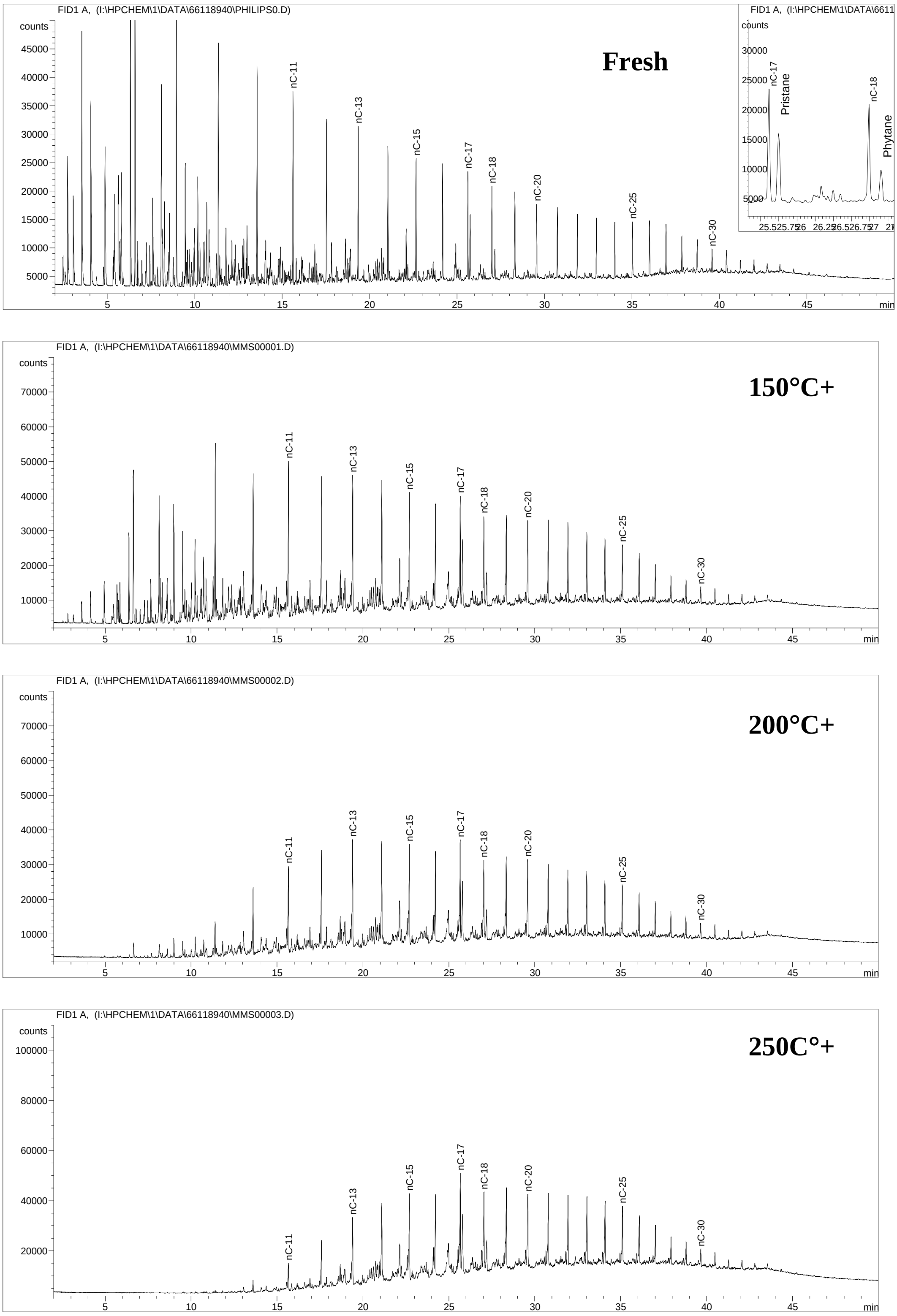


Figure C2: Gas chromatograms for the fresh Alpine Composite and its evaporated residues.

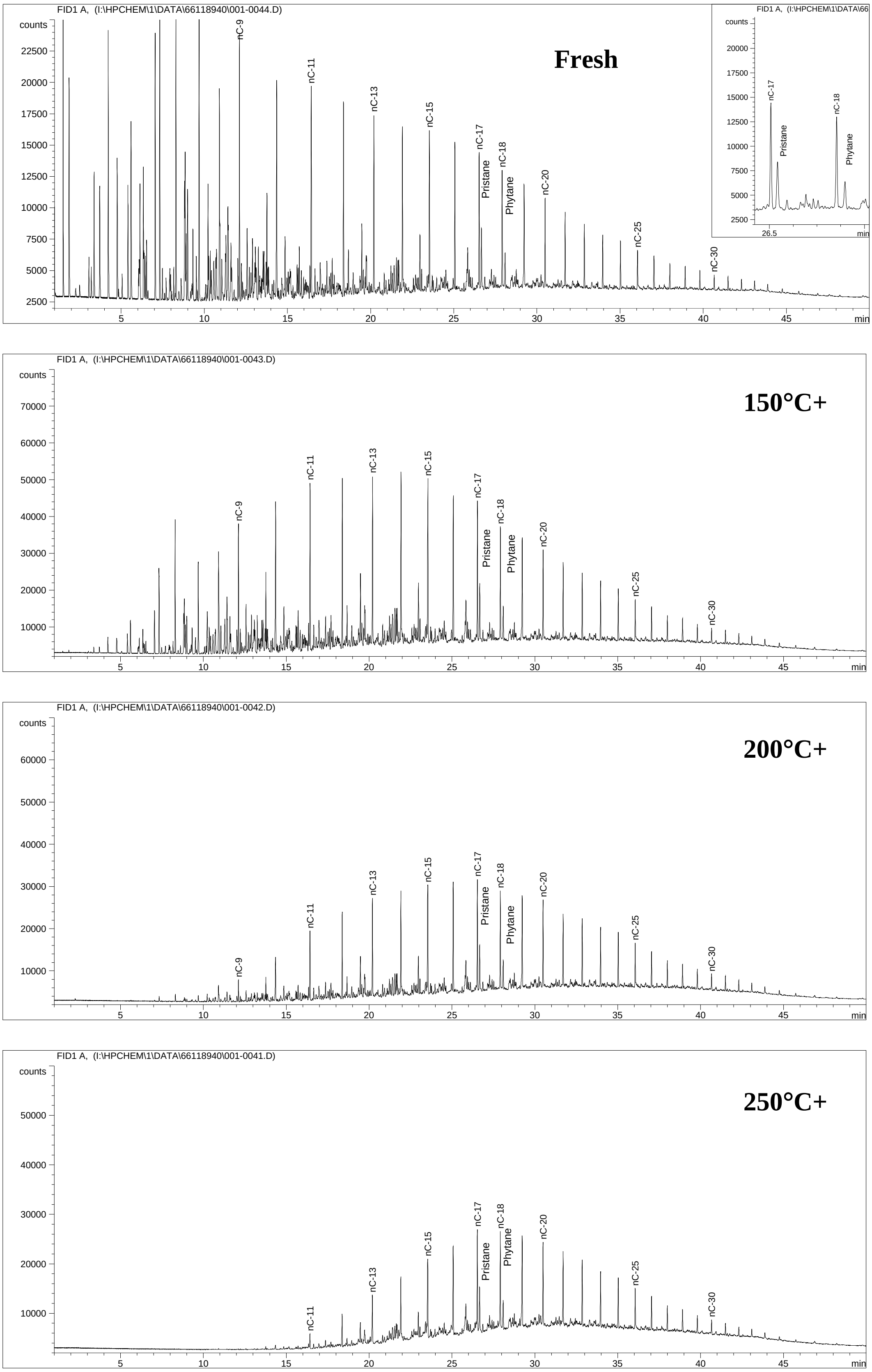


Figure C3: Gas chromatogram for the fresh Neptune Field Composite and it's evaporated residues.

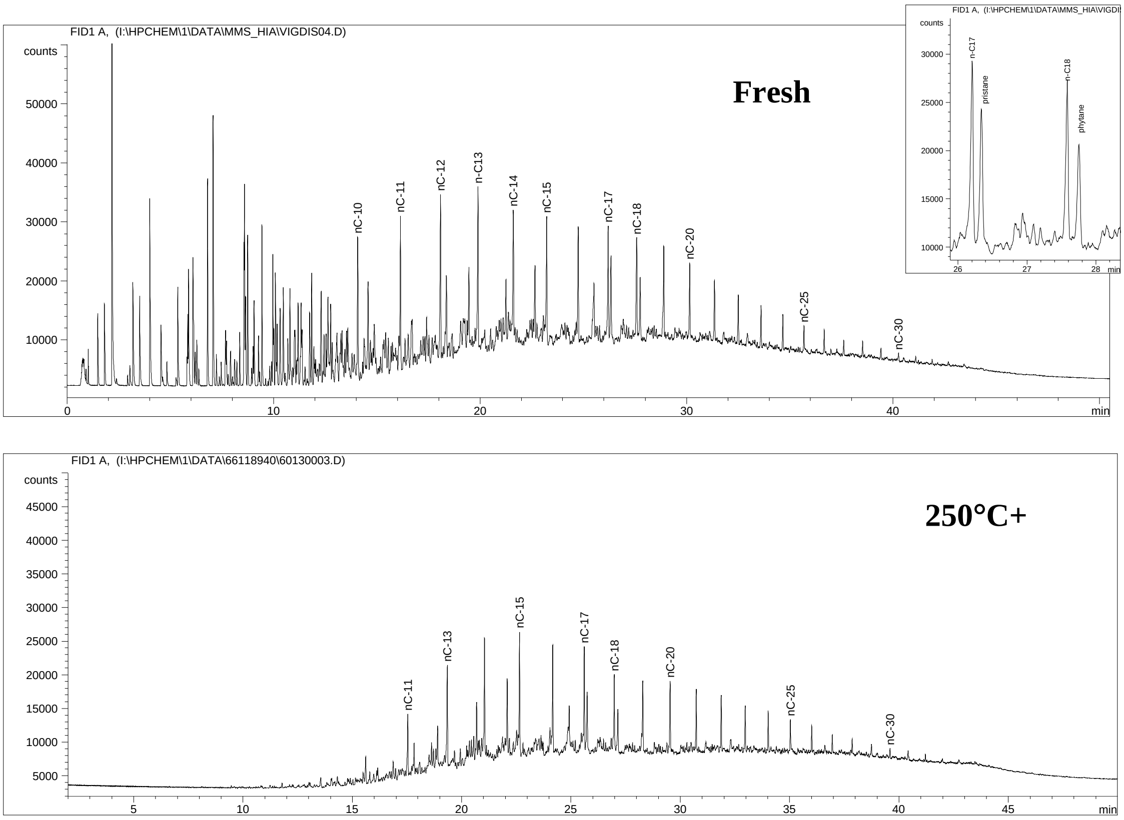


Figure C4: Gas chromatogram for the fresh High Island Composite and the 250°C+ residue.

