SINTEF REPORT

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TITLE

The use of colour as a guide to oil film thickness; Phase 1 - Laboratory experiments

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ABSTRACT

An extensive and systematic laboratory test program have been performed to validate and calibrate present colour code manuals based on visual observations, in order to improve the quantification of oil slicks with thin oil films. An experimental procedure has been established for photographing oil films in small static laboratory tray system, with focus on the apparent colour of the oil film. The test program included experimental series with ten oil types with different physical and chemical properties, and seven different oil film thicknesses in the range of 0.5-200µm. For thin oil films (0.5-5µm) the apparent colour was independent of oil type. Clear rainbow colours were observed in the range of visible light, and became more diffuse at 1µm. For thicker oil films the apparent colour varied very much, both with respect to the intrinsic colour of the oil and the colour intensity. A general colour code guide can therefore not be used for oil films in this thickness area.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Environment	Miljø
GROUP 2	Oil	Olje
SELECTED BY AUTHOR	Oil film thickness	Oljefilmtykkelse
	Colour Code	Fargekode
	Laboratory experiments	Laboratorieforsøk

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1. Introduction

Visual observation from helicopter or aircraft is the most common method of oil spill volume estimation. While experienced observers can achieve positive identification of an illegal discharge, more precise volume estimation based on the colour and area of spills has been identified as a complex task.

Surveillance exercises have shown significant differences in volume estimates from different aircraft. This is due to the following factors:

- During exercises, time from discharge to each aircraft arrival is not constant. Hence, oil evaporation, dispersion, emulsification, oil spreading as well as light conditions varies between each observation.
- Precise area estimation is critical to volume estimation. Area measurements are more complex when a spill is divided into patches. Area of "thick" oil is very critical for total volume estimate. The development in sensor technology will probably reduce the uncertainty of area calculations.
- Level of experience is not identical for each crew.

While basic colour and thickness correlation, i.e. the colour code, may be a good indicator for thin oil films, SINTEF believes a significant improvement to the understanding of this correlation is possible, hence improving oil volume estimation accuracy.

The current colour code used by most European countries is based on exercises and research conducted more than 10 years ago, particularly in The Netherlands. Since illegal spills are easily identified, the main purpose of the colour code is to classify an oil spill as "combatable" or "non-combatable". Volume estimation is also important for response commanders when assessing need for recovery equipment and tank storage capacity of recovered oil.

Oil film thickness varies over a very wide range - sub-micron up to several millimetres. A small difference in colour reflects a significant difference of film thickness. Hence, colour perception - together with precise area calculation - is important for volume estimation.

In this report we have addressed the colour perception of oil with respect to:

- Visual viewing conditions.
- Type of oil.

SINTEF has also identified the need of field trials based on findings in this report.

1.1 Literature review conclusions

A literature review has been accomplished as part of this project (Lewis, 1997). The available literature show that the appearance of the colour of oil films on the sea surface depends on several factors. The main conclusions were;

1. Very thin oil films, below the wavelengths present in white light (about 0.15 µm) will appear silvery or grey, irrespective of oil type. The light is reflected from the sea surface and is only slightly modified by the presence of oil.

   The current Bonn Agreement Code 1 - Silvery at 0.02 microns - is below the oil film thickness that is generally considered to be the thinnest that can be observed in perfect viewing conditions and which has been determined as such in previous, experimentally-validated literature such as Hornstein (1972 and 1973).

   The current Bonn Agreement Code 2 - Grey at 0.1 micron - is similar to the 0.075 micron onset of metallic lustre observed by Hornstein (1972)

2. Oil films between 0.15 microns and 3 microns thick will cause rainbow colours because of interference effects at the wavelengths of white light (0.38 microns to 0.75 microns). This effect is independent of oil type and is only caused by oil film thickness.

   The current Bonn Agreement Code 3 - Rainbow at 0.3 microns - is in very good agreement with all theoretical and experimental observations. However, the current Bonn Agreement Code 4 - Blue at 1 micron - is in conflict with theoretical and experimental findings.

3. Oil films from 3 um to around 50 um can give rise to blue tinted reflections by filtering the white light from the underlying oil/water boundary. This effect is oil type dependent, such as colour and optical density of the oil involved.

   Hence, the assumption that Bonn Agreement Code 5 - Blue/brown at 5 microns for all oil types - is not supported by theoretical considerations or measurements made in the laboratory.

4. Most of the colour exhibited by oil films 50 µm to 200 µm thick is due to the light reflected from the oil surface, and is therefore purely dependent on the colour of the oil. Black oils will appear black, brown oils will appear brown and light coloured oil products may exhibit the false colours caused by filtration of reflected light.

5. Oil or emulsion films thicker than 200 µm will appear as the true colour of the oil or emulsion. The colour of an emulsion depends on many factors including ‘parent’ oil colour. Water content and water droplet size.

   The current Bonn Agreement Code 7 - Dark brown/black over 100 microns - is in agreement with generally accepted values, but these are known to be minimum values and not averages for the full range of thickness that can occur.

The laboratory experiments have focused only on pure oil films and in the thickness range of 0.5-200µm. The conclusion #1 and #5 were therefore not considered in the experimental work.

1.2 Objectives of laboratory experiments

The general principles and problems regarding the observation of oil slicks on the sea are well known. When viewed from oblique viewing angles, an oil slick is only apparent as a modification to the reflection of the sky in the sea; the wave-damping effect of the oil generally produces an area that looks lighter (less grey or more silvery) than the surrounding sea. Similar effects producing light streaks on the sea surface is caused by variations in sea surface roughness caused by the interaction of wind and waves in the absence of oil. Viewing from oblique angles cannot therefore be used in an attempt to quantify the amount of oil on the sea. Vertical observation from directly above an oil slick reveals large variations in local appearance and colour and therefore should be used when estimating the thickness and subsequently calculating the volume of spilled oil. The appearance and colour of an oil slick on the sea is known to be influenced by many factors including: prevailing light conditions, observer positioning, sea and sub-sea features and conditions, oil properties, and the oil slick thickness.

The main objective of the laboratory experiments was to verify the conclusion from the literature review. This was done using small-scale tray testing equipment with oil films on the water surface. The experimental condition was optimised towards photographic conditions giving the largest apparent colour difference, under conditions that may be reproduced in any laboratory. This should not necessary be representative for the field situation.

Through the experimental work the rainbow area of the oil film thickness was illustrated through photos. The variation of the colour of the oil film as a function of oil film thickness should also be given, as well as the difference between different oil types and petroleum products. A total of ten oils, including crude oils, petroleum products and petroleum wastes, with a wide different chemical and physical properties were included in this study.

A total of 7 different oil film thicknesses was used with the 10 oils. All oils were tested with the same oil film thickness variation between the different oils in colour intensity. The photos of the different oils and the oil film thickness should be a basis for making a guide for observers in aircraft.

The laboratory work performed during this project should be the first step towards an oil type dependent colour code manual for the behaviour of oil types on the sea surface. This could also in the future be included in the existing SINTEF manuals on weathering and behaviour of oils at sea (e.g. Daling et al., 1997).

2. Materials and methods

2.1 Materials

2.1.1 Test oils

The following oils have been used as test oils in this small-scale tray experiments:

Balder crude
Balder (Norway) is an asphalthenic, heavy crude (density = 0.914 kg / l), and is therefore not a typical North Sea crude. It is a dark viscous oil, and reminds in many ways on an intermediate bunker fuel. Example of other North Sea crudes in the same category is Captain (UK) and Grane / Hermod crudes (Norway).

