NORDTEST Method

NT CHEM 003
Approved 2002-11

UDC 614.7

PREPARATION OF WATER-IN-OIL EMULSION FOR TESTING OF OIL SPILL RESPONSE EQUIPMENT

Key words: Oil spill, oil, water, emulsion

1 APPLICATION

This document describes a method for preparation of water-in-oil emulsion in quantities appropriate for testing of full-scale oil spill response equipment. The procedure was designed to accompany the "Standard for Performance Testing of Oil Spill Skimmers" (Ref. [1]).

The procedure provides guidelines with respect to selection of base oil, design/dimensioning of mixing arrangement and emulsion preparation methodology; all with the objective to produce a test emulsion of the desired physical properties.

The procedure is based on the use of Bunker oil for emulsion preparation. The document may, however, also provide valuable guidance for emulsification of other oils, for instance crude oils.

The main purpose of this document is to provide a method by which test emulsions may be produced repeatedly with a limited variation in physical properties, thus promoting comparable tests of oil spill response equipment at different locations/laboratories and at different times. Emulsions prepared according to this method may or may not be representative of those formed in the real environment following an oil spill.

The stability of emulsions is dependent on many chemical/physical factors, only partly understood. The use of this procedure does not guarantee the stability of the emulsion, nor the physical properties of the fluid. All quantitative information provided in this procedure should be understood as a guideline and should be verified by measurements and observations, followed by adjustments of the preparation method when appropriate.

2 TERMINOLOGY

Terminology used in this document is generally according to "ISO/FDIS 16165; Terminology relating to oil spill response" (Ref. [2]). Some main terms used in this document are defined below:

- **Asphaltene** – A polyaromatic component of some crude oils that has a high molecular mass, and also high sulphur, nitrogen, oxygen and metal contents. Asphaltenes are usually defined operationally by using a standardised separation scheme. One such scheme defines asphaltenes as those components of a crude oil or bitumen that are soluble in toluene but insoluble in *n*-pentane. Asphaltenes are effective as w/o emulsion stabilisers.
- **Base oil** – the original oil, before water is incorporated.
- **Bunker oil** – Intermediate or heavy fuel oil, primarily used for marine and industrial boilers.
- **Continuous phase** – The host fluid in the emulsion, in which the second fluid is incorporated as droplets.
- **Emulsifier** – Any agent that acts to stabilise an emulsion. The emulsifier may make it easier to form an emulsion by providing stability against aggregation and coalescence. Emulsifiers are frequently but not necessarily surfactants.
- **Emulsion** – A system of two immiscible liquids, in which one liquid is dispersed (the dispersed phase) as droplets in another liquid (the continuous phase).
- **Emulsion stability** – The ability of the emulsion to retain the dispersed phase over time and maintain its physical properties. A stable emulsion is one in which the droplets do not participate in aggregation, coalescence or creaming at a significant rate.
- **Microemulsion** – An emulsion with very small droplets, usually smaller than 1/2 µm.
- **Shelflife** – Period of time that an emulsion may be stored without significant breakdown or change in physical properties.
- **Surfactant** – Any substance that lowers the surface or interfacial tension of the medium in which it is dissolved.
- **Volume changes** – The number of times the entire volume is circulated through the pump (number of passes through the pump).
- **Water/Oil emulsion** – An emulsion in which water is the dispersed phase and oil is the continuous phase
- **Water injection rate** – The rate at which water is injected, expressed as a fraction of the total fluid circulation rate.

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Internet: www.nordtest.org

ISSN: 1459–2770
Project: 1508-00/2

3 BASIC EMULSION THEORY

Water/oil emulsions are systems in which water droplets are dispersed in a continuous oil phase. The water droplets are held in suspension by a combination of viscous and interfacial forces. Emulsification occurs in nature when oil on water is exposed to dynamic sea conditions.

The ability of the emulsion to retain its state over time when left at rest is called the emulsion stability. Whether an emulsion is stable or not depends on the water droplet dimensions, the oil viscosity and the chemical composition of the oil, in particular the content of emulsifiers (emulsion stabilising agents). Emulsions are stabilised by the emulsifiers accumulating at the oil water interface, forming a barrier against droplet coalescence.

The main naturally occurring emulsifiers in oils are asphaltenes, resins and waxes. Of these, the asphaltene content is believed to be most important, being the most effective emulsion stabilising agent. Literature suggests that the asphaltene content should exceed 3% for a stable emulsion with high water content to be produced, findings that are supported by studies carried out by Det Norske Veritas.

4 GENERAL DESCRIPTION OF METHOD

In this method w/o emulsion is prepared by gradually injecting water into a fluid circulation loop as illustrated in Figure 1. The water is injected at the suction side of the circulation pump, hence utilising the pump's shearing energy to break water into smaller droplets. After a number of passes through the pump, the water droplets are sufficiently small not to drain out of the fluid by gravity, but are kept in suspension by viscous and interfacial forces.

Generally, the emulsions should be stabilised by the natural emulsifiers of the oil, mainly asphaltenes, resins and waxes. However, in cases where there are insufficient natural emulsifiers, the addition of small quantities of extra emulsifiers may be considered (see Section 10). This procedure does not, however, recommend the use of chemical emulsifiers.