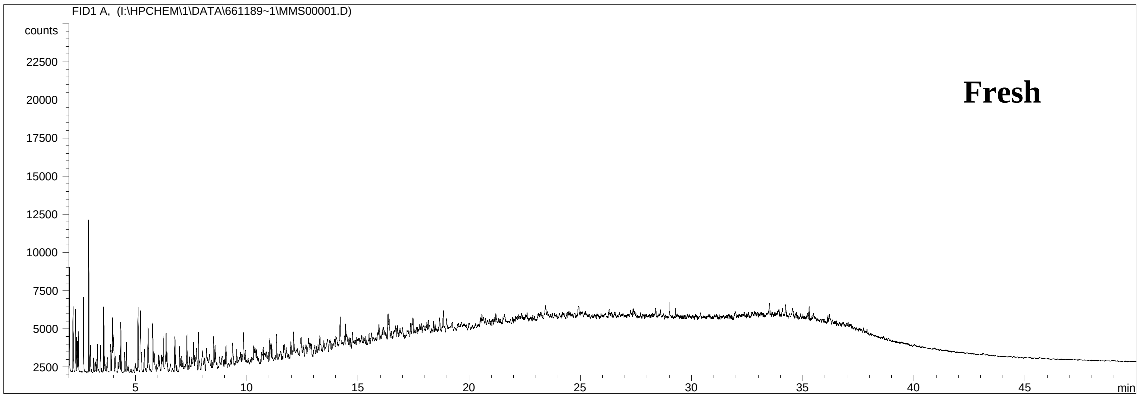


Figure C5: Gas chromatogram for the fresh Milne Point Unit oil.

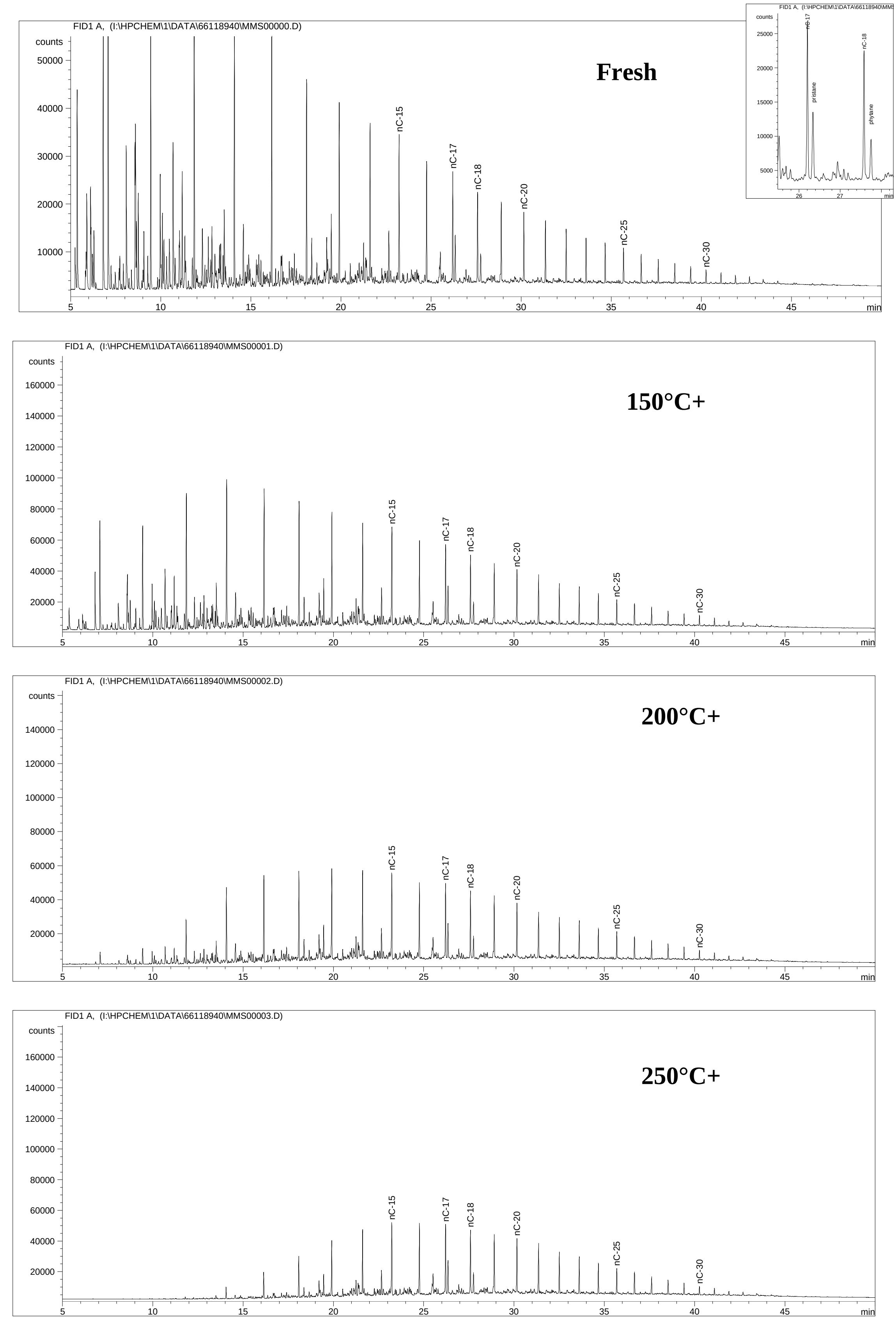


Figure C6: Gas chromatogram for the fresh North Star oil and it's evaporated residues.

C1.1.2 Asphaltene and wax content

Wax and asphaltenes are important parameters for water uptake ability and w/o-emulsion stability. The ("hard") asphaltene and wax content of Endicott, the Alpine Composite and the Neptune Field Composite and their evaporated residues are given in Table C3.

C1.1.3 Classification of the oil samples

From the experimental results all the crude oil sample, but the Milne Point Unit and the High Island Composite are classified as paraffinic crude oils. Endicott is the heaviest of the paraffinic oils with an asphaltene content of 1,6 wt% and a wax content of 5,5 wt%. The Alpine Composite has the lowest asphaltene and wax content of the three oils. The Neptune Field Composite contains a large amount of lighter weight compounds and has a relatively low asphaltene content (0,3 wt%).

Milne Point Unit is a heavily biodegraded heavy crude oil. Information obtained from the chromatogram indicates a low wax content. The extreme stability of the emulsion could indicate a high amount of asphaltenes.

The High Island oil is also biodegraded but not to the same degree as the Milne Point Unit oil.

C1.2 Physical properties

C1.2.1 Evaporative loss

Endicott, Alpine Composite, Neptune Field Composite and North Star were distilled to a vapour temperature of 150, 200 and 250°C. The volume percent evaporated during the distillation is given in Figure C7

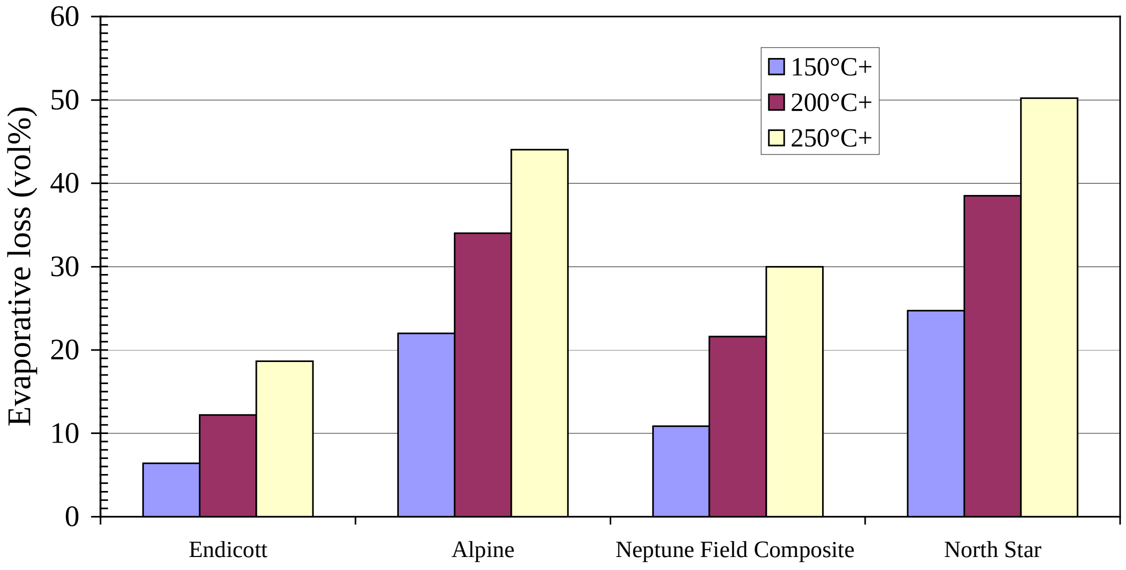


Figure C7: *Evaporative loss of Endicott, the Alpine Composite ,the Neptune field composite and the North Star crude oils.*

Endicott contains a larger amount of higher weight compounds and the volume spilled on the sea surface will decrease slowly. The Alpine and North Star oils have a high amount of lighter components, and evaporative loss will yield great changes in physical properties for the oil.