Statfjord crude
Statfjord (Norway) is a typical paraffinic North Sea Crude. Relatively light (density = 0.835 kg / l) with a high fraction of volatiles that will evaporate (up to 40 to 45%) when weathered 2-3 days on the sea surface. The remaining oil residue is rapidly forming a brown w/o-emulsion with up to 80% water

Forties crude
Forties (UK) is also a paraffinic North Sea crude, and even lighter than Statfjord (density = 0.822 kg / l), and has a lighter brown colour. A fraction of 35 to 40 % volatiles will evaporate when weathered on the sea surface. The remaining oil residue forms a w/o-emulsion with water content of 50-70% water. The emulsion may therefore be darker than the Statfjord emulsion.

Kristin condensate
Kristin (Norway –Haltenbanken) is a relatively “heavy” condensate or more correct a very light crude (density = 0.798 kg / l). Fresh Kristin is relatively transparent. About 70 % of the condensate will evaporate on the sea surface remaining a yellow / light brown waxy residue.

Marine Gas oil (diesel)
Marine diesel is a refinery product that is a blend of Kerosine and more heavy Gas oil giving a boiling point range of 150-360 ^{o}C. The density is 0.84 kg / l. Due to lack of heavy ends (or max 5%), the marine diesel is transparent. Diesel will spread very easily on the surface, and about 60-80 % will evaporate. The remaining residue is not forming emulsion, and is easily dispersed naturally into the water column.

IF-30 (Low Sulphur) Intermediate bunker fuel oil
This bunker fuel came from the Norwegian Esso Refinery. It is a dark high-density refinery product (density = 0.92 kg / l), IF-30 consist of about 35% gas oil and 65 % Bunker C.

IF-40 (Normal Sulphur) Intermediate bunker fuel oil
This bunker fuel sample came from Germany (used at the Bonn-Ex-1997). It is a dark high-density refinery product (density = 0.95 kg / l), IF-40 consist of about 25 % gas oil and 75 % Bunker C. Due to the higher viscosity, it will likely not spread as much on the sea surface as the IF-30.

Slop oil
The slop oil is a sample from a slop oil tank (Esso) in Trondheim. The composition of this oil is not known, but have a density of 0.85 kg/l.

Bilge oil 2
Artificial oil prepared of diesel, lubricant, heavy bunker in a ratio of 20:20:60. The density is 0.907 kg / l.

Bilge oil 3
Artificial oil prepared of diesel, lubricant, heavy bunker in a ratio of 40:20:40. The density is 0.87 kg / l. Due to a higher content of bunker, this sample should therefore be a darker oil than the Bilge 2.

2.1.2 Small-scale static tray system

Each experiment was performed in a small –scale tray system. For this purpose standard polypropylene trays were used. The trays were 55x35x13cm, length, width and height, respectively.

The bottom of the tray was not uniform and could be seen easily. The bottom was therefore covered with one-coloured thick paper sheet. This was attached to the trays using double-sided adhesive tape.

2.1.3 Oil application

Oil was applied to the water phase using syringes of different size with needle, determined by the amount of oil that should be applied. The diameter of the needle was as small as possible. An oil volume of 10-100% filled the syringe. To control the amount of oil applied to the tray the syringe was weighted before and after oil application.

2.1.4 Photo equipment

The photographic equipment used to take photos of the oil films were:

Camera (6x7cm format), Pentax 67 with 75mm lens for normal film
Camera (6x7cm format), Pentax 67 with 75mm lens for Polaroid film
Lightmeter, Minolta 5F
Blitz, Broncolor impulse
Softbox, 1x1m
Tripods
Cables

To be able to reproduce the colour of the object it is important to use a neutral positive film. Many positive films give warmer colours and better contrast for special effects, resulting in a false reproduction of the colour of the oil film. The film used for this purpose was therefore;

Positive film, Agfa RSX100-120
Polaroid film, Fuji HCP-100

2.1.5 Equipment set-up

The equipment set-up, including the small-scale static tray system and the photographic equipment used to establish the oil films and take photos are shown in Figure 2.1. Both the camera and the light source, blitz and softbox, were mounted at tripods and placed as close to the tray as possible to maximise the photo angle.

The experimental set-up was located in a temperature-controlled room with no other light sources.

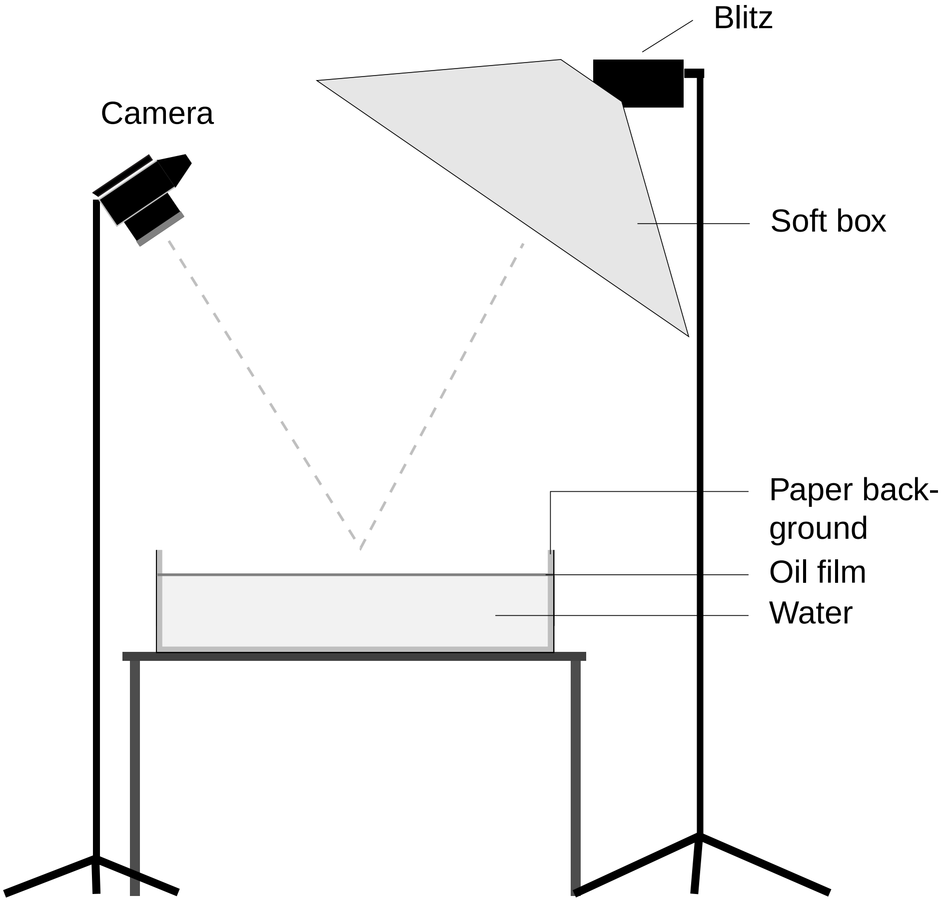

Figure 2.1: Experimental set-up

2.2 Methods

2.2.1 Preparation of oil films

The tray was washed using a convenient detergent and rinsed thoroughly prior to initiation of the experiments. A convenient paper sheet was fastened in the bottom and one side of the plastic trays using double-sided adhesive tape. The tray was filled with tap water to a level of approximately 8cm. The temperature of the water was the same as the room temperature. The tray system was moved to the table for establish oil-film.

When no longer water movement could be observed in the tray oil was applied to the water. This was done through different procedures depending on the thickness of the oil film. For thin oil films, 0.5 and 1µm, the oil was applied directly on the surface of the water.

Larger amount of oil, necessary to prepare oil films in the range of 5-200µm, was injected into the bulk water phase. The small oil droplets were transported to the water surface and an oil film was established. A time interval of 3 minutes was allowed for establishment of an "uniform" oil film.

