SINTEF REPORT

SINTEF Applied Chemistry

Address: N-7034 Trondheim, NORWAY
Location: S.P. Andersens vei 15 b
Telephone: +47 73 59 28 73
Fax: +47 73 59 70 51

Enterprise No.: NO 948 007 029 MVA

TITLE

The use of colour as a guide to oil film thickness; Phase 1 - A literature review.

AUTHOR(S)

Alun Lewis

CLIENT(S)

SFT, Norwegian Pollution Control Authority : Jørn Harald Andersen
MPCU, NL: Jan Huismann MPCU, UK: David Bedborough
Finnish Env. Agency: Tuula Kuusela
Kustbevakningen: Thomas Fågö/Dan Thorell

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ABSTRACT

A literature review of the basis of current 'colour code' (the correlation between apparent colour and oil film thickness) used by the Bonn Agreement surveillance flights has been carried out.

The code consists of seven categories of colour and thickness. In the range up to 3 microns thickness (between Codes 4 and 5), the available literature and theoretical considerations strongly supports most of the colour classifications used, independent of oil type or viewing conditions. This area of the colour code is that which is most often used in assessing discharges from ships. The basis of Code 4 (blue, equivalent to 1 micron thick) and Code 5 (blue/brown, equivalent to 5 microns thick) is not totally supported by the available literature or theoretical studies.

At higher oil film thickness, the region from 5 microns and upwards, there is less evidence to support a rigorous colour/thickness correlation. Assessing the thickness of oil films that are 10 to 50 microns thick (Code 6; Brown/black, equivalent to 15 - 25 microns) by colour alone is likely to be misleading if all oil types are considered to exhibit similar characteristics. The apparent colour for a particular oil thickness will vary depending on oil type. However, a uniform colour (blue, brick red etc.) typical for this film thickness supports the conclusion that the film is beyond 5 microns.

Oil film thickness in around, or in excess of 100 microns (0.1 millimetre), Code 7 in the Bonn Agreement categorisation, cannot be determined by the colour of the film. In this thickness range the colour observed is the true colour of the oil, or emulsion formed from it, and is due to the surface colour. Oil films in this thickness range will only be observed at significant oil spills. The presence of large areas of black oil or brown emulsion will probably indicate that some response (mechanical recovery or dispersant use) is needed, while the absence of areas of these colours will indicate that the oil will probably disperse naturally, provided that it has enough time to do so before it hits the shore. However, a brown colour typical for this film thickness for the specific oil supports the conclusion that the film is beyond 50 to 100 microns.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Environment	Miljø
GROUP 2	Chemistry	Kjemi
SELECTED BY AUTHOR	Oil Spill	Oljesøl
	Oil Film Thickness	Oljefilmtykkelse
	Colour Code	Fargekode

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1. Sources of oil at sea

Crude oil or refined oil products can enter the sea from several sources. Intentional discharges from ships or oil production installations are governed by national and international laws. Unintentional oil pollution, resulting from incidents involving oil production or transportation or other shipping accidents, occurs from time to time.

1.1 International regulations concerning discharge of oil from ships into the sea

According to MARPOL regulations, oil may only be released from ships under certain conditions. These are:

For oil tankers larger than 150 brt, referring to cargo releases;

- Outside "special areas" (as defined by IMO).
- While the vessel is en route.
- Minimum 50 nautical miles from coast (including islands).
- Maximum discharge limit of 30 litres/ nautical mile.
- Maximum amount of 1/15 000 of cargo volume for older ships, 1/30 000 cargo volume for newer ships.
- The vessel must have a monitoring system for oil in water releases.

For other types of ship above 400 brt and tankers, referring to engine room releases;

- Outside "special areas" (as defined by IMO).
- While the vessel is en route.
- Maximum limit of 15 ppm oil in discharged water.
- The vessel must have a monitoring system for oil in water releases.

All other releases of oil from ships are illegal, irrespective of quantity or oil concentration.

1.2 Other sources of oil pollution

Releases of produced water containing oil from oil production installations are covered by separate national regulations. Acute sources of pollution caused by accidental oil spills are breaches of anti-pollution regulations, but cannot be regulated in the same way as permissible low level chronic discharges.

The quantity of oil released in accidental oil spills tends to be much larger than that in intentional releases and may require some form of oil spill response (mechanical recovery or the use of dispersants) to minimise the environmental damage that could be caused.

2. The purpose for aerial surveillance of oil spilled at sea

There are two distinct requirements for aerial surveillance flights and visual observation of oil spilled at sea:

(i) There is a need to ensure that the quantity of oil in any intentional discharge from ships is within the permitted levels, as described in the appropriate regulations.