C1.2.2 Density

The density of Endicott, the Alpine Composite the Neptune Field Composite, the North Star and their evaporated residues are given in Figure C8.

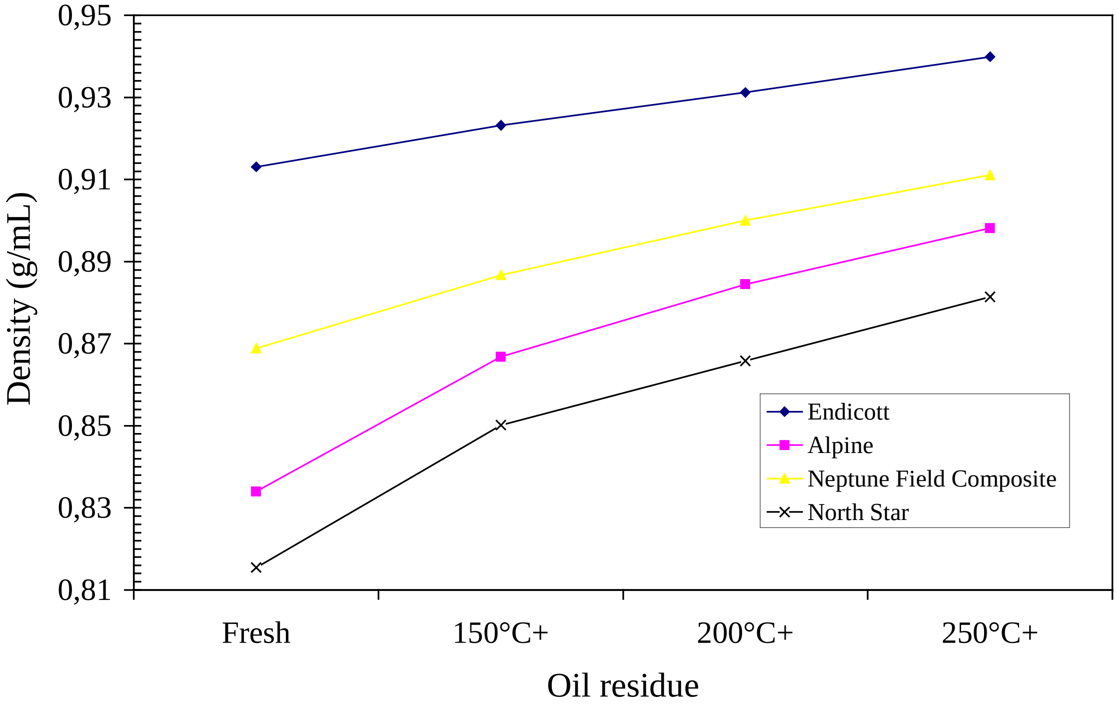


Figure C8: *Density of Endicott, the Alpine Composite and the Neptune Field Composite and their evaporated residues at 15,5°C.*

The densities of the water free oil residue increase with evaporation, see Figure C8. Fresh Endicott has the highest density of the three crude oils indicating that it contains fewer lower weight molecules and a larger amount of heavier compounds than the others do. The North Star crude oil is the lightest of the four crude oils. This is in agreement with the results obtained from the GC analysis and the evaporation data (see chapters C.1.1 and C1.2).

C1.2.3 Pour Point

The pour points of fresh Endicott, the fresh Neptune Field Composite, the North Star and their evaporated residues are given in Figure C9.

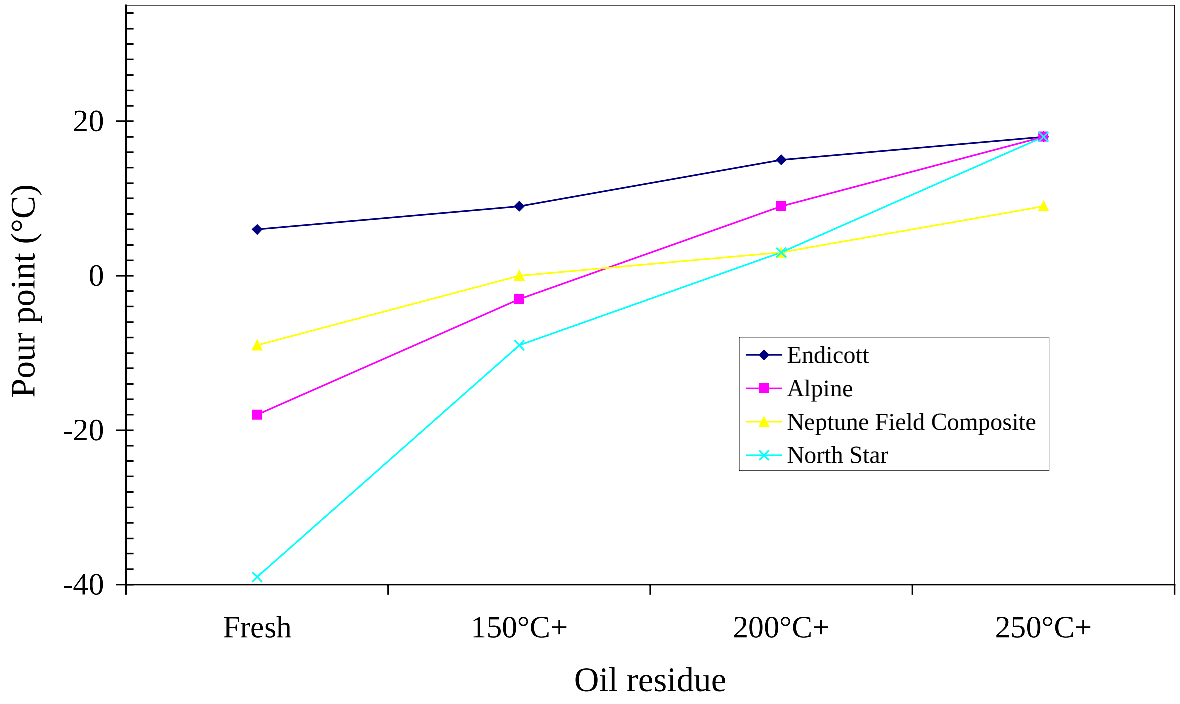


Figure C9: Pour points of Endicott, the Alpine Composite and the Neptune Field Composite and their evaporated residues.

The Alpine Composite and the North Star oil have the lowest initial pour points at –18°C and –39°C respectively. The low pour points are due to high amounts of light components in the oils, keeping heavier components as wax in solution. Upon evaporative loss the chemical composition changes, and as e.g. wax is allowed to precipitate the pour point is getting higher. As the Alpine and North Star oils have the greatest evaporative loss of the four, they also display the greatest change in pour point with evaporation.

C1.2.4 Viscosity

The viscosity of the fresh crude oils and their evaporated residues measured at shear rate 10 s^{-1} is given in Table C2.

Table C2: Measured viscosity for fresh Endicott, the Alpine Composite, the North Star, the Neptune field Composite and The High Island Composite.

Oil type			Viscosity at $10s^{-1}$ [cP]	Pour point [°C]
Alaskan North Slope	Endicott 10°C	Fresh	510	6
		150°C+	840	9
		200°C+	1 630	15
		250°C+	5 150	18
	Alpine Composite 10°C	Fresh	100	-18
		150°C+	120	-3
		200°C+	840	9
		250°C+	1 160	18
	North Star 10°C	Fresh	10	-39
		150°C+	45	-9
		200°C+	380	3
		250°C+	2272	18
Gulf of Mexico	Neptune Field Composite 23°C	Fresh	10	-9
		150°C+	50	0
		200°C+	110	3
		250°C+	300	9
	High Island Composite 23°C	Fresh	23	-36
			-	-
			-	-
		250°C+	83	-15

As the more volatile components are lost by evaporation, the viscosity of the remaining residue will increase. This is seen in Table C2 for all five crude oils.

The viscosities of Endicott 150°C+, 200°C+, 250°C+ , Alpine Composite 250°C+ and North Star 250°C+ were measured close or below their pour points and the values obtained are therefore quite high.

C1.2.5 Flash point

The flashpoint of the fresh crude oils and their evaporated residues were determined and are given in Table C3.

C1.2.6 Interfacial tension

The interfacial tension of the fresh crude oils and their evaporated residues were determined and are given in Table C3.

The experimental results showed that the Neptune Field Composite did not form stable w/o-emulsions. One normally would expect that a crude oil with a wax and asphaltene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This suspicion is supported by the low interfacial tension value measured for the fresh crude (6 mN/m). SINTEF proposes that MMS inquire if offshore chemicals are present in this crude oil sample and that a follow up study be discussed based on the findings.

Table C3: A summary of the physical and chemical variables for Endicott, the Alpine Composite and the Neptune Field Composite, The High Island Composite and the North Star. The viscosities for Endicott, the Alpine Composite, the North Star, the Neptune Field Composite and the High Island Composite and the were measured at 10°C, 10°C , 10°C, 23°C and 23°C respectively.

Oil type			Evaporated [vol%]	Residue [wt%]	Density at 15,5°C [g/mL]	Pour point [°C]	Viscosity at 10 s^{-1} [cP]	Flash point [°C]	Interfacial tension [mN/m]	Wax content [wt%]	Asphaltenes “hard” [wt%]
Alaskan North Slope	Endicott	Fresh	0	100	0,913	6	510	<20	24	5,5	1,6
		150°C+	6	95	0,923	9	840	56	24	5,7	1,7
		200°C+	12	89	0,931	15	1630	85	25	6,1	1,8
		250°C+	19	84	0,940	18	5150	121	25	6,5	1,9
	Alpine Composite	Fresh	0	100	0,834	-18	103	<20	18	3,2	0,06
		150°C+	22	81	0,867	-3	118	38	20	3,9	0,07
		200°C+	34	69	0,885	9	839	82	27	4,6	0,09
		250°C+	44	60	0,898	18	1160	123	16	5,3	0,1
	North Star	Fresh	0	100	0.816	-39	10	<20	20	5,8	0,016
		150°C+	24.7	78.5	0.850	-9	45	37	21	7,3	0,021
		200°C+	38.5	65.3	0.866	3	380	77	23	8,8	0,025
		250°C+	50.2	53.8	0.881	18	2272	119	24	10,7	0,030
Gulf of Mexico	Neptune Field Composite	Fresh	0	100	0,869	-9	10	<20	6	3,7	0,3
		150°C+	11	90	0,887	0	50	46	6	4,1	0,4
		200°C+	22	81	0,900	3	110	93	7	4,6	0,4
		250°C+	30	73	0,911	9	300	128	8	5,0	0,4
	High Island Composite	Fresh	0	100	0,847	-15	23	-	14	1,6	0,03
		150°C+	-	-	-	-	-	-	-	-	-
		200°C+	-	-	-	-	-	-	-	-	-
		250°C+	33	70	0,879	0	83	-	16	2,3	0,04

C1.3 W/o emulsion properties

The formation of w/o-emulsions on the sea surface delay the evaporation and the natural dispersion weathering processes increasing the lifetime for the oil on the sea surface. When determining the most effective plan of action after an oil spill it is important to know the emulsifying properties (e.g. the rate of formation and stability) of the oil that has been spilled.