2.2.2 Experimental oil film

For each oil type tested a total of seven different oil film thicknesses was prepared. These were;

0,5µm
1µm
5µm
10µm
50µm
100µm
200µm

In addition a set of test and control experiments was performed in order to optimise the photo experimental set-up.

2.2.3 Procedure for photographing

Exposure of the film was determined using an exposure meter and test polaroid pictures. The pictures were compared with *in-situ* visual observations, and the conditions were adjusted if necessary.

Pictures of thin oil films (0.5, 1 and 5µm) were taken with direct light and a black colour background. For thicker oil films (5 to 200µm) indirect light and a white colour background were used. For some series of experiments a combination of black and white colour background and direct and indirect light was employed.

When an "uniform" oil film was established at the water surface, photos were taken using positive film. Normally three pictures were taken from each experiment using different apertures on the camera.

2.2.4 Photo processing

After processing of the film, the pictures (6x7cm) were studied using a light table. If necessary the experiments were repeated. At the end of the project the necessary pictures were transferred to photo-CD format. A segment of this picture with the correct combination of background and light exposure was transferred into Adobe Photo-shop. Segments of the pictures were stored as "eps"-files, and figure layout and insertion of text was done in Adobe Illustrator. For reproduction of the information from the original pictures, use of a high quality colour printer will be prerequisited.

3. RESULTS AND DISCUSSION

3.1 Optimisation of conditions for photographing oil films on water surface

Through the project a large number of parameters have been tested to optimise the conditions for taking photos of oil films on water surface. In addition, the effect of a number of experimental conditions was studied.

3.1.1 Static small-scale tray system

To produce a large number of oil film thickness/oil type combinations in the laboratory under controlled conditions, a simple reproducible system should be established. The plastic transport trays were chosen because they are available in large quantities at low cost. They can easily be cleaned using conventional detergents. Interference between the plastic material and the oil itself is special critical for heavy oils. All oil residues have to be removed prior to initiation of a new experiment. If not, even very small amounts oil will not spread over the available water surface.

The bottom of the plastic tray was not uniform, and it was therefore necessary to introduce a bottom cover. This could be done with any material that does not interfere with the behaviour of the oil at the water surface after application. In this project thick paper sheets were chosen, which were disposed after use. 8-10 different paper qualities and colours were tested, but only a very limited number could be used as components in the paper released to the water phase affected the spreading behaviour of the oil at the water surface. This phenomenon occurred within a short time after the paper was inserted into the water phase.

The experimental set-up was located in a room were there surroundings could be controlled completely. This is necessary to give the best possible conditions for oil film formation and photographing. Factors that could affect the results of the oil film colour include temperature, light exposure and air circulation.

3.1.2 Light

For correct reproduction of the oil film colour on the water surface it is essential to use a neutral white light source. This can best be achieved using a photo blitz. The waste majority of traditional in-door light sources do not fulfil these requirements. Interference with such light must be avoided when photos are taken. Also daylight should be avoided, as this will vary from one day to another, by blinding any window in the room with the experimental set-up.

Different arrangements of light expose of the oil film in the static tray system was tested and evaluated during the project. This includes combination of direct and indirect light and various variants of the light source. No light arrangement was optimal for all oil film thickness. In the experiments a softbox was used to give a more diffuse light source and a uniform light intensity in all parts of the tray system. To observe the colour of the thin oil films in the rainbow area, it is an absolute requirement for a direct light exposure (light from the blitz/softbox is reflected directly from the object to the camera). Whereas direct light makes the colour of thicker oil films more diffuse. The size of the softbox allowed, however, arrangement giving both direct and indirect light expose at the oil film surface in the small-scale tray system.

In Figure 3.1 (a and b) are given pictures of oil film in the thickness range studied for two very different oil types, a light petroleum product (marine diesel) and a intermediate bunker oil (IF30), with both direct and indirect light exposure. This shows that the 0.5µm and 1.0µm oil films are visible only in the direct light area. For thicker oil films no or limited information can be achieved from this area. This is, however, dependent on the background colour, which will be discussed in Chapter 3.1.3. For the thicker oil films, were the intrinsic colour of the oil will be dominant, reflection of the softbox surface makes the colour of the oil film more diffuse. In the field the situation will be more complex as the light source will be more diffuse and larger, depending on the weather conditions.

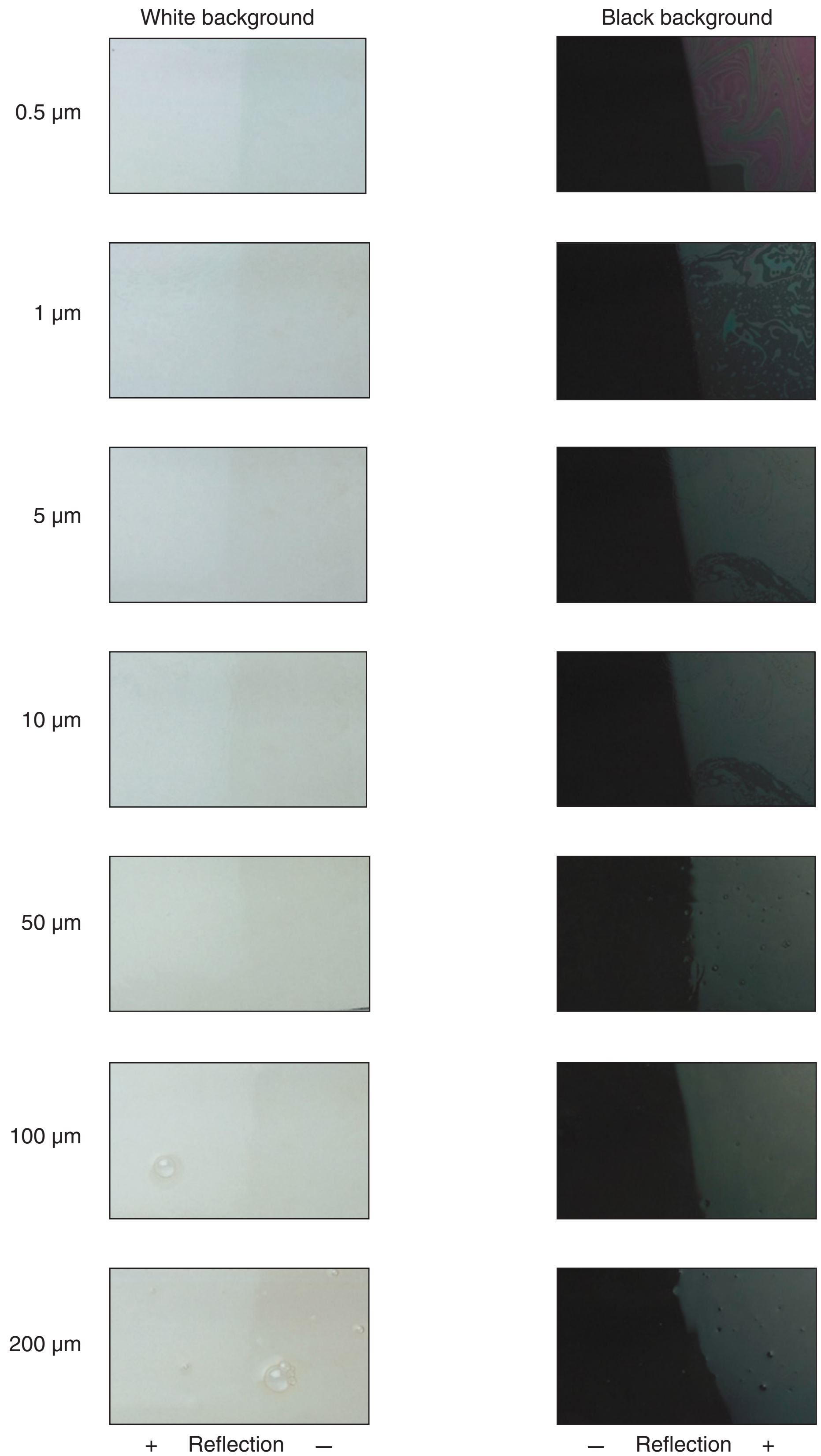

Figure 3.1a: Photos of Marine diesel with all combinations of black and white background and direct and indirect light.