The following ranges are recommended for the mixing arrangement:

Emulsion preparation arrangements and adjustments	
Pump type	Gear or Centrifugal
Pump rate	Min 50% of full capacity
Minimum volume changes	20 (after all water has been injected)
Max water injection rate	1:20 up to 50% water, reduction to 1:30 – 1:40 above 50%
Water injection point	At pump inlet

Emulsions prepared by this procedure will normally obtain water droplets in the 10–20 μm range. Testing has shown that the viscosity of the emulsion is relatively unaffected by water droplet dimensions as long as the dominating droplet size is above 5 μm.

The predicted viscosity of the resulting emulsion as a function of base oil viscosity and water content is given in Figure 2 to Figure 4.

5 EMULSION MIXING ARRANGEMENT

The general emulsion preparation arrangement is illustrated in Figure 1, and includes the following resources.

- Mixing tank
- Water tank
- Mixing pump
- Water injection pump
- Valves
- Pressure gauges
- Flow meters for water and oil
- Hoses and/or pipes
- Storage tanks for the emulsion after preparation.

It is recommended that emulsion mixing is carried out in batches if the required oil quantity exceeds several tons. Table 1 suggests dimensions of the various components of the emulsion preparation arrangement for different batch sizes.

5.1 Mixing pump

The mixing pump must meet the following requirements:

1. Must provide sufficient shearing force to break the water into droplets.
2. Is able to maintain acceptable pumping rate as emulsion properties change as a result of emulsification.
3. Has a pumping capacity that allows recirculation of the entire emulsion batch a minimum of 20 times per hour.
4. Provides sufficient suction (if not submerged in the fluid) to pump the base oil and the resulting emulsion at all stages of preparation.

The pump may be attached to the mixing tank bottom by a short suction line or be submerged in the tank. The length of the suction line must be minimised (preferably less than 2 m) to avoid excessive flow resistance and risk of cavitation on the suction side of the pump as the emulsion viscosity increases.

Overall, the most suitable pump is a positive displacement pump with aggressive shearing action, such as a gear pump. Centrifugal pumps have also proved suitable for emulsifying oil, but this pump type has limited suction and must be submerged in the fluid to allow sufficient inflow to the pump. Centrifugal pumps also have limited pumping capacity for highly viscous emulsions.

5.2 Water injection pump

The water injection pump must meet the following requirements:

1. Must have a pumping capacity up to 1/10 of the expected pumping rate of the mixing pump, against 1 bar pressure.
2. Must be adjustable down to zero (or very low) flow rate.
3. Must withstand salt water.

5.3 Main mixing tank

The main circulation tank must meet the following requirements:

1. Cone shaped or sloping bottom.
2. Discharge port at lowest level of tank.
3. Must have the appropriate volume to match the circulation pump capacity.
4. If larger than 2 m^3, should be equipped with a low-energy stirring mechanism to ensure that the entire volume in the tank is recirculated. This requirement may be avoided by using a submerged and movable pump.

5.4 Hoses and piping

Hoses and piping must be kept as short as possible to minimise pressure drop at high viscosities and high pump rates. This is especially a concern at the suction side where the length should be less than 2m and the pipe diameter should be no less than 4" for an emulsion preparation set-up for batches larger than 1 m^3 (see Table 1 for suggested dimensions).

It is imperative that the suction side of the pumping system is completely sealed since air that is entrained into the fluid may affect the emulsification process.

5.5 Pressure gauges and flow meters

Pressure gauges must be installed on the suction and discharge sides of the mixing pump to provide data required for safe and proper operation.

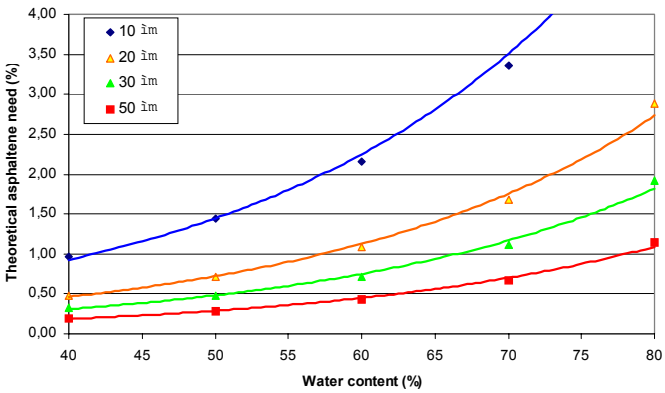
The flow rate in the main circulation line should be monitored by a flow meter. Alternatively the flow rate may for some pumps (positive displacement) be estimated from the pump rotation speed. The water injection flow rate should be monitored with a flow meter or by level measurements in the water tank.

6 SELECTION OF BASE OIL

This procedure is based on the use of Bunker oils (fuel oils) for emulsion preparation. Bunker oils are preferred from considerations of product property variability, international availability, emulsion stability and work environment.