C1.3.1 W/o-emulsion rate of formation

The rates of formation of the Endicott, the Alpine Composite, the Neptune Field Composite and the North Star w/o-emulsions were mapped using the rotating cylinder method (Mackay, 1982) at 10°C, 10°C, 23°C and 10°C respectively. The kinetics of formation are expressed by the $t_{1/2}$-values, which is the time (in hours) it takes for the emulsions to reach half of their maximum water content. The calculated $t_{1/2}$-values for Endicott, Alpine Composite, the Neptune Field Composite and the North Star are given in Table C4.

The maximum water content of the Endicott w/o-emulsions is quite high (all are above 50%). The rate of formation is relatively slow, after approximately 10 hours the Endicott emulsions have reached their maximum water content. A slow rate of formation is typical for crude oils with a high asphaltene content.

The maximum water content of the Alpine Composite w/o-emulsions is high (all are above 80%). The rate of formation is relatively fast, after approximately 30 minutes the Alpine Composite w/o-emulsions have reached a water content above 50 vol%.

The Neptune Field Composite w/o-emulsions contain little water (all water contents are below 10 vol%). The rate of formation is fast, after approximately ½ hour the emulsions have reached their maximum water content. These w/o-emulsion were not stable, see C1.3.2.

The North Star oil has a fast initial water-uptake and reaches 45% within 10 minutes. The water content gradually increases to a maximum water content of 70-80%.

The fast emulsification rates are typical for the Alpine Composite and the North Star oil is typical for paraffinic crude oils

Table C4: The calculated $t_{1/2}$–values and the maximum water content for Endicott, the Alpine Composite, the North Star and the Neptune Field Composite w/o-emulsions at 10°C, 10°C, 10°C and 23°C respectively.

Oil type			$t_{1/2}$ [h]	max. water content [vol%]
Alaskan North Slope	Endicott	150°C+	0,6	82
		200°C+	1,2	79
		250°C+	2,8	64
	Alpine Composite	150°C+	0,1	80
		200°C+	0,2	80
		250°C+	0,5	80
	North Star	150°C+	0.11	68
		200°C+	0.14	69
		250°C+	0.09	83
GOM	Neptune Field Composite	150°C+	0,1	6
		200°C+	0,2	8
		250°C+	0,1	7

C1.3.2 Stability of the w/o-emulsions and the effect of an emulsion breaker

Unstable w/o-emulsions may dehydrate at storage or upon mechanical influence (e. g. stirring or pumping). Stable w/o-emulsions, on the other hand, increase the volume that has to be collected considerably. This can give storage problems. Responding boats are therefore recommended to have an emulsion breaker available and it is important to know its effectiveness. A reduction of the water content in a w/o-emulsion from 80 to 20% will decrease the volume of the emulsion 4 times. One of the most common emulsion breakers is Alcopol O 60% (Ross, 1986).

From the experimental results the fractional dehydration factor, D, is calculated using equation C-1.

$$D_x = \frac{WOR_{ref} - WOR_x}{WOR_{ref}} \qquad \text{(C-1)}$$

where:

WOR_{ref} = Volumetric water-to-oil ratio in the emulsion after 24 hours rotation
WOR_x = Maximum volumetric water-to-oil ratio in the emulsion after 24 hours rotation and x hours settling

The fractional dehydration value lies between 0 and 1. An emulsion is defined as totally stable if no water is separated from the emulsion during a 24 hour settling period (D = 0) and an increasing D means reduced stability after the application of an emulsion breaker.

The calculated fractional dehydration factor for the Endicott, the Alpine Composite and the North Star w/o-emulsions with and without application of Alcopol O 60% are given in table C6.

Table C5: The calculated fractional dehydration of the Endicott, the Alpine Composite, and the North Star w/o-emulsions with and without the application of Alcopol O 60% (500 ppm and 2000 ppm) after 10 min settling and 24 hours settling with and without rotation at 10°C.

Oil residue		Alcopol O 60% [ppm]	$D_{24\ hours}$	$D_{24\ hours\ +\ rot}$
Endicott	150°C+	0	0	0
	200°C+		0,1	0,1
	250°C+		0	0
	150°C+	500	0,2	0,2
	200°C+		0,2	0,4
	250°C+		0,3	0,3
	150°C+	2000	1,0	1,0
	200°C+		1,0	1,0
	250°C+		0,7	0,9
Alpine Composite	150°C+	0	1,0	1,0
	200°C+		0	0
	250°C+		0,2	0,2
	150°C+	500	1,0	1,0
	200°C+		0,93	0,93
	250°C+		0,93	0,93
	150°C+	2000	1,0	1,0
	200°C+		1,0	1,0
	250°C+		1,0	1,0
North Star	150°C+	0	0	0
	200°C+		0	0
	250°C+		0	0
	150°C+	500	0,82	0,82
	200°C+		0,89	0,89
	250°C+		0,90	0,90
	150°C+	2000	0,92	0,92
	200°C+		0,92	0,92
	250°C+		0,97	0,97

The asphaltene and wax content in Endicott stabilise the w/o-emulsion by preventing the fusion of water droplets. In order to effectively dehydrate the Endicott w/o-emulsions when using Alcopol O 60%, a minimum dosage of 2000 ppm should be applied in an oil spill situation. This will enable an effective dehydration of all of the Endicott w/o-emulsions.

The wax content and asphaltene content in the Alpine Composite oil sample is quite low, however, the relative amount of these stabilising components increase with weathering. This will increase the stability of the w/o-emulsions formed. In addition the increase in viscosity of the continuous phase (especially the 200°C+ and 250°C+ residues) decreasing the diffusion of water droplets will lead to a more stable w/o-emulsion. A dosage of 500 ppm Alcopol O 60% will dehydrate emulsions of the Alpine Composite oil to a water content of 6%, which should be sufficient for most practical purposes. A total dehydration demands a higher ratio of demulsifier.

The experimental results showed that the Neptune Field Composite obtained a water content below 10 %, however, these w/o-emulsions were completely dehydrated after a settling period of 24 hours. The initial spill volume of the Neptune Field Composite will not increase significantly. One normally would expect that a crude oil with a wax and asphaltene content similar to the Neptune Field Composite will form stable w/o-emulsions. SINTEF suspects that production-/process-chemicals are present in the oil sample thereby reducing the w/o-emulsion process. This is supported by the low interfacial tension value measured for the fresh crude (6 mN/m), and as mentioned earlier, a follow up study is recommended.

The North Star crude has a low asphaltene content, but will form emulsions stabilised by the high wax content of the oil. Emulsions of the North Star oil is dehydrated to a water content of approximately 7% at an emulsion/demulsifier rate of 500ppm. For further dehydration of the emulsion a higher dosage (e.g. 2000ppm) will be needed.

C1.3.3 Viscosity of the w/o-emulsions

The viscosities of the Endicott and the Alpine Composite w/o-emulsions with different water contents were measured at 10°C, the results are given in Table C6. The viscosities measured are used as input to the SINTEF Oil Weathering Model. Emulsification of Endicott will cause a dramatic increase in viscosity. The viscosity of the Alpine Composite w/o-emulsion could not be determined due to the emulsion’s unstability.

Table C6: Viscosities of the Endicott and Alpine Composite w/o-emulsions (0 vol%, 50 vol%, 75 vol% and maximum water content) measured at 10°C.

Oil residue		Water content [vol%]	Viscosity at shear $10s^{-1}$ [cP]
Endicott	150°C+	0	840
	200°C+		1 630
	250°C+		5 150
	150°C+	50	1 530
	200°C+		3 330
	250°C+		7 910
	150°C+	75	6 240
	200°C+		12 200
	250°C+		-
	150°C+	82 (max)	15 300
	200°C+	79 (max)	21 400
	250°C+	64 (max)	21 700
Alpine Composite	150°C+	0	120
	200°C+		840
	250°C+		1 160
	150°C+	50	120
	200°C+		920
	250°C+		2 940
	150°C+	75	780
	200°C+		2 970
	250°C+		7 130
	150°C+	80 (max)	-
	200°C+		5 960
	250°C+		11 700
North Star	150°C+	0	45
	200°C+		380
	250°C+		2272
	150°C+	50	305
	200°C+		405
	250°C+		882
	150°C+	75	624
	200°C+		1034
	250°C+		1967
	150°C+	68	421
	200°C+	69	850
	250°C+	83	752

-: measurement not possible

C2 Meso-scale laboratory testing of the High Island Composite

In this chapter the experimental results obtained for High Island oil in the meso-scale laboratory testing are presented. The High Island oil were emulsified at arrival SINTEF. The emulsion was difficult to break, and thus the untreated emulsion were used in the meso-scale laboratory test. The experimental test temperature was 23°C. Results from the meso scale experiment are given in table C8.