(ii) There is a need to determine whether the quantity of oil released in an accidental discharge is sufficient to warrant the mobilisation of oil spill response equipment.

iii) Guidance support during oil spill combat operations.

These two requirements are normally dealing with very different quantities of oil; slicks caused by intentional discharges are localised and can be on the borderline of visibility (see Section 5.1) because of the very low quantities of oil involved, whereas accidental discharges can involve up to several thousand tonnes of crude oil spread out over a vast area.

3. Visual observation of oil on the sea

Oil on the sea can generally be seen quite easily from a surveillance aircraft, provided that there is sufficient oil present and that viewing conditions are suitable. The general principles and problems regarding the visual observation of oil slicks on the sea surface are well known.

The shape and appearance of the slick depends on the way the oil has been discharged;
oil-in-water mixtures discharged from a moving ship produce a thin trail of oil of a very low thickness in the ship's wake. Oil spilled during an accidental spill may be of a much larger quantity and the form of the slick will be different. Oil that form stable emulsions will create a slick area of emulsion within a thinner area of oil and there will also be an extensive area of sheen (oil film about 1 micron or less thick). Vertical observation from directly above an oil slick reveals large variations in local appearance (texture and effect on waves) and colour that can be used by trained observers to estimate the oil film thickness and therefor the volume of spilled oil.

There are several separate, but connected, problems quantifying the amount of oil on the sea by visual observation:

- Visibility of oil and influence of viewing conditions.
- Colour (or apparent colour) / oil film thickness correlation.
- Converting thickness estimates into volume estimates.

3.1 Visibility of oil

A great deal of work has been done over a prolonged period to determine the lower limit of oil concentration at which an oil discharge is visible to an observer in a surveillance plane. The work has been conducted in the USA (House of Representatives, 1930 and Hornstein 1972 and 1973), in Europe in the past (Wardley Smith, 196?) in recent times (Rijkswaterstaat, 1992)

The intention of all these experiments has been to determine the lowest amount of oil that can be seen from the air. This minimum amount of oil has been expressed in different ways, such ppm in water effluent or litres/mile. Although associated to this project, the visibility of oil, i.e. the minimum quantity of oil, either as film thickness or as some other measure of quantity, has not been specifically addressed in this literature survey, other than the theoretical and experimental limits in near perfect viewing conditions as described in Section 5.1.

3.1.1 The influence of viewing conditions

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. Observations made towards the sun or a low sun angles suffer from interference due to sun glitter, and the reflection of the sun of a rough sea can prevent even thick layers of oil from being seen. Viewing from oblique angles cannot therefore be recommended in any attempts to accurately quantify the amount of oil on the sea.

The level of overall brightness is important; oil slicks are obviously more difficult to see if the light level is very low (near dark), however the best light conditions for observation is not bright sunlight. The absence of direct sunlight improves visibility of oil slicks (Hornstein, 1973), and bright overcast conditions are best when the overall brightness and sun angle produce maximum visual contrast between the sea and oil colour. The presence of cloud shadows can be confusing.

The apparent sea colour depends on sky reflection, depth of water, bottom colour and sediment load in the water and is influenced by sea state (presence of waves and wave breaking) and this will influence the contrast with the colour of the oil film. Actual oil colour varies. Marine diesel is almost colourless at the thickness it is present when spilled on the sea. Crude oils vary from light brown to black and this alters from pale orange through light brown to black depending on oil composition and water content, when they have become emulsified.

4. Correlation of oil film thickness and colour

The main purpose of this report has been to concentrate on the Bonn Agreement Colour Code. The presence of any colour in the observed oil obviously indicates that the quantity present is above the minimum that is visible, otherwise it would not be observed.

4.1 References reviewed

Within the scope of this literature review, only a limited number of references specifically dealing with the correlation of oil film thickness and colour have been identified.

The main reference to the correlation between oil colour and oil film thickness that many publications refer to is the *American Petroleum Institute (API) Manual on Disposal of Refinery Wastes: Volume I Waste Water Containing Oil, 7th edition*, published in 1963 (API, 1963). The relevant regulations controlling these discharges were known as the Federal "Sheen Regulations" and the study was originally performed to see whether these regulations were enforceable on the basis of visual observation. As the title of the report indicates, this work was produced to relate the way that permissible discharges from refineries could be observed, and was not directly relevant to observation of illegal oil discharges at sea from surveillance aircraft.