6.1 Required base oil properties

In order to ensure emulsion stability a certain fraction of natural emulsifiers is required. The main stabilising component in Bunker oil is believed to be asphaltene and the necessary quantity is related to the total water/oil interface area. The figure below suggests minimum asphaltene fractions in the base oil for different water contents and average droplet size. Emulsions formed by the method prescribed here (typically having droplets in the 10 to 20 ìm range) should usually not have less than 2% asphaltene for water content up to 50%. For water content exceeding 60% it is recommended that the base oil has more than 3% asphaltene.



Chemicals with surface active properties are in some cases added in the oil production process or at refineries. Such chemicals may interfere with the emulsion preparation process and lead to instability. Oil/water interfacial tension measurements may give indications of such past chemical treatment. Normally, the interfacial tension of intermediate or heavy bunker oils is in the 18 to 35 mN/m range. Interfacial tension below this range can indicate past chemical treatment that may be detrimental to emulsification. Such oils should be avoided or investigated for emulsification at small scale before use.

Due to particular effects of waxes, the relationships between base oil and emulsion properties outlined in this procedure may in many cases not be valid for oils with very high wax content. It is therefore recommended that the quantity of wax in the base oil should be less than 8%.

The table below summarises recommended property ranges for the base oil:

Recommended base oil properties	
Oil/water interfacial tension range	18–35 mN/m
Min asphaltene content	2% up to 50% water 3% above 50% water
Max wax content	8%

6.2 Preparation of base oil

A base oil with the desired properties, mainly viscosity and density, may be prepared by blending a heavy fuel, such as Bunker C/Fuel oil No. 6, with a lighter fuel oil, such as diesel.

Guidelines for determining blending ratios are specified in ASTM standard D341 "Viscosity – Temperature Charts for Liquid Petroleum Products" (Ref. [3]). In many cases, the terminal can provide users with fuel oils blended to any viscosity.

As the above blending guidelines are crude and often give inaccurate results, all base oil properties must be verified by measurements and blending ratios adjusted to achieve the correct properties at the actual test temperature.

All relationships between emulsion properties and base oil properties in this procedure are for 20°C. Testing may be carried out at other temperatures and the effect of temperature variation on base oil viscosity and emulsion must always be taken into consideration (see Figure 5 and Figure 6).

7 OIL PROPERTY MEASUREMENTS

Oil analytical equipment must be available for measuring the oil properties of the base oil and the emulsion.

Base oil characterisation should include:

- Viscosity (cP) at 20°C. Viscosity should be reported at shear rates 1, 10 and 100 s^{-1}. At least two of these must be measured, while the third may be found by extrapolation
- Density (kg/l) at 20°C
- Water content (%) (to identify any water originally in the oil)
- Pour point (°C) *(optional)*
- Wax content (%) *(optional)*
- Asphaltene content (%) *(optional)*
- Oil/water interfacial tension (mN/m) *(optional).*

The latter four parameters are optional but recommended to predict stability problems.

Emulsion characterisation should include:

- Viscosity (cP) at 20°C and at the test temperature. Viscosity should be reported at shear rates 1, 10 and 100 s^{-1}. At least two of these must be measured, while the third may be found by extrapolation
- Density (kg/l) at 20°C
- Water content (%)
- Droplet size distribution in emulsions, or droplet size range (µm).

8 STEPWISE EMULSION PREPARATION PROCEDURE

The following lists the recommended sequence of actions for preparing an emulsion according to this procedure:

8.1 Prior to mixing

Main steps prior to mixing:

1. Specify the desired viscosity of the emulsion to be produced (at shear rate 10), and the temperature at which the emulsion should be used.
2. Specify the desired water content of the emulsion (%).
3. Estimate the emulsion viscosity at 20°C from Figure 5.
4. Determine the required base oil viscosity from Figures 2 to 3.
5. Determine the quantity of base oil required to produce the desired emulsion quantity (Test oil quantity x (1-water content%/100)).
6. If the base oil is to be prepared by blending heavy bunker and diesel, determine the blending ratio crudely from ASTM D341. Accurately determine the blending ratio by blending small volumes of oil (see 6.2) and measuring viscosity. The base oil viscosity should not deviate by more than 5% from the desired values.
7. Prepare the needed quantity of base oil by blending bunker oil and diesel according to the identified blending ratio.

8.2 Emulsion mixing

The following lists the main steps in the mixing process:

8. Transfer base oil to the emulsion mixing tank.
9. Fill the water tank with the needed quantity of salt water. Ensure that the temperature of the water is close to the temperature of the base oil.
10. Start circulation of the oil. Adjust to the desired pump rate. The pump rate should normally be at least 50% of the maximum pump capacity to provide sufficient shearing energy. The pump should not run at its full capacity at this point since extra power will be needed as the oil is emulsified.
11. Check that both suction and discharge hoses are well submerged in the oil and that there is no sign of air being entrained in the fluid. If air bubbles are seen, stop pumping and seal the system.
12. Check that the pressure on the suction side is well above the required Net Positive Suction Height (NPSH) given by the pump manufacturer. The pressure should not be below 0.7–0.8 bar at this point since pressure will drop as oil is emulsified.
13. Start water injection pump, open water injection valve and adjust water injection to a rate not exceeding 1:20 of the pump rate of the mixing pump.
14. Monitor the pumping rate of the mixing pump and the water injection rate. If the mixing pump rate is reduced due to increased flow resistance, reduce the water injection rate accordingly. If gas bubbles are observed in the system (that has been leak tested) this may be due to pump cavitation and may be avoided by reducing the pumping rate. Observe visually the consistency of the emulsion. If large water droplets are seen, reduce the

water injection rate or increase the speed of the mixing pump.