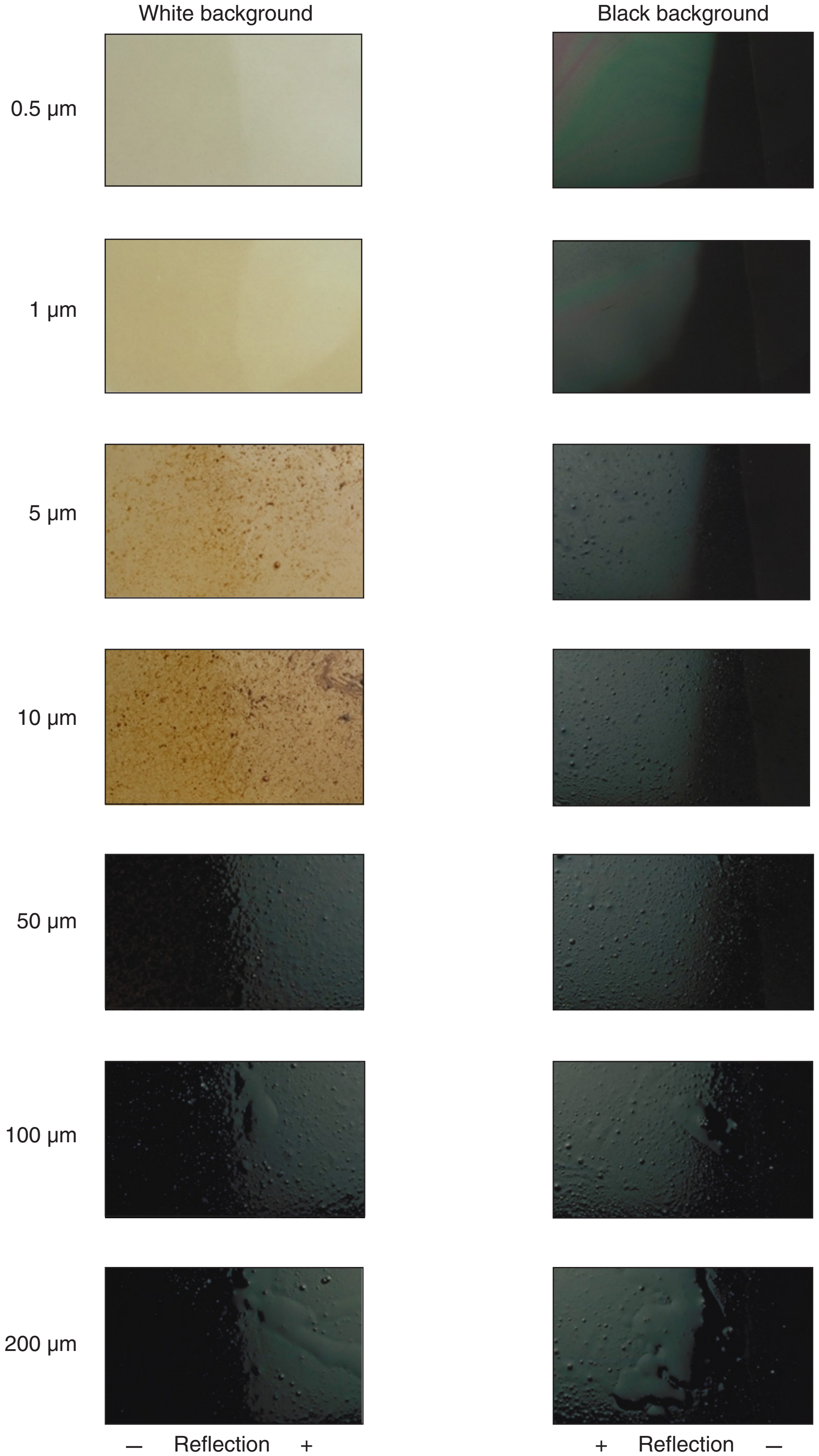

Figure 3.1b: Photos of IF30 with all combinations of black and white background and direct and indirect light.

A correct expose of the pictures was obtained using a photometer and adjustment of the aperture in the camera. The oil films photos were taken normally with three different apertures to ensure a correct light exposure. Comparing these photos, representing different light intensity in a field situation, it is clear that some information was lost when suboptimal conditions were employed. Therefore the light intensity will affect the observations made in the field after an oil spill or release to the sea. The effect of light intensity was, however, not focused or quantified during these experiments.

3.1.3 Photo/observation angle

During observations of an oil slick from an aircraft, observations can and will be made from many directions and angles. In the laboratory experiments the photos were taken as close to perpendicular (90°) on the water surface as possible. Due to practical difficulties related to the equipment and to avoid the reflection of the camera, a deviation from perpendicular of approximately 5° was used.

The effect of different observation angles was studied with some oil film thickness – oil type combinations. The most pronounced effect in the laboratory system was found for thin oil films in the rainbow area. In Figure 3.2 are given pictures on the same oil film from different observation angles.

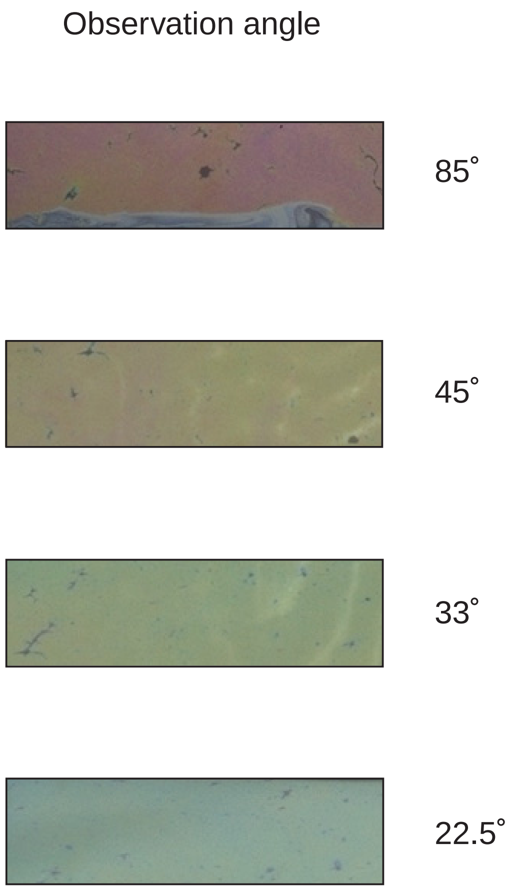

Figure 3.2: Colour appearance of 0.5µm oil film (Statfjord crude) from different observation angles.

The colour of the oil film varies with observation angle. At vertical observation the film is reddish, going through yellow/orange greenish to pale blue with decreasing observation angle. The main reason, for the change in colour of this oil film, is that the thickness of the oil layer which the light have to go through increases with decreasing observation angle. The generation of the oil film colour in the rainbow area will be discussed in more detail in Chapter 3.2.1. For thicker oil films the effect of the colour was less pronounced. This could, however, be affected by the light intensity, which were not controlled or varied systematically during these experiments.

The findings from the laboratory experiments indicate that the observation angle will affect the impression of the colour of the oil film also in a field situation. In the field the situation is, however, normally more complex than with the laboratory experiments. The water surface will never be as smooth as a millpond, but the waves will give rise to a "continuous" variation of the observation angle. The observation angle from the aircraft will, however, most probably be of less importance than indicated through the photo series in Figure 3.2. The effect of the waves could also give rise to different interpretation of the oil slick colour using observations from for example boats and aircraft as the water surface area observed will be very different. By introducing the small waves in the tray systems by shaking or blowing, the colour of the oil slick turned from a uniform colour to a full rainbow spectrum. This was due to variation in the observation angle following the length of the wave.