C2.1 Visual observations

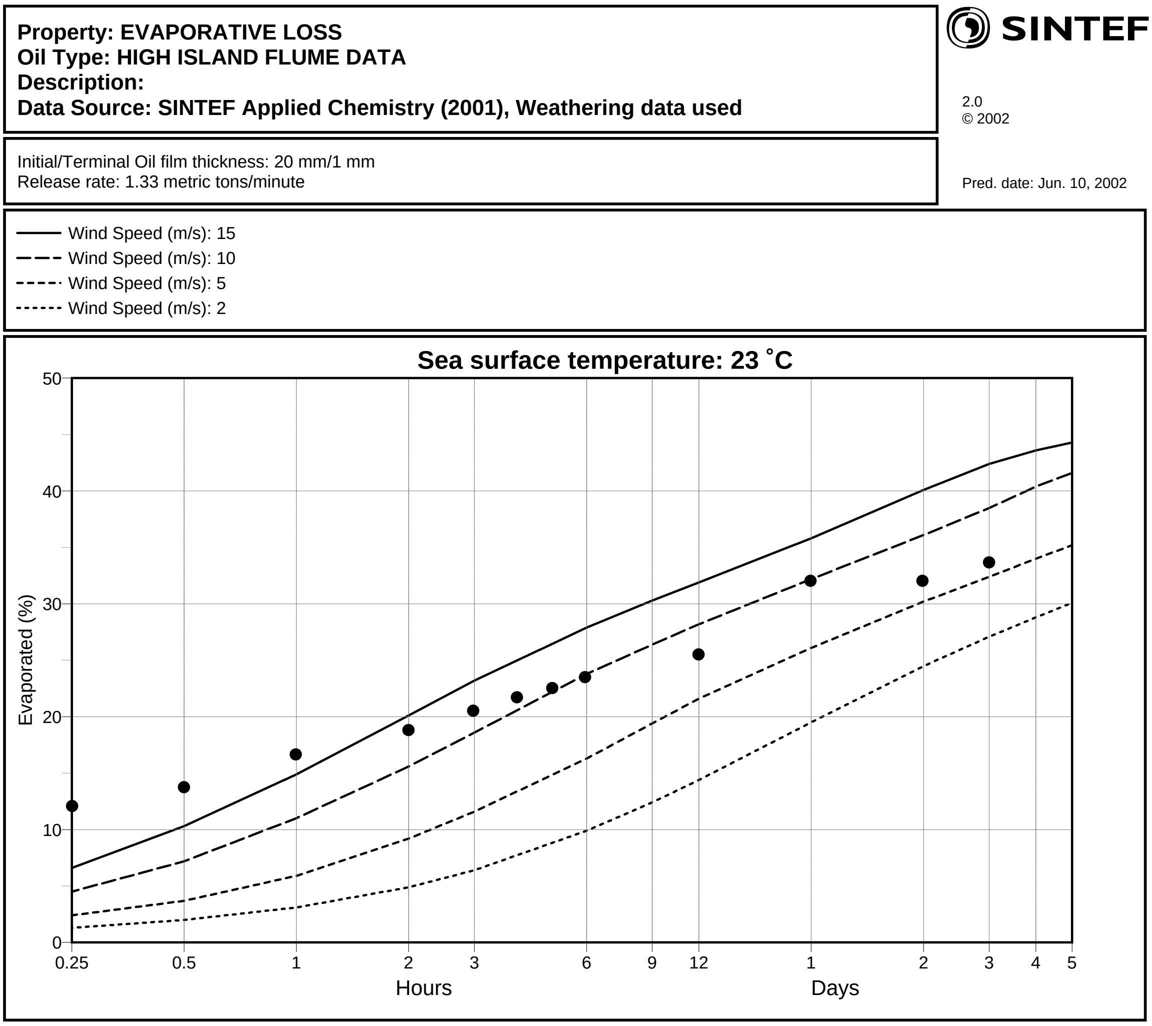
The High Island Composite oil sample spread quickly after its application to the water surface in the flume (Figure C14), an estimated 80-90% of the water surface was covered with oil within one hour. The formation of a w/o-emulsion could be observed during the first hour after application of High Island Composite.

An increase in the viscosity of the w/o-emulsion was observed throughout the experiment. The surface w/o-emulsion samples taken 5 hours after application of High Island Composite were dehydrated after a one-hour settling period, indicating the instability of the w/o-emulsion formed. The w/o-emulsion formed after 6 hours weathering is seen in Figure C15

Figure 16 shows the w/o-emulsion formed after 3 days of weathering in the flume. The w/o-emulsion formed after 3 days of weathering has a darker colour and has become more viscous. Immediately after the first application of dispersant the w/o-emulsion was dehydrated (Figure C17) and after 10 minutes most of the surface oil had dispersed (Figure C18). A second dispersant application was therefore not necessary.

C2.2 Evaporation

The evaporation results obtained in the meso-scale laboratory testing of High Island oil are presented and compared with the predicted evaporation results from the SINTEF OWM in Figure C10.



Property: EVAPORATIVE LOSS
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering data used

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

2.0
© 2002

Pred. date: Jun. 10, 2002

Figure C10: The evaporation results obtained for High Island Composite in the meso-scale laboratory testing and the predicted results from the SINTEF OWM.

Predicted evaporative loss is in good accordance with results form the meso scale flume.

C2.3 W/o-emulsification

The w/o-emulsification results obtained in the meso-scale laboratory testing are plotted with the predicted results from the SINTEF OWM in Figure C11 to Figure C12.

C2.2.1 Water uptake

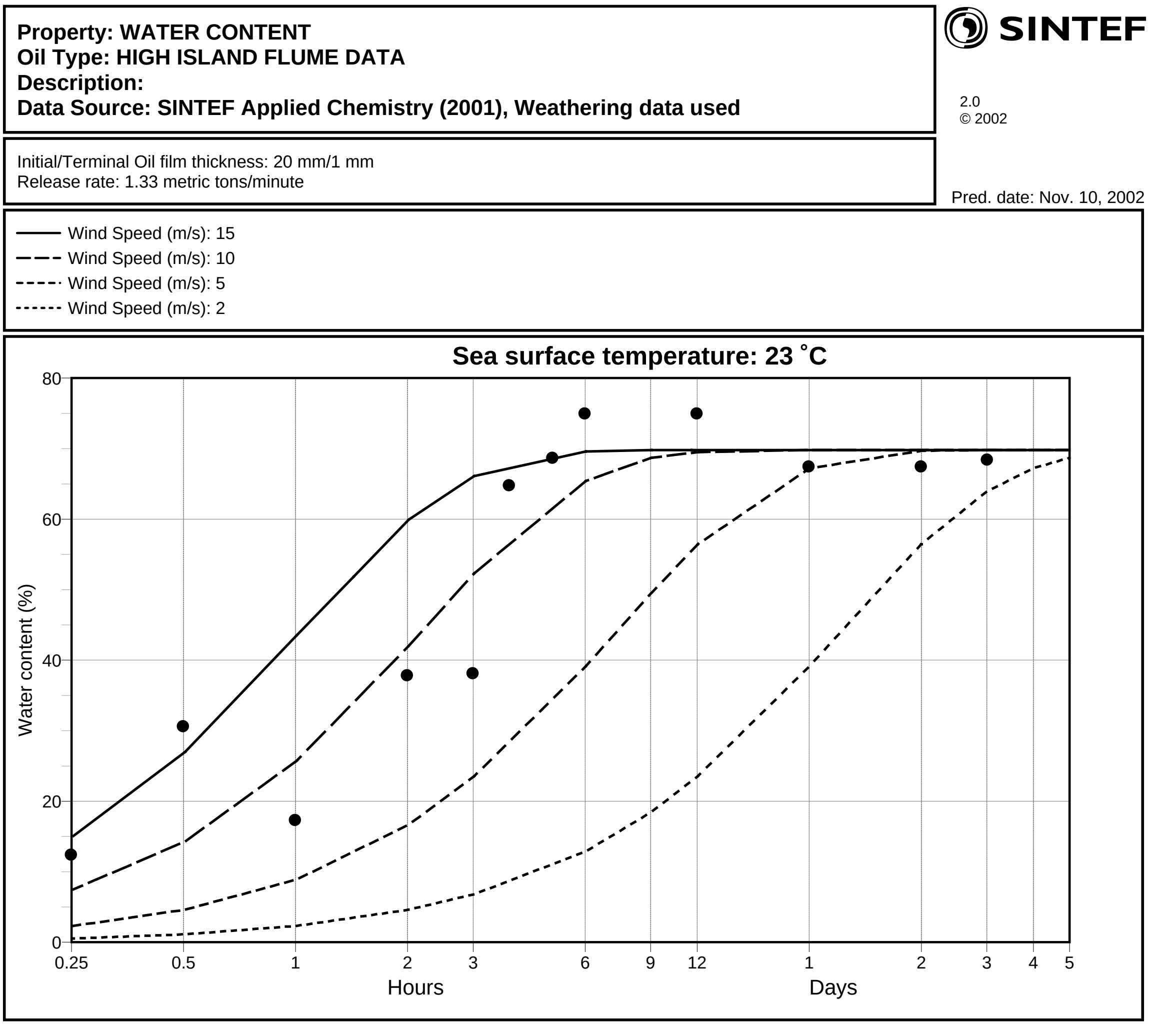


Figure C11: Predicted water uptake for High Island Composite and the results obtained from the meso-scale laboratory testing.