15. When water content in the emulsion exceeds 50% reduce the water injection rate to 1:30 – 1:40.
16. Visually observe the emulsion as water content increases. If there are any indications that water and oil are separating, the injection rate should be increased. Monitor the pressure on the pump suction side and reduce pump rate if the pressure is near the NPSH requirements of the pump. Any cavitation problems will be heard as clicking noises in the pump and should be avoided by reducing the pump rate.
17. After the desired water quantity has been injected, stop the water pump and continue recirculating the emulsion for another 20 volume changes.
18. Inspect the emulsion and continue mixing if there are indications of free water in the fluid.

8.3 After mixing

After mixing is completed carry out the following:

19. Take several samples of the emulsion for property measurements and stability assessment.
20. Measure water content and viscosity (see Section 7). Assess emulsion stability (see Section 9).
21. Transfer the emulsion batch to the main emulsion holding tank.
22. If additional emulsion batches are to be made, return to point 8.

9 ASSESSING EMULSION STABILITY

For purpose of equipment testing, the emulsion is considered stable if:

1. The water content is not reduced by more than 3% after 1 week of storage at test temperature.
2. The droplet size distribution is not significantly changed during the same period.

Emulsion stability may only be properly assessed by measuring water content after storage of extended duration. However, experience shows that unstable emulsions will show signs of this at an early stage and in most cases within the first day after production.

The following may be early stage indications of instability:

1) An emulsion droplet pressed between two thin sheets of glass, should not show water droplets, that are distinguishable by the eye.
2) An unstable emulsion rubbed against the palm of glove covered hands (preferably white plastic gloves) will often show signs of water droplets shearing out of the fluid, while stable emulsions will not.
3) Unstable emulsions will frequently show indications of microscopic bubbles bursting on the fluid surface when inspected at low angle light.
4) When inspected through microscope, unstable emulsions will often show clear indications of droplet coalescence. Note that the heating by the microscope light may accelerate this process and samples should therefore be inspected at low light level and allowed short time to heat.

10 COMMENTS ON THE USE OF CHEMICAL EMULSION STABILISING AGENTS

In cases when the natural content of emulsifiers is too low to form stable emulsions, stability may be achieved by the addition of small quantities of chemical emulsion stabilisers, which are widely available commercially.

The emulsion stabiliser can promote emulsion formation and stability by two main mechanisms:

- Most emulsifiers reduce oil/water interfacial tension, thereby reducing the energy required to break large droplets into smaller ones.
- Emulsifiers accumulate at the oil/water interface where they form a protective layer that counteracts the tendency of contacting droplets to coalesce.

The addition of chemical emulsifiers is not recommended when emulsions are prepared according to this procedure. The reason for this is that emulsifier addition easily results in the formation of emulsions with extremely small droplets, often below μm level, due to the high shearing energy of the mixing pumps and the interfacial tension reduction. The physical properties of such emulsions are highly unpredictable since viscosity increases dramatically when droplet dimensions are reduced below approximately 5 μm.

If the use of emulsion stabilising chemicals is the only solution for obtaining a stable emulsion, the following is recommended:

- An emulsifier should be used that has a minimum effect on interfacial tension, but yet acts as a stabiliser.
- The quantity of emulsifier used should be reduced to the minimum required to obtain stability.
- Measurements should verify that the emulsifier has minimum effect on other physical properties of the emulsion.

11 REFERENCE DOCUMENTS

[1] Standard for Performance Testing of Oil Spill Skimmers. Det Norske Veritas 2002.

[2] ISO/FDIS 16165. Ships and marine Technology. Marine Environmental Protection. Terminology relating to oil spill response.

[3] ASTM Standard D341-93(1998). Standard Viscosity-Temperature Charts for Liquid Petroleum Products.

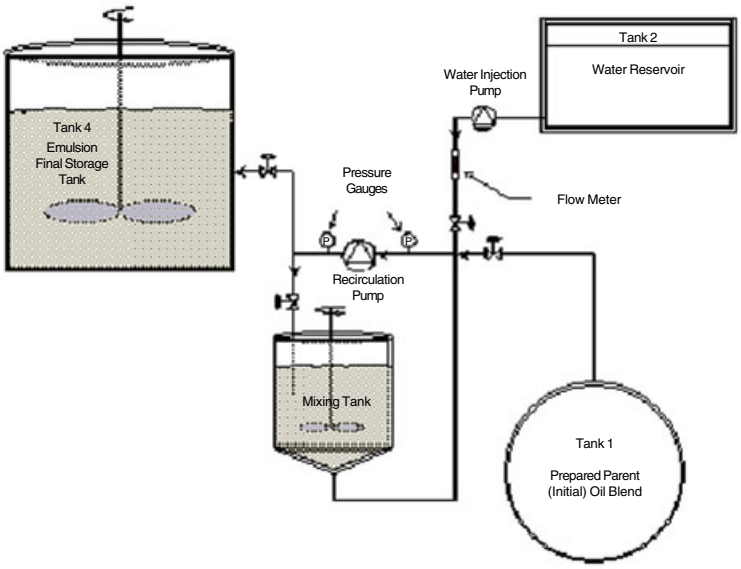


Figure 1. Suggested emulsion preparation arrangement.