Bernard Hornstein of the U.S. Environmental Protection Agency (EPA) examined whether the colour/thickness correlation was relevant to aerial observation of spilled oil and illegal oil discharges. This work was reported as *The Appearance and Visibility of Thin Oil Films on Water* in an EPA report in 1972 (Hornstein, 1972) and, for more general availability as *The Visibility of Oil-Water Discharges* at the 1973 Joint Conference on the Prevention and Control of Oil Spills (Hornstein, 1973), the forerunner of the biennial International Oil Spill Conferences.

From the late 1970's, the emphasis has been on remote-sensing techniques for oil spill surveillance. Little or no scientific work has been conducted, although the original colour/thickness correlation has frequently been re-published and, in some cases extended. CONCAWE published a colour/thickness correlation covering an oil thickness range of 0.1 to 10 µm in 1981 (CONCAWE, 1981), although the reference from which it is taken is a 1979 EPA reference (EPA, 1979), which in turn quotes Hornstein's 1972 reference.

ITOPF (The International Tanker Owners Pollution Federation) published a Technical Information Paper on Aerial Observation of Oil at Sea (ITOPF, 1981) with a "Guide to the Relation between Appearance, Thickness and Volume of Floating Oil". CONCAWEs publication in 1988 (CONCAWE, 1988) of an extended correlation is supported by photographs

The Bonn Agreement has produced several documents on this topic. The latest edition of the Bonn Agreement Manual (Bonn Agreement, 1993 with annual amendments) contains the latest version of the "colour code".

4.2 Colour perception

Before considering the correlation between the different 'colour codes' that have been published, it is useful to consider what causes the colours observed in oil films.

Human vision and the perception of colour by the eye is a complex process. Newton's work, the Opticks (1704), is considered to be the start of the science of colour perception. It is a complex science in its own right and only a simplified description is given here to explain some of the effects that occur when oil films are observed at sea.

The colour of any object that is observed by the human eye depends on many factors:

- the mixture of wavelengths (detected as colour) of the prevailing light.

- the way the wavelengths (and therefore detected colour) of the observed light is altered by being:

    - transmitted (filtered) through,
    - absorbed and reflected off,

  or
    - refracted by the object.

- the way the human eye detects different light wavelengths (the rod and cone detectors within the eye) and interprets them as colours.

The visible spectrum is from 400 to 750 nanometres (0.40 to 0.75 microns). This is detected by the human eye as a colour range from blue to red. The colour of light can be mixed. White light is a mixture of all the visible wavelengths of light. All different light colours can be mixed to produce colours in which the constituent colours cannot be identified. White light can be 'coloured' by the use of filters (selective wavelengths are absorbed or removed by the filter). Yellow light is obtained by combining red with green light. If two lights are projected on to a screen, one through a red filter and one through a yellow filter, the light seen reflecting from a white screen will be yellow. White light can be achieved by mixing the light from three principal colours of red, yellow and violet in the appropriate proportion. Any colour in the visible spectrum can be produced by a mixture of three, but not less than three, lights set to appropriate intensities.

However, it is not possible to produce all colours that can be seen by mixing light. Brown is a not a pure colour, it is not in the visible spectrum but, of course, it can be seen. It is not possible to produce brown by mixing red, yellow and violet. It is also not possible to produce metallic colours such as silver or gold by mixing lights. Black is not a true colour: it is the absence of light, caused by absorption of all visible wavelengths.

The mixing of different coloured light should not be confused with the colour produced by mixing pigments; a painter that mixes yellow and blue paints to produce green is not mixing light; he is mixing the total spectrum of colours *minus the colours absorbed by his pigments*.

The colour of a solid object that we see is therefore produced by the selective absorbance of some light wavelengths from (normally) white light by the surface of the object. Our eyes detect the light reflected from the object, which is now deficient in some wavelengths, and interpret it as a specific colour. When viewing transparent objects, such as coloured glass, the light that reaches our eyes has had certain wavelengths removed due to absorbance by the pigment in the glass. The colour that we detect is normally the full spectrum of all possible colours (white light) minus some wavelengths that have been removed by absorbance. We generally consider that we detect the 'true' colour of an object, but it is simple to demonstrate that the colour changes if not viewed in pure white light. The colour of an object is therefore a function of viewing conditions and perception, rather than an intrinsic property of the object or substance.

4.3 The colour of oil

Oils spilled at sea range from black fuel oils through brown crude oils to almost transparent, or lightly coloured products such as lubricants or distillate fuels.