In a field situation the incident light will come from different angles towards the oil slick surface. This can hardly be reproduced in a laboratory situation. The light exposure will also vary as a function of among others the time of the day, season, weather conditions and the degree of latitude location. Therefore the light exposure will vary between each observations. It is therefore not possible to define "a typical light exposure conditions". This parameter must be included in the evaluation of the apparent colour of oil slicks on the sea surface.

3.1.4 Background colour

In the field the seawater many forms a variable background colours for an oil slick. The background has a colour determined by several factors as water depth, the properties of the seafloor, concentration of particles in the water, roughness of the sea surface as well as reflection from the sky. The background will also normally be undefined. This is not possible to reproduce in the laboratory experiments, using pure water, a complete horizontal surface and a defined background approximately 8cm below the water surface. Focus was therefore directed towards establishment of condition giving the most pronounced effects and differences using different oil types and film thickness.

In the small-scale tray system a thick paper was attached in the bottom of the tray. This material was chosen because it could be disposed after use, giving no requirement for cleaning. However, any other material could be used which would not interfere with the behaviour of the oil film. Through this project a large number of paper qualities were tested, but only a few could be used without any effect on the oil film behaviour. The spreading of the oil on the surface became restricted and in one extreme situation the oil from the droplet did not spread at all after application on the water surface. The paper material affecting the behaviour of the oil could not be used because the tray coverage could not be estimated straight on, and the oil film thickness should be determined analytically. The effect of oil spreading was most probably due to release of chemicals into the water phase. The chemicals were released at high rates, giving effects within less than a minute on the interfacial spreading of the oils.

Initially, black and white background was used, which gave good pictures of the thin and thick oil films, respectively. The pictures of two oil types, IF30 and marine diesel, are given in Figure 3.1 for the different oil film thickness used. With the black background the rainbow colours can easily be seen in the direct light area for both oil types and the thinnest oil films. In the experiments with white background, the rainbow colours are very difficult to observe with the same oil film thickness. For thicker oil films no information can be collected from the experiments with black background. The reflection of the front surface of the softbox can be seen in the direct light area, but this give no information on the oil film colour. With white background the intrinsic colour of IF30 can be seen easily, and the intensity increases with increasing oil film thickness. In the marine diesel experiment no colour could be observed, which was expected as this petroleum product are close to colourless. The combination of black and white background can be used to give a good reproduction of the oil film colours in the film thickness area of 0.5-200µm. This is, however, not optimal, as these colours are not relevant to the field situation and a single background colour for all oil film thickness would be preferred. This would be of importance in the transition range when the alternative is to chance from black to white background.

Due to the various surfactant-leaching properties of the paper materials, a limited number of background colours could be tested in the tray system. Different gradations of grey, blue, and green were tested in addition to black and white. Figure 3.3 shows pictures of the 0.5 and 5µm films with four different backgrounds. The background colours are charcoal grey, grey, cyan and black. For the 0.5µm film the colour of the oil is different with the different background, and the grey backgrounds no rainbow colours could be seen. The differences of “colour” observations could also be due to small variation in the oil coverage in the tray systems. For the 5µm films the colours of the oil films are similar with charcoal, black and cyan, whereas the grey background gave a considerably brighter colour. For thicker oil films the oil films were similar pictures with black colour background as shown in Figure 3.1.

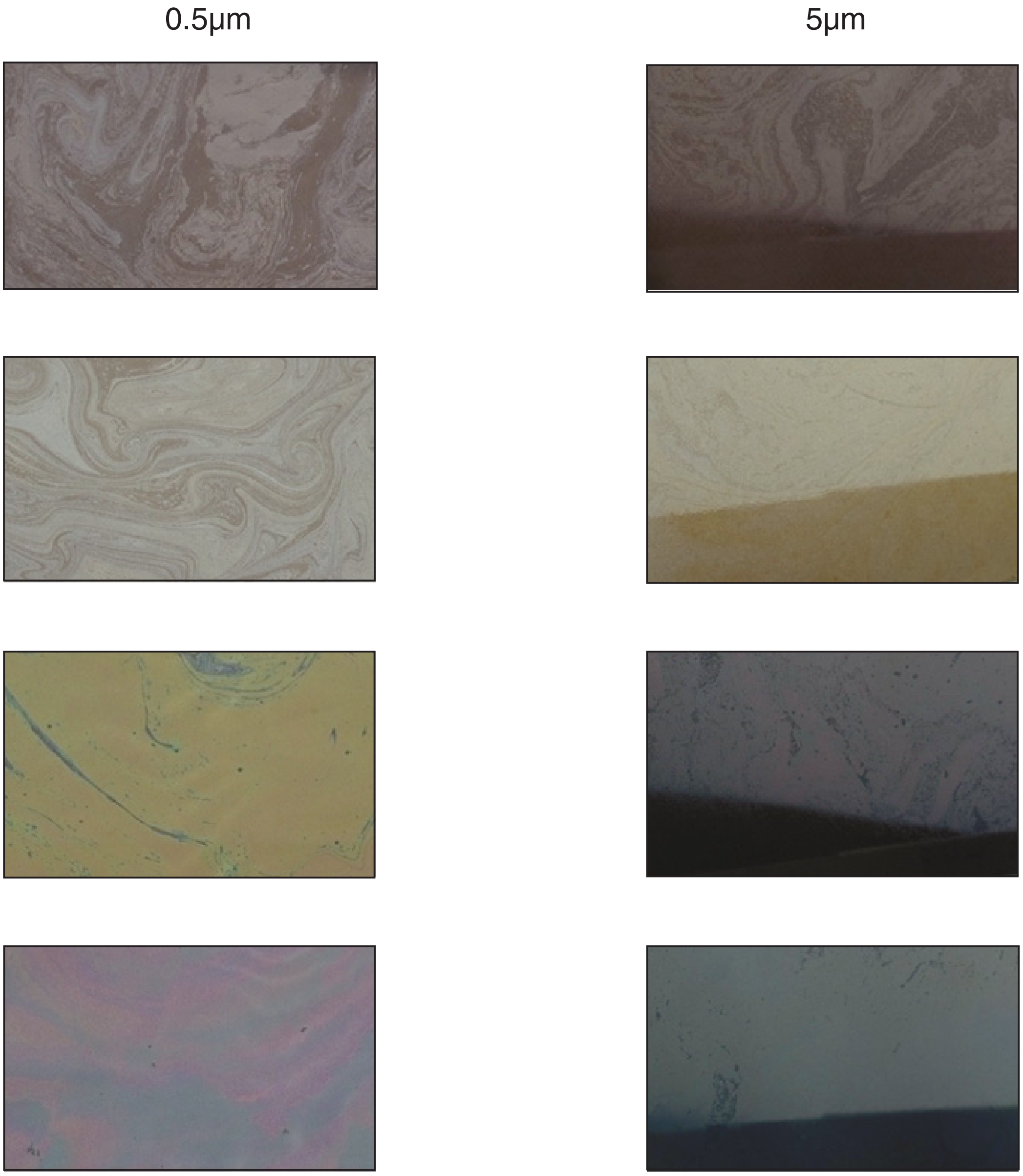

Figure 3.3: Colour appearance of 0.5 and 5μm oil films using different background colour

These experiments show that the best result of the oil film colours will be achieved using a combination of black and white background. No other background colour could be used for oil films in the oil film thickness range studied under the experimental conditions used. In the experiments a combination of black and white background were used, with an overlap using both backgrounds for 5μm-film thickness. This will be further discussed in Chapter 3.2.3.