Table 1. Suggested scaling of the emulsion preparation system according to the volumes of emulsion batches to be produced.

Emulsion batch volume (tank volume) (m^3)	0,1	0,5	1	2	5	10
Mixing pump, min capacity (m^3/h)	3	15	30	60	150	300
Water injection pump, min capacity (m^3/h)	0,3	1,5	3	6	15	30
Suction line min dimensions (" inner diam)*	2	3	4	4	5	6
Pressure line min dimensions (" inner diam)*	2	3	3	3	4	4

* – assumes 2 m length, based on 4000 cP effective viscosity of the emulsion, the diameter reduction may be compensated with a similar length reduction.

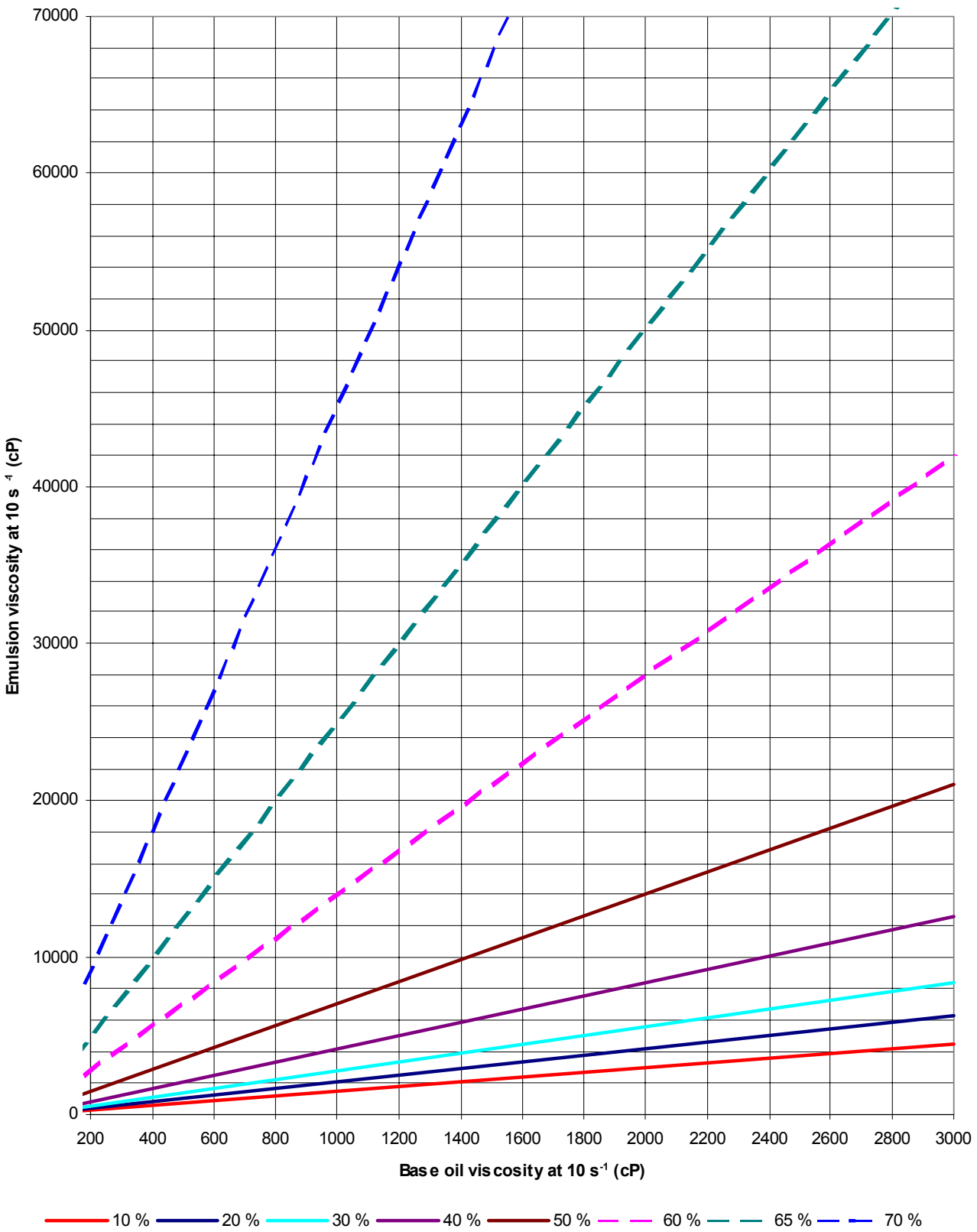


Figure 2. Suggested emulsion viscosity as a function of water content (at shear rate 10 s^{-1}).