Residual fuel oils are black because they contain high molecular weight components such as asphaltenes which absorb all the visible wavelengths. Isolated asphaltenes are black. Other residual oil components are brown, but appear black because of the high proportion of asphaltenes dissolved in them. The ability of the oil to block light is known as its optical density. Normally this is quoted for a particular light wavelength. Residual fuel oils with a high optical density can block all light passing through them, even when present in relatively thin layers. Black oils block all the wavelengths in white light to the same degree, but not to the same extent. Even within groups of oils that all look black, there are differences in optical density; some black oils are blacker than others. Thinner layers of the most optically dense black oils will block more light than the same thickness of less optically dense black oils.

Crude oils vary in colour from pale brown to black. This is due to the proportion of heavier components that they contain. Some components of crude oils, described as chromphores, have quite intense colours due to their chemical structure. The precise structure of these components is not relevant to this report. Their colour and concentration in crude oils varies over a wide range. Crude oils also vary in their optical density and in the wavelengths that they block most (see Figure in section 4.5.3). The amount of white light that can pass through, or is reflected from, crude oils varies over a wide range.

Distillate fuels and lubricants are produced from the lightest and middle range components of crude oils by the refinery distillation process. The coloured components are concentrated in the residue which is used to make residual fuel oils. Distillate fuels and lubricants tend to have pale colours such as very light brown and they have very low optical density, i.e. only block light to a very limited degree. When spilled on the sea they form very thin layers which are almost transparent, light passes readily through them with little absorption, but they will reflect light from their surface.

The general colours that are seen at oil spill tend to be metallic silvers, browns and black plus apparent colours caused by other effects. Assigning a description to these colours is difficult because they are not optically pure colours.

5. Theory of oil thickness / colour correlation

There are certain effects that can be described in terms of colour and depend only on oil film thickness and others that depend on oil film thickness and the way the apparent colour is altered by reflection from, or transmission through, different coloured oil films.

5.1 Very thin films (below 0.15 μm)

Below approximately 0.04 microns thickness oil films are invisible, even in perfect viewing conditions. There is not enough oil present to affect the appearence of the sea surface. In less favourable viewing conditions, or in the presence of substantial waves, even much thicker oil films cannot be reliably detected by the human eye. Extremely thin films of oil, less than 0.1 micron thick, are only visible because they reflect white light slightly more effectively than water (Figure 1).The apparent colour of silvery or grey is due to this effect and not the colour of the oil itself. The oil film is too thin for any actual colour to be observed. All oils will appear the same if they are present as extremely thin films.

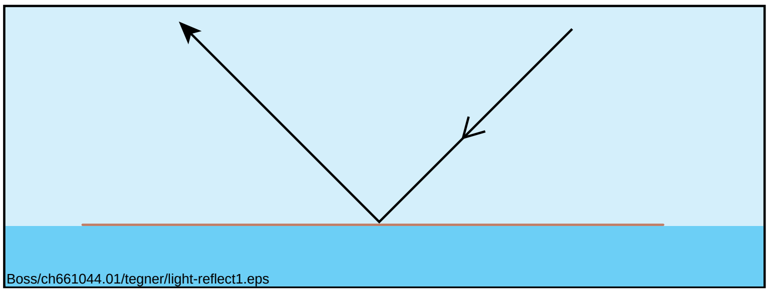


Figure 1 Light reflecting from very thin oil films (below 0.15 microns). The oil layer reflects white light slightly more effectively than the water. Silver or grey colour observed.

5.2 The 'rainbow region' (from 0.15 μm to 3 μm)

The rainbow colours observed for thin (around 1 micron) oil films are caused by destructive and constructive interference between different wavelengths (colours) that make up white light. When white light (a mixture of colour from blue to red, wavelengths of 400 to 750 nm, i.e. 0.4 to 0.75 microns) illuminates a thin film of oil it is reflected from the both the surfaces of the oil and of the water (Figure 2).