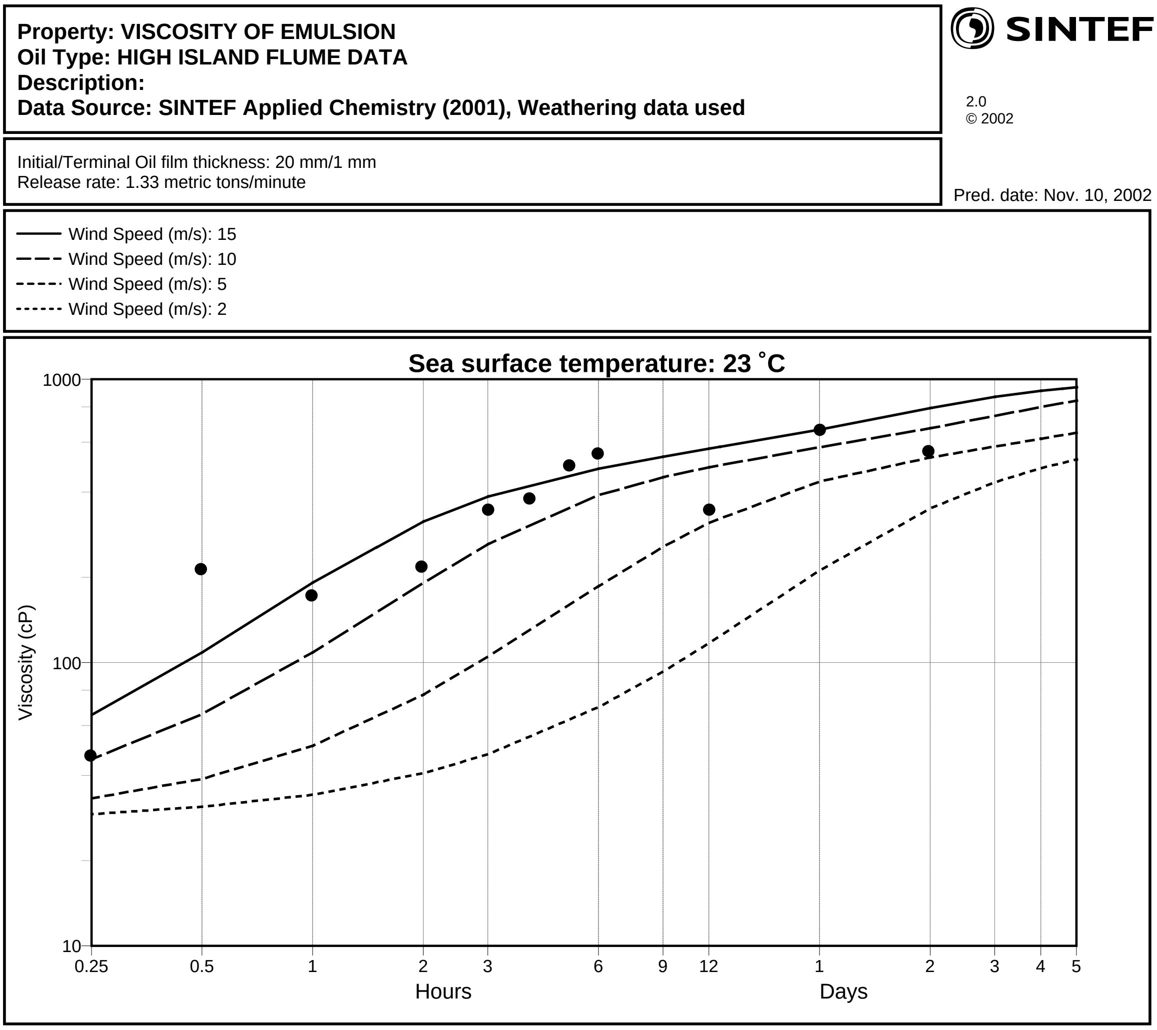
The water uptake observed in the meso scale flume experiment is used as input to the OWM. As shown in figure C11, the predicted emulsification rate correlates with the results from the flume experiment.

C2.3.2 Stability of the w/o-emulsions

The surface w/o-emulsion samples taken 5 hours after application of High Island Composite were dehydrated after a one-hour settling period, indicating an unstable emulsion. An increase in the stability of the w/o-emulsions, however, was observed throughout the experiment.

C2.3.3 Viscosity of the w/o-emulsion

Viscosities of the emulsion formed in the meso scale flume is compared to predicted viscosities in figure C14. As results form the meso scale flume experiment are used as input to the OWM, good correlation is expected between predicted and measured values. Evaporation- and emulsification rates in the meso scale flume is calibrated to simulate weathering conditions at 5-10m/s wind speed. Measured viscosities are in good accordance with predicted values in this wind speed interval.



Property: VISCOSITY OF EMULSION
Oil Type: HIGH ISLAND FLUME DATA
Description:
Data Source: SINTEF Applied Chemistry (2001), Weathering data used

Initial/Terminal Oil film thickness: 20 mm/1 mm
Release rate: 1.33 metric tons/minute

2.0
© 2002

Pred. date: Nov. 10, 2002

Figure C12: Predicted viscosity of the High Island Composite w/o-emulsions and the results obtained from the meso-scale laboratory testing.

C2.4 *In-situ* chemical dispersion

In situ chemical dispersion of the surface emulsion was performed on the High Island oil after 3 days of weathering in the meso scale flume. The efficiency of the dispersant on the emulsion was tested by analysing the concentration of dispersed oil in sub surface water.

At the application of the dispersant the emulsion were quickly dehydrated from approximately 70% to a water content of 10%. As the water content decreased a decrease in viscosity were visually observed (to little surface oil for measurements). Analysis of the sub surface water in the meso scale flume shows a high dispersibility compared to other oils tested in the flume, and emulsions of the high Island oil is probably dispersable for at least 3 days in an oil spill situation. Re-emulsification of the surface oil were slow and a second dispersant application were not thought to be necessary.

C2.5 Mass balance

The main elements in a mass balance for a crude oil spilt at sea are:

- Evaporative loss
- Surface oil
- Dispersed oil

However, the initial sample and water volume in the flume is reduced throughout the test, therefore the following parameters must taken into consideration:

- Amount of oil sampled
- Amount of water sampled
- Amount of oil adsorbed to the flume walls

The amount of oil evaporated, dispersed and sampled was calculated, and the oil adsorbed to the flume walls was estimated. Table C7 shows the mass balance for High Island oil during weathering in the meso-scale flume at 23°C.

Table C7: Mass balance for High Island Composite during the meso-scale laboratory test at 23°C.

	After 72 hours of weathering (%)	After the application of dispersant (%)
Evaporated	35.2	35.2
Oil on water surface	53.1	30.7
Dispersed	4.1	26.3
Sampled amount of oil	2.6	2.8
Adsorbed to the flume walls	5.0	5.0

The mass balance for High Island Composite during the meso-scale laboratory testing was predicted by the SINTEF OWM at 23°C and is given in Figure C13

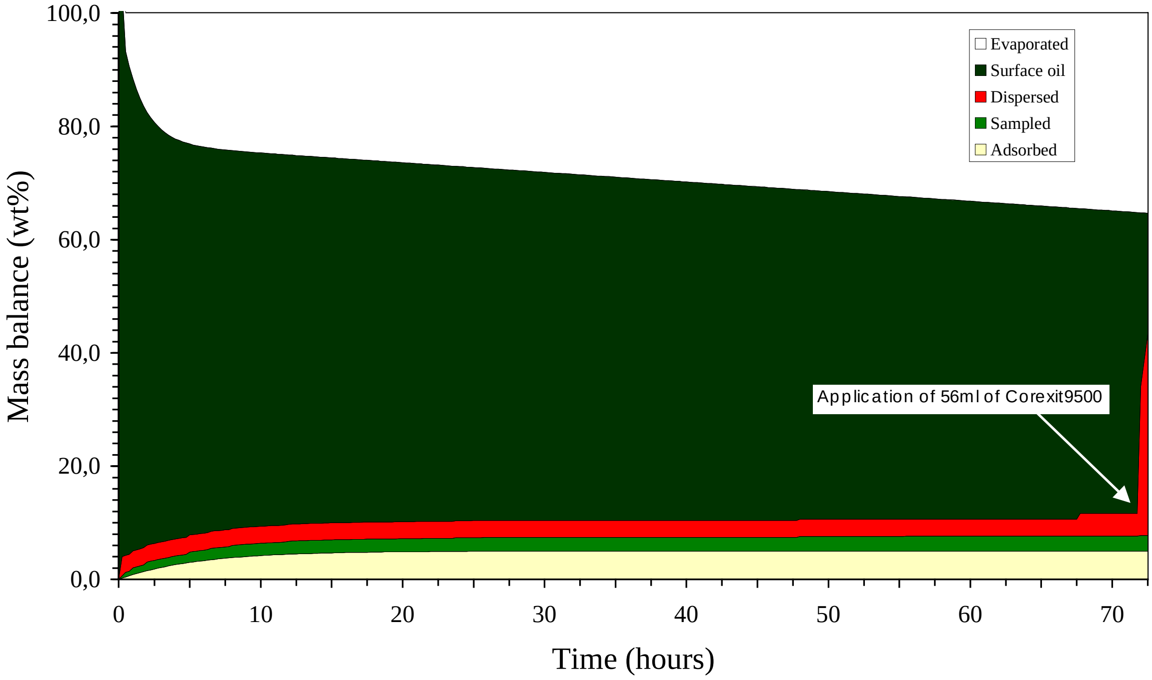


Figure C13: Mass balance for High Island Composite in the meso-scale laboratory test at 23°C.

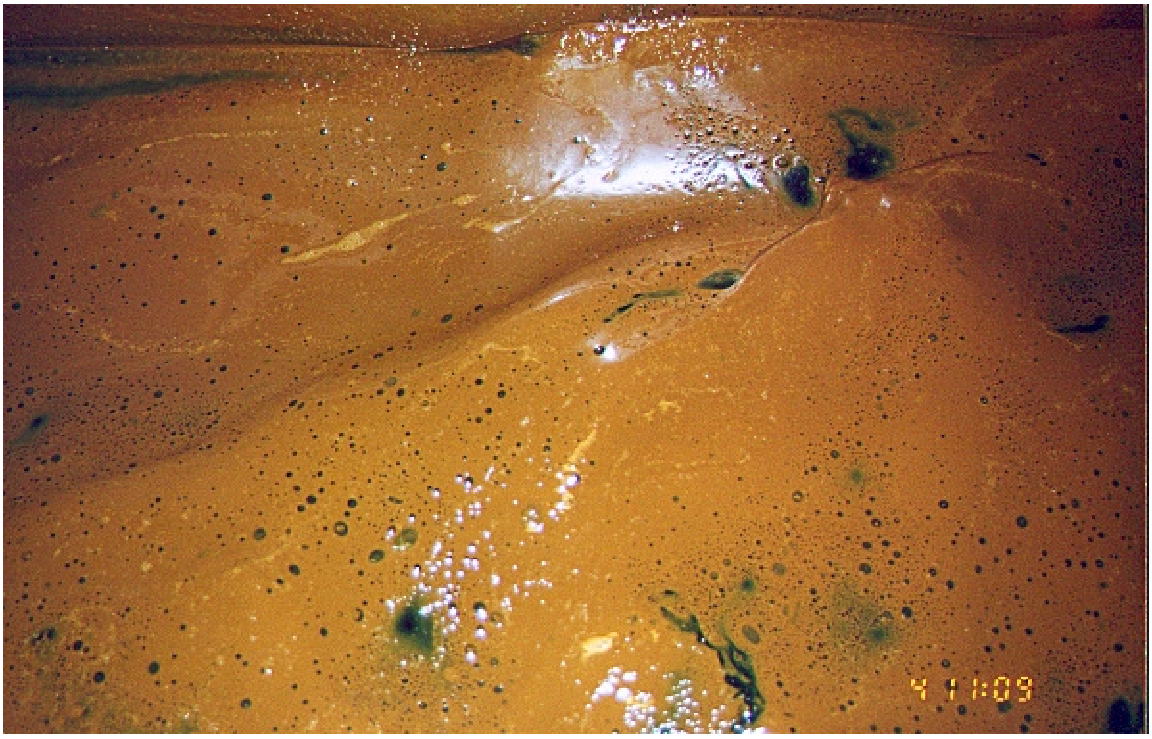


Figure C14: High Island Composite 30 minutes after application in the meso-scale flume.