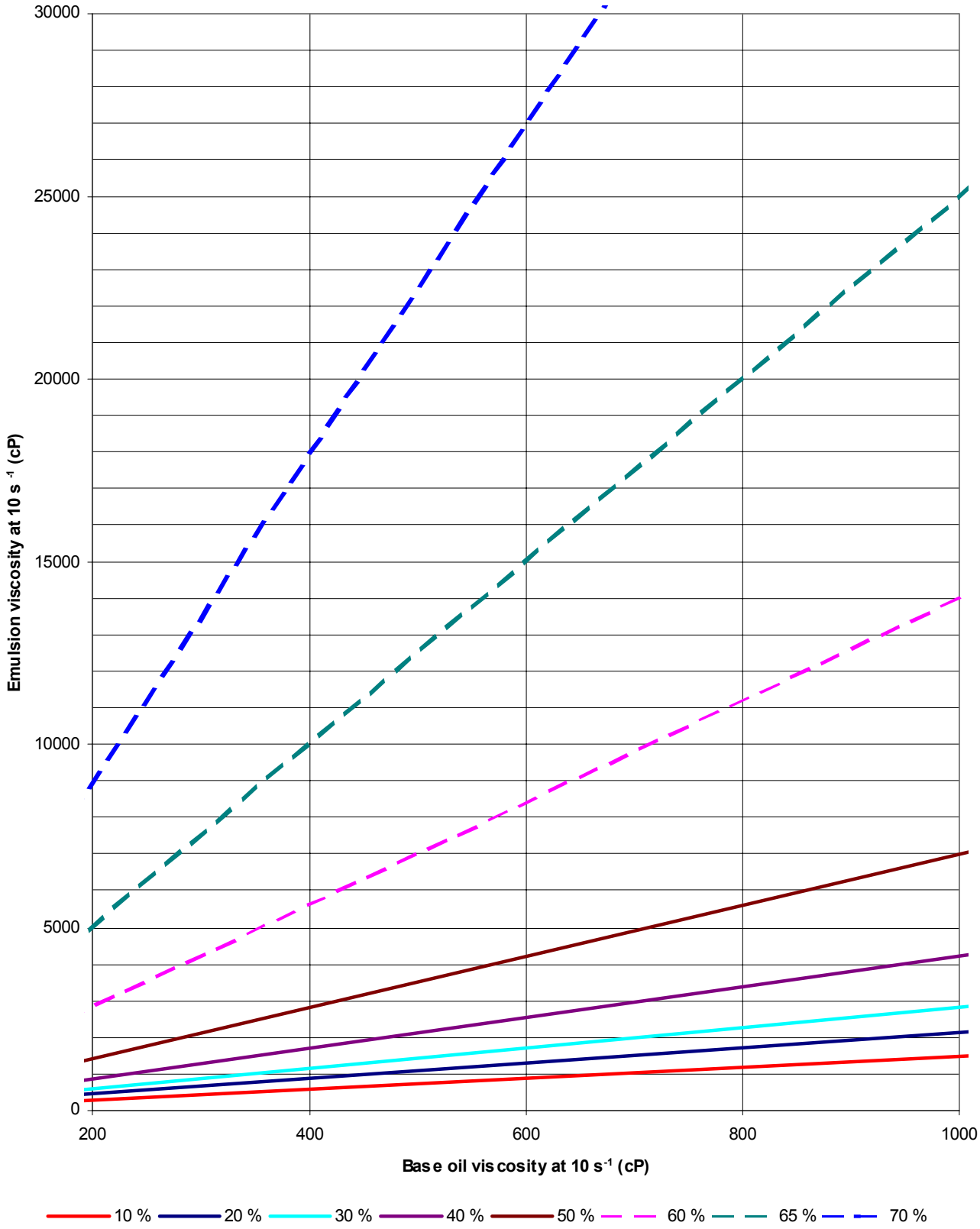


Figure 3. Suggested emulsion viscosity as a function of water content at shear rate 10 s^{-1} – (low range extract of Figure 2).