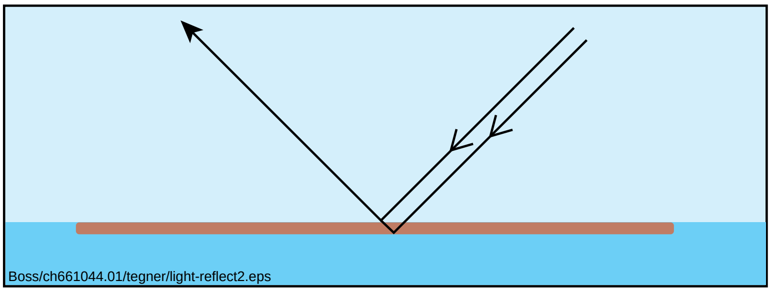
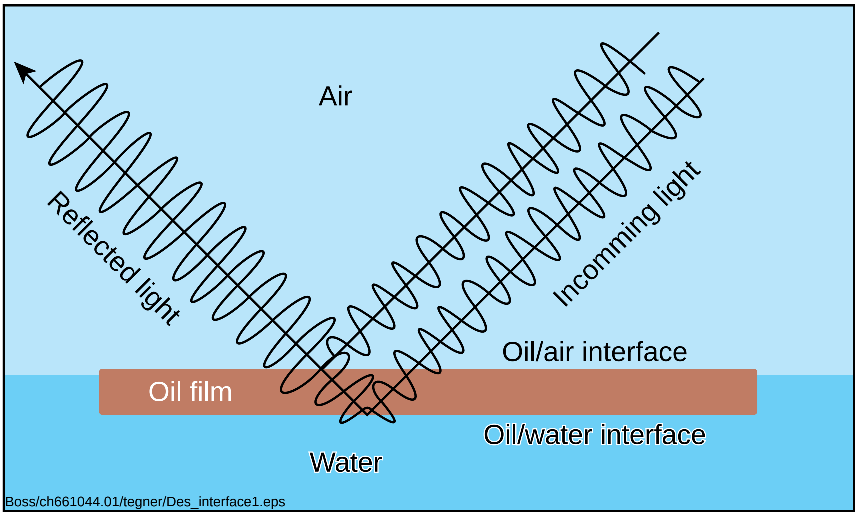


Figure 2 *The rainbow region (0.15 to 3.0 microns). Light reflected from both oil/water surface (the sea surface) and oil/air surface (the oil surface)*

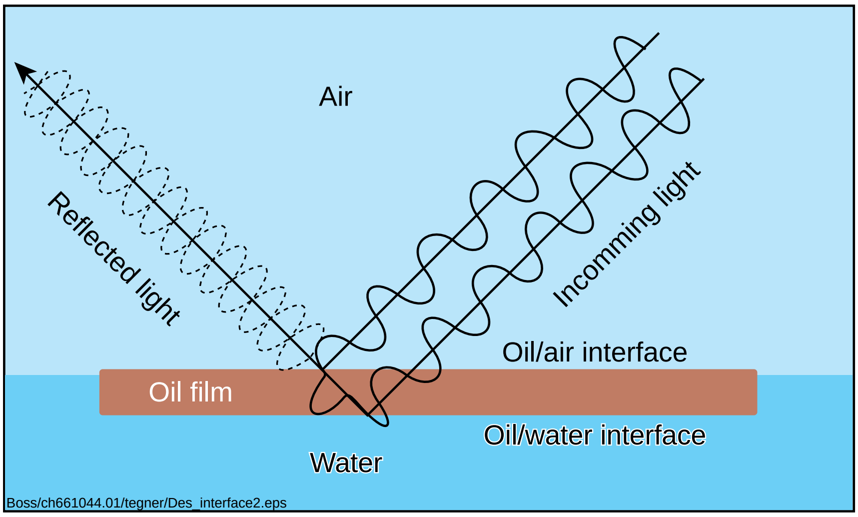
The light that is reflected from the lower (oil / water) surface combines with the light that is reflected from the upper (oil /air) surface. If the light waves reinforce each other (i.e. they are ‘in step’ as in Figure 3), the colour will be present and brighter in the observed colour.



Constructive interface (light waves reinforce each other)
Wavelength (colour) appears brighter

Figure 3 *Constructive interference of light wavelengths. The light waves reinforce each other and the particular wavelength (colour) looks brighter.*

If the light waves cancel each other (i.e. are ‘out of step’ as in Figure 4), the colour will be absent and the colour that is seen will be white minus the cancelled wavelength. For example, where green has been destroyed, the film will have a red appearance. The interference was discovered in about 1800 by Thomas Young. The colours are therefore brightest when the oil film is of the same order of thickness as the light wavelength; about 0.2 to 1.5 µm thick and less evident above and below this thickness.



Destructive interface (light waves cancel each other out)
Wavelength (colour) appears darker

Figure 4 *Destructive interference of light wavelengths. The light waves cancel each other out and colour is reduced in reflected light.*

All oils present in films of this thickness will show a similar tendency to produce this ‘rainbow’ effect. The effect will also be noticeable, although not as pronounced, for layers that are somewhat thicker (up to approximately 3 microns). Very black or opaque oils will show this effect less than transparent oils.