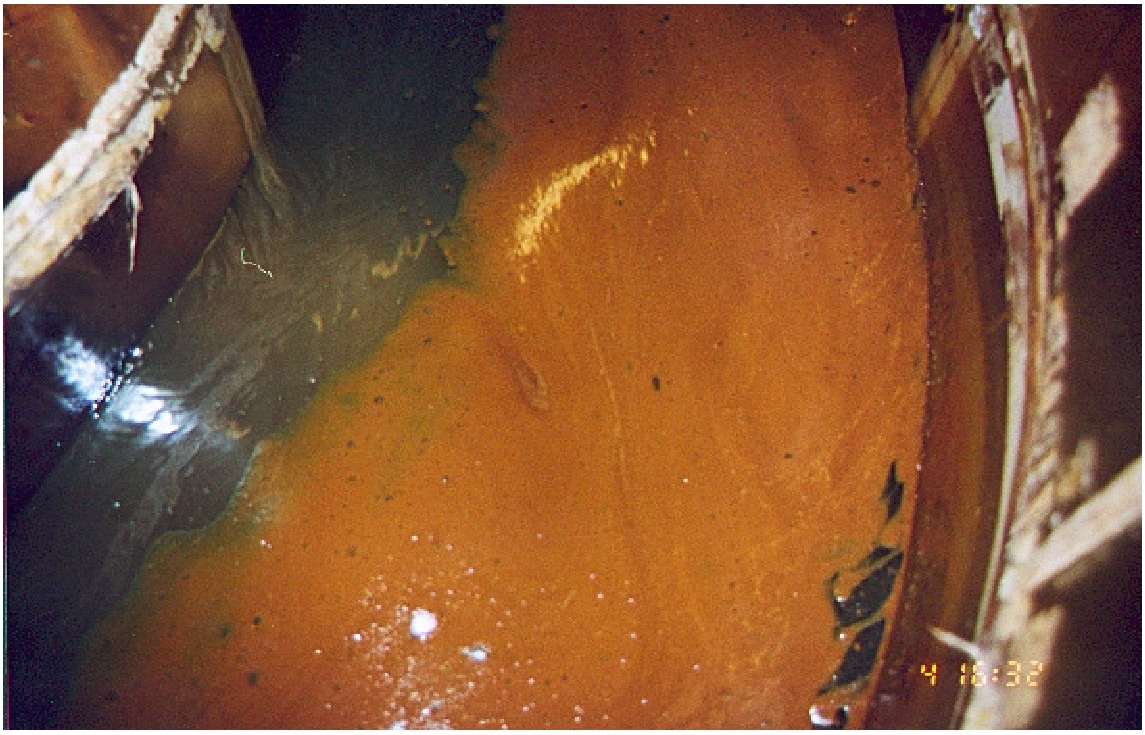


Figure C15: High Island Composite 6 hours after application in the meso-scale flume.

Figure C16: High Island Composite 3 days after application in the meso-scale flume.

Figure C17: High Island Composite immediately after application of dispersant in the meso-scale flume.

Figure C18: High Island Composite 10 minutes after application of dispersant in the meso-scale flume.

Table C8 Results from the meso-scale flume testing of the High Island Composite at 23°C

		Emulsion		Waterfree residue	
Sample	Time (hours)	Water content (vol%)	Viscosity (cP)	Evaporative loss (wt%)	Dispersed oil (wt%)
0	0.0	0	23	0	0
1	0.25	13	43	13	3.3
2	0.50	31	230	15	3.0
3	1.00	19	185	17	3.0
4	2.00	38	220	19	3.0
5	3.00	38	345	21	3.0
6	4.00	66	370	21	3.0
7	5.00	69	450	22	3.0
8	6.00	75	510	23	3.0
9	12.0	75	345	26	3.0
10	24.0	68	675	33	3.0
11	48.0	67	-	33	3.0
12	72.0	67	490	34	4.1
Application of 56 ml of Corexit 9500					
13	72.05	12	-	34	26,3
14	72.2	12	-	34	30,9
15	72.5	20	-	34	35,6

Appendix D: Input data for the SINTEF Oil Weathering Model

D1 Endicott

Geographical area:	Alaskan North Slope
Initial oil film thickness:	20 mm
Terminal oil film thickness:	2 mm
Release rate:	1,33 metric tons/minute
Sea temperature:	0°C and 10°C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to the SINTEF OWM for Endicott are given in Table D.1 to Table D.3.

Table D.1: Physical and chemical data for Endicott

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0,913
Pour Point	6°C
Reference temperature #1	10°C
Viscosity at reference temperature #1	510cP
Wax (wt%)	5.5
Asphaltenes (wt%)	1.6

Table D.2: The true boiling point values used for Endicott (obtained from Crude Assay at http://www.etcentre.org/main/e/db/db.html).

Temperature [°C]	Evaporated [vol%]
66	0
93	1
121	3
149	6
204	11
232	16
260	21
287	27
315	34
343	40
371	46
427	57
482	66
537	74
565	77

Table D.3: Experimental results from the bench-scale laboratory testing (see chapter C1) at 10°C:

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]	-	190	185	275
Evaporation [vol%]	0	6	12	19
Residue [wt%]	100	95	89	84
Specific gravity [g/L]	0.913	0.923	0.931	0.9340
Pour point [°C]	6	9	15	18
Viscosity at shear 10s^{-1} [cP]	510	840	1630	5150
Viscosity of 50% emulsion at shear 10s^{-1} [cP]	-	1540	3330	7910
Viscosity of 75% emulsion at shear 10s^{-1} [cP]	-	6240	12200	-
Viscosity of max water emulsion at shear 10s^{-1} [cP]	-	15300	21400	21700
Maximum water content in emulsion [vol%]	-	82	79	65
Halftime for water uptake [h]	-	0.6	1.2	2.8
Stability ratio	-	0.96	0.98	1.0

-: not determined

D2 Alpine Composite

Geographical area:	Alaskan North Slope
Initial oil film thickness:	20 mm
Terminal oil film thickness:	2 mm
Release rate:	1,33 metric tons/minute

Sea temperature:	0°C and 10°C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to the SINTEF OWM for the Alpine Composite are given in Table D4 to Table D6.

Table D.4: Physical and chemical data for the Alpine Composite

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.834
Pour Point	-18
Reference temperature #1 (°C)	10
Viscosity at reference temperature #1 (cP)	103
Wax (wt%)	3.2
Asphaltenes (wt%)	0.06

Table D.5: The true boiling point values used for the Alpine Composite sample.

Temperature [°C]	Evaporated [vol%]
85	8
105	13
135	19
175	27
205	33
235	38
265	45
310	54
350	62
420	72
525	89

Table D.6: Experimental results from the bench-scale laboratory testing (see chapter C1) at 10℃:

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]	-	167	246	296
Evaporation [vol%]	0	22	34	44
Residue [wt%]	100	81	69	60
Specific gravity [g/L]	0.8340	0.8668	0.8845	0.8981
Pour point [°C]	-18	-3	9	18
Viscosity at shear 10s^{-1} [cP]	103	118	839	1160
Viscosity of 50% emulsion at shear 10s^{-1} [cP]	-	120	920	2940
Viscosity of 75% emulsion at shear 10s^{-1} [cP]	-	780	2970	7130
Viscosity of max water emulsion at shear 10s^{-1} [cP]	-	-	5960	11700
Maximum water content in emulsion [vol%]	-	80	80	80
Halftime for water uptake [h]	-	0.1	0.2	0.5
Stability ratio	-	0	1	0.8

-: not determined

D3 North Star oil

Geographical area:	Alaska North slope
Initial oil film thickness:	20 mm
Terminal oil film thickness:	1 mm
Release rate:	1.33 metric tons/minute
Sea temperature:	0°C and 10°C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to the SINTEF OWM for High Island Composite are given in Table D7 to Table D9.

Table D.7: Physical and chemical data for North Star

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.816
Pour Point (°C)	-39
Reference temperature #1 (°C)	10
Viscosity at reference temperature #1 (cP)	20
Wax (wt%)	5.8
Asphaltenes (wt%)	0.016

Table D.8: The true boiling point values used for the North Star.

Temperature [°C]	Evaporated [vol%]
60	1.3
100	6.9
120	11.9
140	18.3
160	25.5
180	31.3
200	36.4
220	41.3
240	46.0
250	48.6
310	61.1
360	69.2
420	75.2
525	86.2

Table D.9: Experimental results from the bench-scale laboratory testing (see chapter C1) at 23°C.