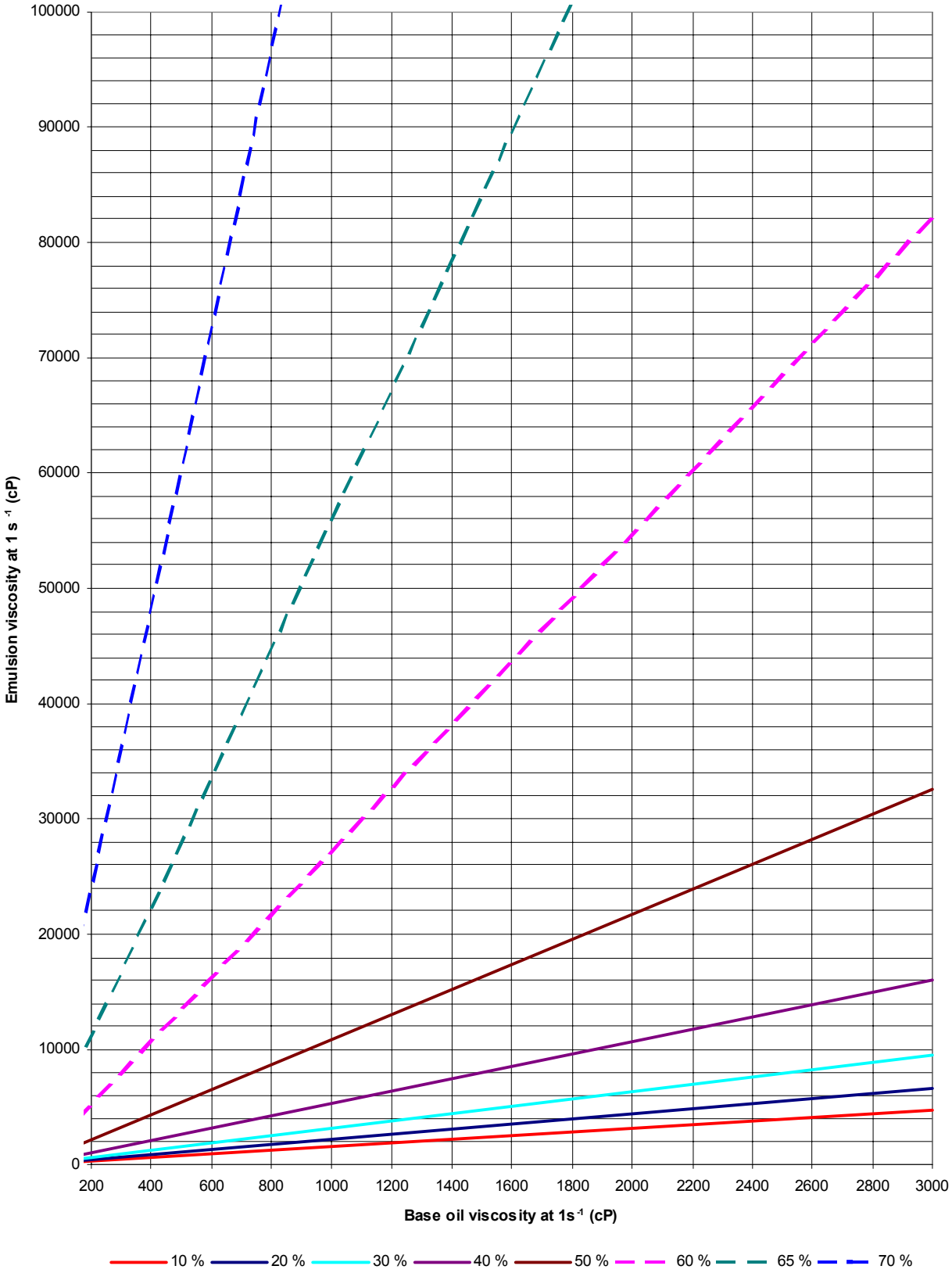


Figure 4. Suggested emulsion viscosity as a function of water content at shear rate 1 s^{-1}.

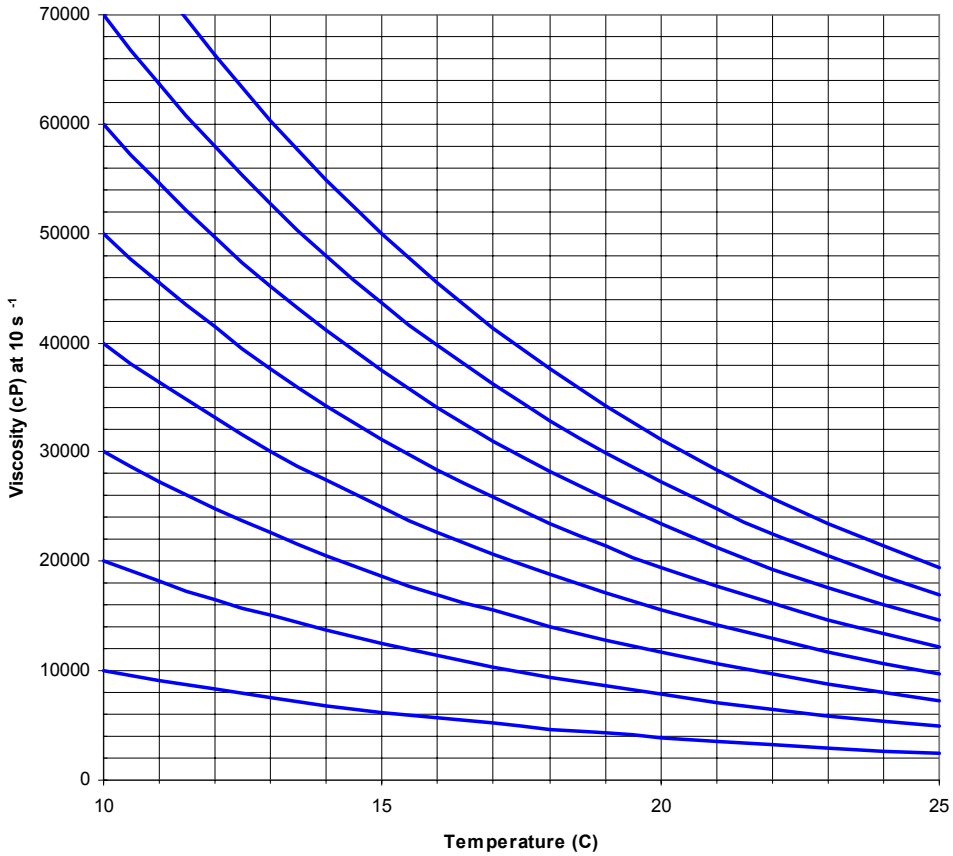


Figure 5. Typical viscosity-temperature relationships for w/o emulsions of bunker oil.