5.3 Oil films from 3 μm to around 50 μm thick

Oil films above 3 microns thick will not exhibit interference colours. The thickness of the film is four times the wavelength of red light and the average effect of multiple interference is to produce no overall ‘rainbow’ effect. However, the ‘true’ colour of the oil will not be evident because oils do not have sufficient optical density (they are not opaque enough) to block all the light. Some of the light will pass through the oil and be reflected off of the water surface. The oil will therefore act as a filter to the reflected light.

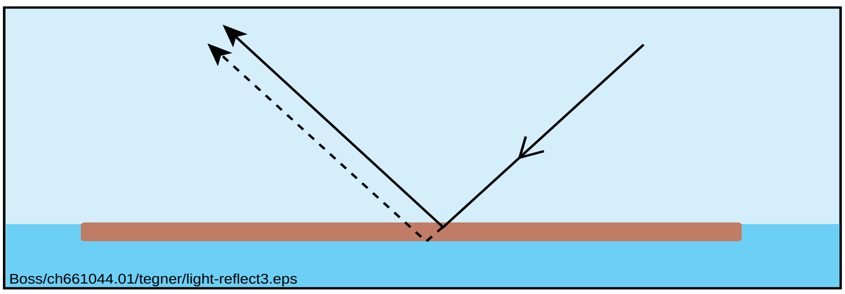


Figure 5 *Intermediate thickness oil films (3 to 50 microns) Majority of light is reflected from oil surface, but a minority passes through oil film and is reflected from sea surface.*

The extent of filtering will depend on the optical density of the oil and the thickness of the oil film. Black oils such as Bunker C fuel oil will reduce the total amount of light reflected from the water surface and the area covered by a film of Bunker C fuel oil will appear darker than its surroundings. Many crude oils are brown in colour.

As described in Section 4.2, white light is a mixture of all wavelengths and can be considered to be a mixture of red, green and violet light. This is called additive mixing of colour. Thin films of brown oil contain the chromophores which act as pigments. These absorb some of the red and green components from the white light leading to an enhancement of the blue component in the reflected light. Although the oil is brown, the reflected light that has been filtered through it (twice its film thickness - see Figure 5) can appear to have a blue tint.

Unlike the rainbow interference colours, which are independent of oil colour and only depend on oil film thickness, the modification of reflected light by filtering by the oil film will depend on oil colour and optical density (and therefore oil type) plus the oil film thickness.

5.4 Oil films from 50 µm to 200 µm thick

Oil films considerably thicker than 50 µm start to appear as the true colour of the oil. The light is being reflected from the oil surface rather than from the sea surface.

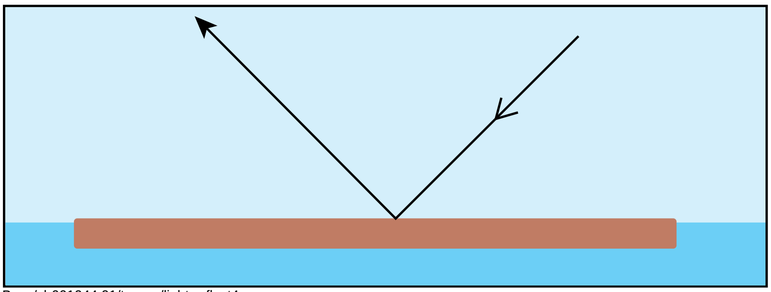


Figure 6 Thick oil films (50 to 200 microns and thicker, depending on oil type)

The colour observed depends on the optical density (or conversely, the transparency) of the oil and therefore the observed colour depends on oil type. Relatively transparent oils, such diesel or marine diesel fuel and many lubricants, will have no apparent colour when present as thin layers, provided that they have not emulsified. They will also not modify the reflected light buy absorbing components from it. They will act as in Figure 5, but without modification to the reflected light colour if the oils are not coloured.

Heavy bunker fuel oils, such as IF 240, have a dense black colour and will start to appear as such on the sea surface where the film thickness exceeds around 50 µm (Figure 6).

Crude oils will generally appear as brown, although their true colour will only become apparent in thicker layers (from about 50 to 100 µm or more) because many crude oils have a low optical density and are only slightly coloured when present as a thin films. The colour of the oil film is therefore not a direct indication of oil film thickness.