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]		160	231	280
Evaporation [vol%]	0	24.7	38.5	50.2
Residue [wt%]	100	78.5	65.3	53.8
Specific gravity [g/L]	0.816	0.850	0.866	0.881
Pour point [°C]	-39	-9	3	18
Viscosity at shear $10s^{-1}$ [cP]	10	45	380	2272
Viscosity of 50% emulsion at shear $10s^{-1}$ [cP]		305	405	882
Viscosity of 75% emulsion at shear $10s^{-1}$ [cP]		624	1034	1967
Maximum water content in emulsion [vol%]		68	68	83
Viscosity of max water emulsion at shear $10s^{-1}$ [cP]		421	850	752
Halftime for water uptake [h]		0.11	0.15	0.09
Stability ratio		1	0.99	1

D4 The Neptune Field Composite

Geographical area:	Gulf of Mexico
Initial oil film thickness:	20 mm
Terminal oil film thickness:	0.5 mm
Release rate:	1.33 metric tons/minute
Sea temperature:	20°C and 29°C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to the SINTEF OWM for the Neptune Field Composite are given in Table D10 to Table D12.

Table D.10: Physical and chemical data for Neptune Field Composite

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.869
Pour Point (C°)	-9
Reference temperature #1 (C°)	23
Viscosity at reference temperature #1 (cP)	10
Wax (wt%)	3.7
Asphaltenes (wt%)	0.3

Table D.11: The true boiling point values used for the Neptune Field Composite.

Temperature [°C]	Evaporated [vol%]
53	1
93	4
125	9
150	13
173	17
195	20
213	23
240	28
267	33
288	36
321	42
370	50
450	62

Table D.12: Experimental results from the bench-scale laboratory testing (see chapter C1) at 23°C.

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]	-	200	256	305
Evaporation [vol%]	0	11	22	30
Residue [wt%]	100	90	81	73
Specific gravity [g/L]	0.869	0.887	0.900	0.911
Pour point [°C]	-9	0	3	9
Viscosity at shear $10s^{-1}$ [cP]	10	50	110	300
Maximum water content in emulsion [vol%]	-	0	0	0
Halftime for water uptake [h]	-	0	0	0
Stability ratio	-	0	0	0

-: not determined

D5 High Island Composite

Geographical area:	Gulf of Mexico
Initial oil film thickness:	20 mm
Terminal oil film thickness:	0,5 mm
Release rate:	1.33 metric tons/minute
Sea temperature:	20°C and 29°C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to the SINTEF OWM for High Island Composite are given in Table D13 to Table D15.

Table D.13: Physical and chemical data for High Island Composite

Chemical/physical property	
Specific Gravity (60°F/15.56°C)	0.846
Pour Point (C°)	-15
Reference temperature #1 (C°)	23
Viscosity at reference temperature #1 (cP)	23
Wax (wt%)	1.6
Asphaltenes (wt%)	0.03

Table D.14: The true boiling point values used for the High Island Composite.

Temperature [°C]	Evaporated [vol%]
120	3.0
140	5.7
150	7.0
160	8.6
170	10.7
180	12.8
190	15.3
200	18.2
210	20.3
220	23.0
230	25.5
240	26.8
250	31.9
280	40.0
300	45.0
350	56.0
380	61.0
400	64.0
425	68.0
450	72.0

Table D.15: Experimental results from the bench-scale laboratory testing (see chapter C1) at 23°C.

Chemical/physical property	Fresh	150°C+	200°C+	250°C+
Boiling point [°C]	-	-	-	285
Evaporation [vol%]	0	7.0b	18.2b	32.7
Residue [wt%]	100	93.9c	83.5c	70
Specific gravity [g/L]	0.847	0.853c	0.864c	0.879
Pour point [°C]	-36	-20*	-10*	0
Viscosity at shear $10s^{-1}$ [cP]	23	40*	60*	83
Maximum water content in emulsion [vol%]	-	70f	70f	70f
Viscosity of max water emulsion at shear $10s^{-1}$ [cP]	-	200f	400f	500f
Halftime for water uptake [h]	-	0.25f	0.25f	0.25f
Stability ratio	-	0f	0f	0f

-: not determined
f: From meso scale flume data
b: From boiling point curve
c: Calculated from boiling point curve
*constructed data

The High Island Composite sample received for the weathering study were in fact an emulsion. This disabled a proper weathering study, and a lot of the weathering data had to be extracted from data obtained in the meso scale flume, calculated, or constructed with background in experience from studies of similar oils. The results from the meso scale flume is, however, regarded realistic compared to a real weathering situation, and should provide relevant input data to the OWM.

Appendix E: List of abbreviations, symbols and acronyms

Term	Abbreviation, symbol or acronym
Benzene, toluene, etylbensen, *o*-, *m*- and *p*-xylenes	BTEX
Carbon	C
Centi Poise	cP
Cubic meters	m^3
American Petroleum Index	API
Degrees Celsius	°C
Dehydrating	D
Flame Ionization Detector	FID
Gas Chromatograph/Gas Chromatography	GC
Gram	g
Hours	h
Hydrogen	H
Kilo Pascal	kPa
Liter	L
Meter	m
Microliter	µL
Micrometer	µm
Milligram	mg
Milliliter	mL
Millimeter	mm
Millimeters	mm
Minute	min
Nickel	Ni
Nitrogen	N
Nitrogen, Sulfur and Oxygen	NSO
Oil Weathering Model	OWM
Oil-in-water	o/w
Oxygen	O
Parts per million	ppm
Percent	%
Polynuclear Aromatic Compounds	PAH
Reciprocal second	s^{-1}
Rotations per minute	rpm
Second	s
Sulfur	S
The American Society for Testing and Materials	ASTM
The fractional dehydration factor after 24 hours rotation and x hour settling	D_x
The fractional dehydration factor after 24 hours rotation and x hours settling	D_{24}
The fractional dehydration factor after 24 hours rotation, 24 hours settling and 10 rotations	$D_{24 + rot}$
The time it takes in hours before the oil has emulsified half of its maximum water content	$t_{1/2}$
Unresolved Chromatographic Material	UCM
Vanadium	V
Volume percent	vol%
Volumetric water-to-oil ratio in the emulsion after 24 hours rotation and x hours settling	WOR_x
Dispersant to Emulsion ratio	DER
Dispersant to Oil Ratio	DOR
Volumetric water-to-oil ratio in the emulsion after 24 hours rotation	WOR_{ref}
Water Soluble Fraction	WSF
Water-in-oil	w/o
Water-to-oil ratio	WOR
Weight percent	wt%

Appendix F: Literature list

Bridiè, A. L., Wanders, T. H., Zegweld, W. V. and den Heijde, H. B., 1980: Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse. *Mar. Poll. Bull.*, **11**, 343-348.

Daling, P. S., Brandvik, P. J., Mackay, D. og Johansen, Ø., 1990: Characterization of crude oils for environmental purposes. Paper at the 13th AMOP seminar, Edmonton, Canada 1990. DIWO-report no. 8. IKU rapport 02.0786.00/08/90. Open, 22pp.

Daling, P. S. and Strøm, T., 1999: Weathering of Oils at Sea: Model/Field Data Comparisons. *Spill Science and Tech. Bull.*, **5** (1), 63-74.

Fiocco, R. J., Daling, P. S., DeMarco, G., and Lessard, R., R., 1999: Advancing Laboratory/Field Dispersant Effectiveness Testing. OSC, pp 177-185.

FOH, 1984: Oljers skjebne og effekter i havet, Avslutningsrapport, Miljøverndepartementet, Norge.

Hokstad, J. N., Daling, P. S., Lewis, A., Strøm-Kristiansen, T., 1993: Methodology for testing water-in-oil emulsions and demulsifiers. Description of laboratory procedures. In: Proceedings Workshop on Formation and Breaking of W/O Emulsions. MSRC, Alberta, June 14-15, 24pp.

ITOPF 1986, Fate of Marine Oil Spills. Technical information paper no. 11/86. The InternationalTankers Owners Pollution Federation Ltd., London, England.

Johansen, Ø., 1991, Numerical modelling of physical properties of weathered North Sea crude oils. DIWO-report no. 15. IKU-report 02.0786.00/15/91. Open.

Leirvik, F.,Moldestad, M.Ø., Johansen, Ø., 2001: Kartlegging av voksrike råoljers tilflytsevne til skimmere. SINTEF report STF 66F01157.

Mackay, D, Buist, I., Mascararenhas, R. and Paterson, S., 1980: Oil Spill Processes and models. Report EE-8, Environment Canada, Ottawa, Ontario.

Mackay, D. and Zagorski, W., 1982: Studies of W/o Emulsions. Report EE-34: Environment Canada, Ottawa, Ontario.

Martinsen, E.A., 1994: The operational oil drift system at DNMI. The Norwegian Meteorological Institute, Technical Report No 125, Oslo, Norway, 51 pp.

McDonagh, M., Hokstad, J. N. og Nordvik, A. B., 1995: Standard procedure for viskosity measurement of water-in-oil emulsions. Marine Spill Response Corporation, Washington D. C., MRSC Technical Report Series 95-030, 36pp.

Moldestad, M., Singsaas, I., Resby, J. L. M., Faksness, L.-G. og Hokstad, J. N., 2001: Statfjord A, B og C. Egenskaper og forvitring på sjøen, karakterisering av vannløselige komponenter relatert til beredskap. SINTEF rapport nr. STF66 A00138. Åpen. 121pp.

National Research Council (NRC), 1985: Oil in the sea. Input, fates, and effects. National Academy Press, Washington D. C.

Nordvik, A., B., Daling P., S. and Engelhardt, F. R., 1992: Problems in the interpretation of spill response technology studies. *In:* Proceedings of the 15th AMOP Technical Seminar, June 10-12, Edmonton, Alberta, Canada, pp. 211-217.
Singsaas, I., Daling, P. S. and Jensen, H. V., 1993: Meso-scale laboratory weathering of oils. IKU report 22.2042.00/04/93, 81pp.

Ross, S. L., 1986: An experimental study of the oil spill treating agents that inhibit emulsification and promote dispersion. Report EE-87, Environmental Canada, Ottawa, Ontario.

Stiver, W. and Mackay, D., 1984: Evaporation rate of spills of hydrocarbons and petroleum mixtures. *Environ, Sci. Technol.*, **18** (11), 834-840.

Strøm-Kristiansen, T., Daling, P.S., 1994: Forvitringsegenskaper på sjøen for Brage Råolje. En håndbok for Norsk Hydro a.s.. IKU report no. 96.116.