3.1.5 Standardised experimental procedure

The procedure for preparation of the oil film in the small-scale tray system was developed during the project towards a simple, time-effective and reproducible method. A number of parameters were varied and control experiments were performed.

An oil spill where a quantification of the oil is necessary will normally take place in the marine environment. However, the availability of seawater could be a limitation in some laboratories. Therefore tap water was used in this experiments. To quantify the effect of water salinity a series of experiments were performed with both tap water and fresh seawater for one oil type. The pictures show that there was only a very slight difference between the series.

The seawater temperature is seasonal, weather and geographical dependent, and will vary over a wide range. An all-purpose temperature for these experiments could therefore not be used. In the experiments the water temperature was the same as the room temperature. This was done to avoid temperature gradients. At room temperature the viscosity of the oils will be significant lower than at field seawater temperature. This allows also a more rapid distribution of the oil film on the water surface. The effect of temperature on the colour of the oil film was controlled through a series of experiments with a water temperature of 10°C and room temperature (20°C). The pictures show that there was no difference between the two series, at the same time interval after oil application for all oil film thicknesses.

The spreading of the oil at the water surface took place rapidly with the smallest amount of oil. With increasing amounts of oil, the spreading was restricted by the oil present at the surface. The spreading of was not affected by the application method for thick oil films. The oil was introduced into the water phase by a syringe and a thin needle at a high rate as pure oil or a 50/50 oil-in-water emulsion. Use of an emulsion was convenient for small oil quantities, whereas with larger volumes the emulsion was not stable during the time necessary to introduce the oil into the bulk water. Therefor the oil was normally applied to the tray systems as pure oils. By the use of this method the oil was divided into small oil droplets, which were transported to the water surface and more evenly spread over the available surface area. The oil phase was allowed to come into equilibrium at the water surface for three minutes before the photos were taken. During this time period a uniform film was not always established. With the thickest oil films a period of more than three hours was necessary to establish a uniform oil film, whereas the thin oil films was established within seconds. Therefore a compromise of three minutes was chosen so the same time interval could be used for all oil films. With a long time interval the chemical composition of the oil could also take place due to evaporation of the light components.

3.2 Laboratory experiments with different types of oil and film thickness

To establish a basis for a better evaluation of the oil film thickness based on visual observations of oil slicks, a systematic work on oil types and film thickness was performed. This includes experimental series with ten different oil types and seven different film thickness. Picture was taken of the oil film at the water surface under optimised conditions. A total of more than 250 experiment have been performed during this project. The resulting pictures are present as 1) the oil film in the rainbow area, 2) the various types of oil (at different thickness), and 3) the different oil film thicknesses of the oil types tested.

3.2.1 The rainbow area

The rainbow colours observed from an oil film are caused by reflection of white light from the oil <u>and</u> water surface through constructive and destructive interference. This phenomenon is described in detail in the literature review in this project (Lewis, 1997). This phenomenon is, however, very complex. This is illustrated in Figure 3.4. In the example an oil film thickness of 0.8μm (800nm) are used. As the figure show a constructive interference arise with 400nm and 533nm, which will give violet and green colour, respectively. A destructive interference will be found with wavelengths of 457nm and 640nm, giving blue and orange colours, respectively. The reflection of light from the 0.8μm oil film will therefore be a mixture of these four phenomenon; a mixture of violet, green, blue and orange. The intensity of the different contributing colours and thereby the resulting colour of the oil film can not be estimated. The intensity of the different colours will, vary with in very small variations of the oil film thickness; changes of just a few nanometer will probably alter the colour of the oil film.

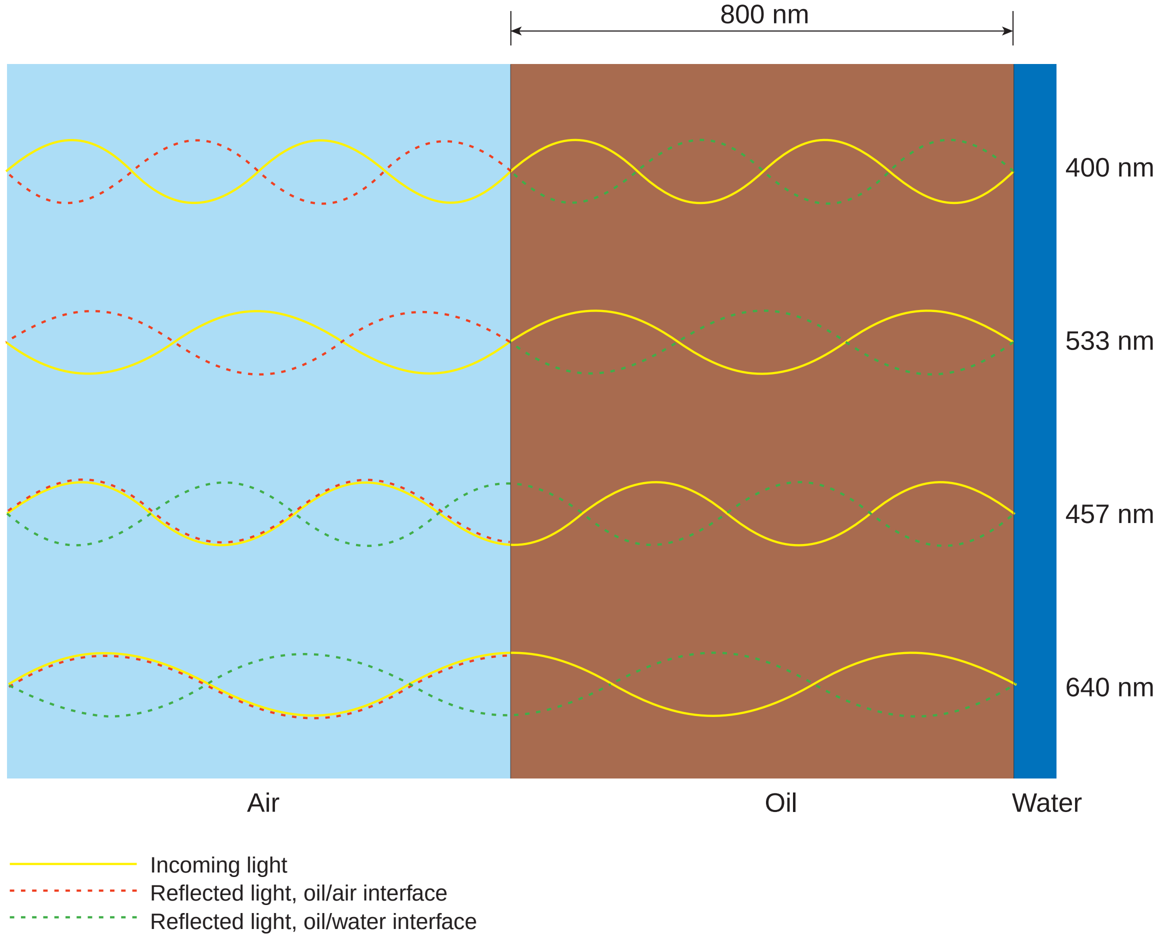

Figure 3.4: Constructive and destructive interference of reflected light

The constructive and destructive interference will arise for oil film thickness and wavelengths according to the following equations;

Constructive interference

$$\lambda = L\,(\tfrac{1}{2}n)^{-1}$$

Destructive interference

$$\lambda = L\,(\tfrac{1}{4} + \tfrac{1}{2}n)^{-1}$$

n is an integral number, λ is the wavelength and L is the oil film thickness. For this equation n should be an integral number which gives a wavelength within the visible light range (400-760nm). For the example given above constructive interference occurs with n = 3,4 and destructive interference with n = 2,3. Based on these equation and that the visible light is the range of 400-760nm, colours should be observed from oil film thickness of 200nm (constructive interference of violet light 400nm). With a thin oil film a limited number of colours will arise due to the interference of the light waves.