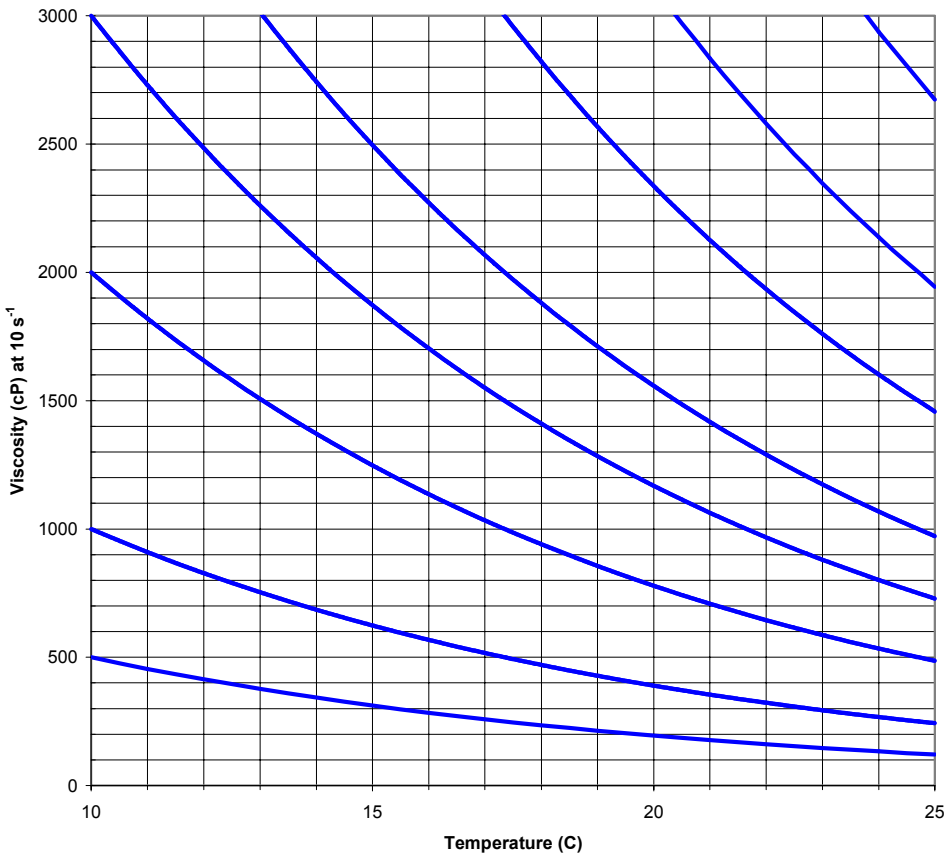


Figure 6. Example of typical viscosity-temperature relationships for bunker oils.

APPENDIX 1. A STEP BY STEP EXAMPLE

A skimmer is to be tested in 60% w/o emulsion. The emulsion should have viscosity 20.000 cP at shear rate 10 s^{-1} at 16 °C test temperature. It is estimated that 10 m^3 emulsion is required for testing.

a. From Figure it is found that the viscosity of the emulsion at 20°C should be 13.000 cP at shear rate 10 s^{-1}.

b. From Figure 3 it is found that in order to form a 13.000 cP emulsion with 60% water, a base oil viscosity of 860 cP is required.

c. The required quantity of base oil is calculated to 10 m^3 x (1–60%/100) = 4 m^3.

d. The blending ratio of heavy fuel oil and bunker is determined according to ASTM D341. The blending ratio may for example be 15% diesel and 85% Bunker C.

e. The required 4 m^3 of base oil is prepared according to the blending ratio.

f. It is decided that the emulsions shall be prepared in five 2 m^3 batches.

g. 0.8 m^3 of the base oil is transferred to the mixing tank for preparation of the first batch. The water tank is filled with 1.2 m^3 of salt water.

h. For emulsion mixing a gear pump with capacity 100 m^3/h is used. The pump is started and adjusted to 60 m^3/h. The operator ensures visually that air is not entrained in the oil (no air bubbles). The operator ensures that the pump has extra capacity to compensate for later viscosity increase due to emulsification.

i. The water injection is started and set to 1:20 of the mixing pump rate, i.e. 3 m^3/h.

j. The operator observes the mixing process and reduces water injection rate if substantial free water is observed.

k. When the water content in the fluid is approximately 50% (i.e. 800 l water has been injected) the water injection rate is reduced to 1:40, i.e.1.5 m^3/h.

l. The operator observes the mixing process and reduces water injection rate if substantial free water is observed.

m. After all water has been injected, the emulsion is allowed to recirculate for additional 20 volume changes, i.e. additional 20 min if the pump rate is still 60 m^3/h. If the emulsion appears to undergo changes even after 20 min mixing, the mixing period is extended until the emulsion appears uniform.

n. Samples of the emulsion are retrieved for characterisation of physical properties.