Films of any oil in excess of about 200 - 500 microns will appear as the true colour of the oil - black for heavy fuel oils and some crude oils, brown (ranging from light to dark) for crude oils or a range of browns (from almost black to chocolate and then to *cafe au lait* or even red or orange) if the oil has emulsified. The colour of an emulsion depends on the colour of the oil, the water content and the size of the incorporated water droplets. The colour is not directly related to the emulsion film thickness.

6. Oil thickness / colour (or appearance) correlations

The potential of using apparent colour as a guide to oil film thickness, and therefore oil volume, has been recognised for many years. The rainbow (or iridescent) colours caused by small quantities of spilled oil (gasoline, diesel fuel or engine oil) are familiar to anybody that has observed them in city streets after rain. The obvious extension from land-based, casual observations to aerial surveillance of oil spilled at sea was made a long time ago.

6.1 US House of Representatives Congress Report 1930

The 1930 US Congress report on oil pollution experiments (House of Representatives, 1930) contains the following correlation for oil film layers in the range of 0.04 to 2 µm (Table 1).

Table 1 Colour / oil film thickness correlation published in 1930.

Approximate film thickness	Approximate quantity of oil in film		Appearance
µm	gallon per square mile	litres per square kilometre	
0.04	25	44	Barely visible under most favourable light conditions
0.08	50	88	Visible as a silvery sheen on water surface
0.15	100	176	First traces of colour may be observed
0.3	200	351	Bright bands of colour
1	666	1168	Colours begin to turn dull
2	1332	2337	Colours are much darker

These values were obtained by actual experimentation, although the precise details are no longer available. The correlation agrees with all theoretical work in that the ‘rainbow’ region is centred on approximately 0.3 microns, 300 nanometres, near to the wavelength of blue light.

6.2 American Petroleum Institute 1963

The colour / oil film thickness correlation published in the API Manual on Disposal of Refinery Wastes (API, 1963) covers the same limited range, between 0.05 to 2 µm thick

(Table 2). With minor variations in the wording and the degree of accuracy to which the film thickness, this is almost identical to the correlation published 33 years earlier

Table 2 Colour / oil film thickness correlation published in 1963.

Film thickness µm	Appearance
0.038	Barely visible under most favourable light conditions
0.076	Visible as a silvery sheen on surface
0.15	First traces of colour may be observed
0.31	Bright bands of colour are visible
1.0	Colours begin to turn dull
2.0	Colours are much darker

These values are also based on experimental work although, once again, the precise details were not available for analysis. However, the strong agreement between theory and the early work strongly suggests that this correlation is correct.

6.3 US Environmental Protection Agency 1972 and 1973

In the work reported by Hornstein in 1972 (Hornstein, 1972) and 1973 (Hornstein, 1973), the colour / oil thickness correlation examined was in a similar range as the earlier work, but concentrated on the region where colour is most apparent (Table 3). This is essentially the region where interference effects (see Section 3.3) occur and is in the range from about 0.15 microns to 2 or 3 microns.

An exact description of the experimental work is contained in both the 1972 and 1973 references, although only the 1972 reference contains the colour photographs on which the written description is based. The experiments were conducted in the laboratory. The colour and appearance of the oil films are that of South Louisiana crude, Light Arabian crude, Agha Jari (Iranian) crude and No. 2 fuel oil. This correlation is the most definitive and well documented of all the correlations that have been published. Its agreement to theory and the care and precision with which it was carried out establishes it as the reference work against which other correlations should be judged. The description of the 'fine structure' of individual colours within the 'rainbow' region is unique.

Table 3 Colour / oil film thickness correlation published in 1973.

Oil film thickness (μm)	Appearance	Description
Up to 0.15	Colourless films	Films reflect more light than water and look brighter. May need adjacent bare water for comparison. Appearance brightness increases with thickness. At about 0.075 μm and thicker, a pearly or metallic lustre is usually apparent.
Approx. 0.15	Onset of colour	First colour seen as a warm tone, more bronze than yellow. As film thickens, deep violet or purple appears; these colours begin the first set of rainbow bands.
0.15 to 0.9	Pure rainbow colours	The set of bands around 0.3 μm are in the sequence; bronze, purple, blue, green, in order of increasing thickness. These colours are pure and intense. The set of bands around 0.6 μm are slightly less intense than at 0.3 μm, and have a modified colour sequence; yellow, magenta (reddish-violet), blue, green. They are quite pure.
0.9 to 1.5	Dull, impure colours	Main characteristic is the reduction in number and quality of colours. Colours at 0.9 μm are a rich terra cotta (brick red) and turquoise (rather bright blue-green). At 1.2 μm and 1.5 μm these colours are progressively duller or less pure looking. These sets of bands may also contain a trace of white or pale yellow.
1.5 to 3.0	Light and dark bands with little colour	Any colour present is merely a tint in the light and dark alternating bands. At 1.8 μm, the contrast between light and dark bands is strong, but weakens as thickness increases. At 3.0 μm, it is apparent that the interference effects are weak and they will quickly disappear as thickness increases

6.4 CONCAWE 1981

CONCAWE's 1981 publication "A field guide to coastal oil spill control and clean-up techniques" presented the oil film thickness and colour as a graph (Figure 7) sourced from a 1979 EPA manual (EPA, 1979).