With increasing film thickness the number of both constructive and destructive interference's including different wavelengths will increase. The number of effects will increase linearly with the increase of the oil film thickness. These effects will probably outweigh each other, and less clear colour would be expected by increasing the oil film thickness.

The peak of the rainbow area is according to the 1997 Bonn Agreement Pollution Observation Log at 0.3µm, and the colour is independent of the oil type according to the literature review. During this project an oil film thickness of 0.5µm was used to represent this part of the scale. A large number of experiments were performed with this oil film thickness, and a clear colour was obtained with all oil types tested. A wide variety of colours were established with the different oil types. The colour of the oil film could also vary from one experiment to another with the same oil type. Based on this observation and the theoretically appreciation above, this is probably due to minor variation of the oil film thickness. Such variation could be due to an uneven distribution of the oil at the surface and small variation in the amount of oil applied to the small-scale tray system. The oil film thickness was not verified by analysis, but the amount of oil applied to the water surface was determined gravimetrically. The gravimetric analysis showed, however, no significant difference was found between the experiments.

The observation from the 0.5µm film thickness experiments and the theoretical appreciation above, indicate the statement that the oil film colour in the rainbow area is not oil type dependent. However, experimental validation of this would require considerably laboratory work. This would include a very large number of oil film thickness experiments with very small thickness intervals. This is behind the scope of this project, and would for an operational point of view not contribute much to the overall understanding of the oil film colour subject.

Based on the experimental result, a rainbow palette including different dominant colours (Figure 3.5) was chosen to represent the 0.5µm oil films. The same palette is therefore used with all different oil types. This should also be relevant for an oil spill situation, as it will always be minor variations in the oil film thickness for oil slicks in this area. The presence of waves, which is the normal situation, will also give a variable observation angle relative to the sea surface. The light path length will therefore vary, giving different colours.

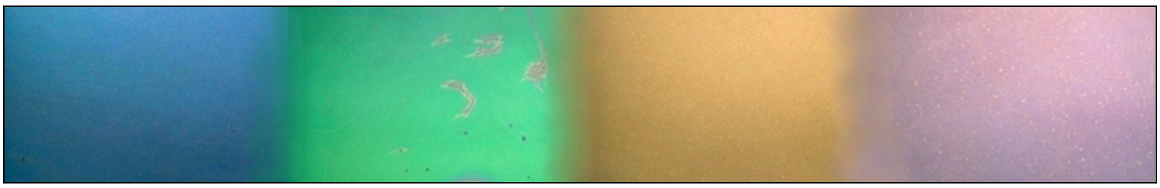

Figure 3.5. The rainbow palette representing the 0.5µm oil film thickness

The thickness range that includes the rainbow colours varies with the different publication reviewed in the literature review. The Bonn Agreement code defines rainbow to be 0.3µm, whereas other defines the rainbow to be up to several microns (cf. Lewis, 1997). The 1.0µm oil film used in this experiment is shown Appendix 2a. With most oil types, a colour is observed also with this oil film thickness. A less uniform film was obtained than with the 0.5µm film, giving more inhomogeneous film colours. The colours are in general, however, more diffuse than the colours with the thinner oil films. The observed more diffuse oil film colours, is most probably due to an increasing number of constructive and destructive interference. The apparent rainbow colours will in the experimental set-up with lighting through the softbox be more diffuse than with for example with direct sunlight. The softbox was, however, necessary to establish an even illumination of the tray-system. The softbox system would most probably represent an overcast weather situation.

Based on the result of the experiments with 0.5 and 1.0µm oil film thickness, it seem that these should be included in the rainbow area, and that the oil film colour is independent on the oil types. From the theoretical considerations above on possible constructive and destructive interference, the lower limit of the rainbow colour appearance should be an oil film of 0.2 µm. The upper limit will be slightly higher than 1µm. This is similar to the colour/oil film thickness correlation presented by USEPA in the early seventies (Hornstein, 1973). In these reports the rainbow area was divided into a range (0.15 – 0.9µm) for "pure rainbow colours", and a range (0.9 – 1.5µm) for "dull, impure colours".

3.2.2 Oil film colour appearance by oil type

During the project, seven different oil film thicknesses were produced from a total number of ten different crude oil and petroleum products. The pictures of the oil films for each oil type is given in Appendix 1.A-J. The same combination of light exposure and background colour was used for all oil types; black background and direct light up to 5µm, and white background and indirect light for the oil films thicker than 10µm. This was chosen to allow a direct comparison of the different oil types for all oil film thicknesses.

With increasing oil film thickness the intrinsic colour of the crude oils and petroleum products becomes more pronounced. This is the situation for all oil and petroleum products tested, except for marine diesel. Within the thickness area studied in these experiments, marine diesel did not cause any colour appearance on the water surface. In a real spill situation, however, an oil slick of marine diesel would be observed with direct light exposure and a darker background (cf. Figure 3.1.A), if the situation allows formation of thicker oil films.

Low colour intensity was also found with the Kristin condensate. An intrinsic colour could not be observed for the condensate until oil film thickness of 50µm. Using higher oil film thickness the condensate film appears to be yellow, which is different from the typical brown colour of the remaining oil types used, which reflect the chemical composition of the oils.

Three different crude oil with different physical/chemical properties were tested, Balder, Statfjord and Forties crude. As with other oil products tested, the intensity of intrinsic colour of the oil film increases with increasing oil film thickness. The colours of the different crude oils are, however, different. Forties crude is the brightest, tending towards an orange colour. On the other side, Balder crude has a pure brown colour. Statfjord crude oil has an intermediate colour. A more defined characterisation of the oil could be obtained by for example scanning UV-spectroscopy in the visible range.

Another group of petroleum products tested in the laboratory experiment was the bunker oils, IF30 and IF40. These two bunker oils should be similar expect that the IF-40 have a slightly higher viscosity. The products are, however, produced in Norway and Germany, respectively, resulting in oil product with different physical properties. The pictures of the oil films show that IF30 is spread more even over the water surface. IF40 forms a more inhomogeneous oil film, with most oil located in spots with higher oil film thickness. The difference in colour appearance is probably less pronounced than the 50 and 100µm film thickness pictures may indicate. The 10µm oil film with both IF30 and IF40 has a clear brown colour. For these two oil types the colour of the oil would be visible also at 5µm if a white background colour have been used. This can be seen in Figure 3.1.B, which show IF30 using different combination of background and light exposure.

Slop oil is waste oil product from ships and normally collected in special tanks in the harbours. In this project, one intact slope oil of unknown composition, and two defined “synthetic” waste products (Bilge 2 and 3) with different composition of heavy bunker oil, diesel and lubricant oil were used. The picture series of the three waste oil product show that the slop oil is the brightest one followed by Bilge 3 and Bilge 2. This indicate that the Slop oil used have a Bunker oil content which is significantly lower than 40%.

3.2.3 Oil film colour appearance by oil film thickness

Seven different oil film thicknesses were used during this project; 0.5, 1, 5, 10, 50, 100, and 200µm. These are given (expect the 0.5µm films) for all oil types in Appendix 2.A-F. As indicated through the discussion on the different oil types used in this project at film thicknesses above 5-10µm, oil types form films at the water surface with different colours and different colour intensity. The colour observed in the laboratory experiments was obtained by using a procedure directed towards maximising the colour differences. The colours observed in the laboratory should, however, give an indication of the oil film appearance on the water surface in a field situation. The most extreme situation was found with marine diesel which do not has any intrinsic colour using white background. This type of petroleum product will not give any colour in a field situation, making it difficult or impossible to quantify the oil film thickness based on visual observations. A similar situation will appear with Kristin condensate and similar products. A slight yellow colour appears for an oil film thickness of 50µm. The colour intensity varies little, giving the same problems with visual observations as for marine diesel in the oil film thickness range studied. The physical properties of these types of oil, however, allow formation of thicker oil films less likely.

The description of the thinnest oil films, i.e. the rainbow range was discussed in a separate chapter (cf. Chapter 3.2.1). The colour appearance for the 0.5µm oil film was gathered in a common rainbow colour box. A similar solution could also be used for the 1µm oil films. The small differences in colour appearances is most probably due to uneven behaviour of the oil itself which will affect the oil distribution and thereby the local oil film thickness. The difference of the oil film colours is therefore most probably not due to the effect of the various oil types.

The pictures of the 5µm oil films are also presented with a black colour background and direct light. Under these conditions the oil film appearance of the different oil film vary to a very little extent. A possible colour appearance by the constructive and destructive interference is less likely as a large number of interference will cancel out the colours. The different 5 µm oil films appears to have a neutral/homogenous colour. As seen previously (cr. Figure 3.1.B) with IF30, some of the oils have a bright colour using a white background and indirect light. The appearance of this colour in a field situation is dependent on the oil type, but will with most oils be very weak. The Bonn Agreement Code 5 giving a colour appearance of blue/brown can not be verified through this laboratory experiments.

The appearance of the intrinsic colour of the oil becomes increasing important with increasing oil film thickness. All types of oil, expect Marine diesel and Kristin condensate, have a clear light brown to yellow colour under the conditions used for the experiments with the 10µm oil films. The colour intensity, however, varies over a wide range, from the brightest colour with Forties crude to the darkest with IF30. Even between the Statfjord and Forties crude oils, which both are relatively light paraffinic crudes, significant differences are observed. The slightly lighter Forties show a more orange/brown colour compared to Statfjord. In a real spill situation with an average oil film thickness of 5-10µm, the oil film thickness will vary within a small scale to a large extent. The film thickness could probably be thin enough to give rise to rainbow colours using observation with high resolution. The appearance of this phenomenon will, however, be dependent on the observation distance and thereby the resolution of the observation made; these colours phenomenon could be observed from a boat but less likely from an aircraft.

A similar situation with large variation in the colour intensity for the different oil types, are also found with the three thickest oil films studied; 50, 100 and 200µm. The oil films becomes darker with increasing film thickness. The darkest oil film was obtained with IF30 and IF-40, giving a black oil film with a 100µm oil film thickness. The oil films also appear black or dark brown with Bilge 2 and Bilge 3 at 200µm thickness. The apparent colour of the different petroleum products varies over a wide range. The colour of the Slop oil film requires approximately ten times more oil than with IF30/IF40. An even more pronounced effect would be found if a very heavy bunker oil (e.g. IF240) had been tested.

A large variation for the thicker oil film was also obtained with the crude oil studied. The Balder crude of 200µm film thickness appears to be dark brown, whereas the Forties crude of the same thickness is brown/yellow. The same colour intensity appeared for Balder crude at an oil film thickness, which was one order of magnitude thinner. From an observational point of view this could result in an incorrect estimate of oil quantity

3.3 Recommandations for renaming and modification of the Bonn agreement codes

Main conclusions:

This project identifies the need for Bonn Agreement Colour Code amendments.

- It has been shown both in literature survey and by laboratory tests that for Colour Code 5 and above, the colour of oil is oil type dependent. Special colour codes for the most common oil types should be developed and included in the amended Colour Code.

- For Colour Code 1 based on the literature study, theory does not support the 0,02µm value. This could be enhanced to a value of 0,05µm. The current Code 1 and 2 could be merged together.

Other preliminary recommendations:

- The rainbow colours appeared in both the 0.5 and 1µm oil film thickness. These observations and theoretical considerations indicate that the rainbow area should be approximately 0.2 – 1.5µm. The appearance of rainbow colours are independent of oil types, and the colours becomes more diffuse with increasing oil film thickness. The current Code 3 should include a broader oil film thickness range.

  The appearance of the intrinsic colour of the oil starts at approximately 5µm, but varies very much with the different oil types. Any general colour code can not be used for this purpose. The colour intensity of the oil used in this project varied by a factor of one order of magnitude. Quantification of the amount of oil in a slick of this thickness can therefore only be obtained with knowledge of the actual oil. A colour code chart for the different types of oil should therefore be available. Based on the findings, the accuracy of colour code 5 and above is oil type dependent.

- The transition range (1.5 to 5-10μm) between the rainbow area and the appearance of the intrinsic colour of the oil is very difficult to characterise. No colour appearance was observed, neither rainbow nor brown. This film thickness range could also easily be confused with oil films thickness within the area below the rainbow range, which have not been studied in this project. An oil film with an average thickness within this range could also locally exhibit other phenomenon, under different environmental conditions. The current Code 4 and 5 is not valid, and should be amended to “metallic” or “homogenous”.

The present recommendations are given based on the laboratory experiments performed under controlled conditions. Conformation and adjustments of these observations will be necessary through larger scale field studies under realistic conditions. This should also be done with a large number of different oil types.

Based on the findings during this project, we recommend the following step-wise procedure for future work:

1. Amendment of documents describing the colour code hence obtaining a scientific basis of the colour code method.
2. Phase 3, field trials; further investigation of colour in outdoor conditions.
3. Possible amendment to the colour code itself

4. Conclusions and recommendations for further work

A laboratory experimental set-up allowing photographing of oil films on a water surface and a standardised procedure for this was established. Conditions were chosen to optimise the appearance of the colour of the oil films. For thin oil films, including the rainbow area, a black background colour and direct light was used. For thicker oil films (above 5-10µm) a white background and indirect light was used. A total of ten oils were used, including three crudes, one condensate, three fuels and three bilge water. Seven different oil film thicknesses were prepared of each oil type.

For very thin oil films (rainbow area; 0.2 – 1.5µm) the apparent colour is not dependent on the oil type. Pure rainbow colours did appear for oil films with a thickness similar to the wavelength of visible light (400 – 760nm). The colour became more diffuse with increasing and decreasing oil film thickness at the edges of this thickness region.

For oil films thicker than 5-10µm the apparent colour is dependent on the intrinsic colour of the oil. The intensity of the colour increases with increasing oil film thickness to 200µm, where most oil films were black/dark brown. The colour intensity, however, varies over a wide range (decades) for the oils tested. The general colour code guide can therefore not be used for oil film thickness within this range. For quantitative determination of the total amount of oil in an oil slick of this thickness information on oil properties should be available. The documentation of oil film appearance should also be included in the existing SINTEF-manuals on weathering and behaviour of oils at sea.

The oil films of thickness 1.5 to 5-10µm appears to have no or very weak colours. The “colour” appearance is difficult to describe; metallic or homogenous could be used. This could probably be mistaken for the Code 1 and 2. Influence of waves on the sea surface and inhomogeneous film thickness could provoke appearance of locally areas of rainbow colours also for this thickness area. .

The observations from the laboratory work constitute a basis for renaming and modification of the current Bonn Agreement Pollution Observation Log. A preliminary amending using the present oils is suggested. However, additional work have to be done prior to preparation of a final operation field guide for quantification of oil slick by visual observations based on colour appearance. Such studies could include:

- extensive laboratory studies including more narrow film thicknesses – particularly in the band from 1 to 200 (500)µm.
- the effect of weathering on oil film colour appearance
- meso-scale flumes including the effect of waves
- controlled outdoor experiments – use of “AL booms”
- verification by field dedicated trials which should revieled; more diverse/dynamic system in real life, inhomogeneous spreading within the slick, effects of waves and light, weathering of the oil, and remote versus near-surface observations.