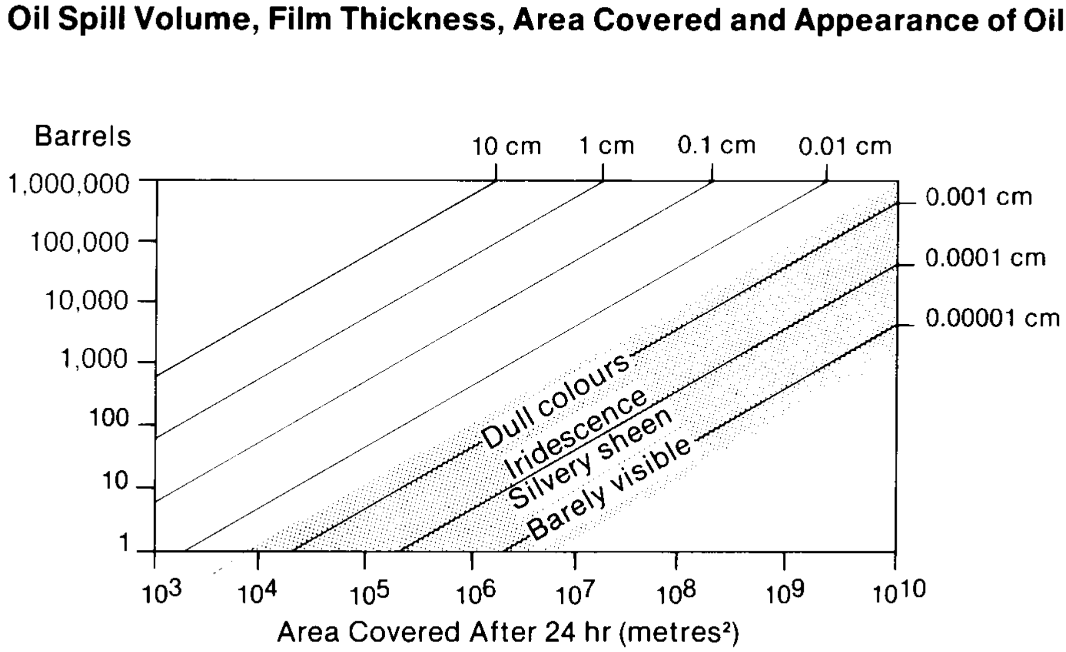


Figure 7 *Oil Spill Volume, Film thickness, Area Covered and Appearance of Oil.* (CONCAWE 1981)

A footnote to this graph states:
"Shaded area indicates the range of oil slick observations for which thickness and area can be determined by appearance. Any value below the shaded area would not be visible, and any value above would be a dark brown or black."

It should be noted that the area covers the range from below 0.00001 cm (0.1 microns) up to just over 0.001 cm (10 microns). The line equivalent to 10 microns is labelled "Dull Colours" which is similar to the 1 μm to 3 μm range in Hornstein's earlier work.

It is not clear from the reference whether the extension in the correlation range, from around 2 μm to 10 μm, in the oil film thickness causing "dull colours" was an error in transcribing the information from earlier references or the result of other work, but it is not in agreement with all theoretical work on this subject (see section 3.3).

The relationship given in Figure 7 is therefore probably wrong and should not be relied upon.

6.5 International Tanker Owner's Pollution Federation 1981

ITOPF's 1981 "Aerial Observation of Oil at Sea" (ITOPF, 1981) contains the following information:

Table 4. A Guide to the Relation between the Appearance, Thickness and Volume of Floating Oil (ITOPF, 1981)

Approximate thickness (µm)	Approximate volume (m^3/km^2)	Oil type	Appearance
>0.1	0.1	Oil sheen	Silvery
>0.3	0.3	Oil sheen	Iridescent
>100	100	Crude and fuel oil	black/dark brown
>1000	1000	Water-in-oil emulsions ('mousse')	brown/orange

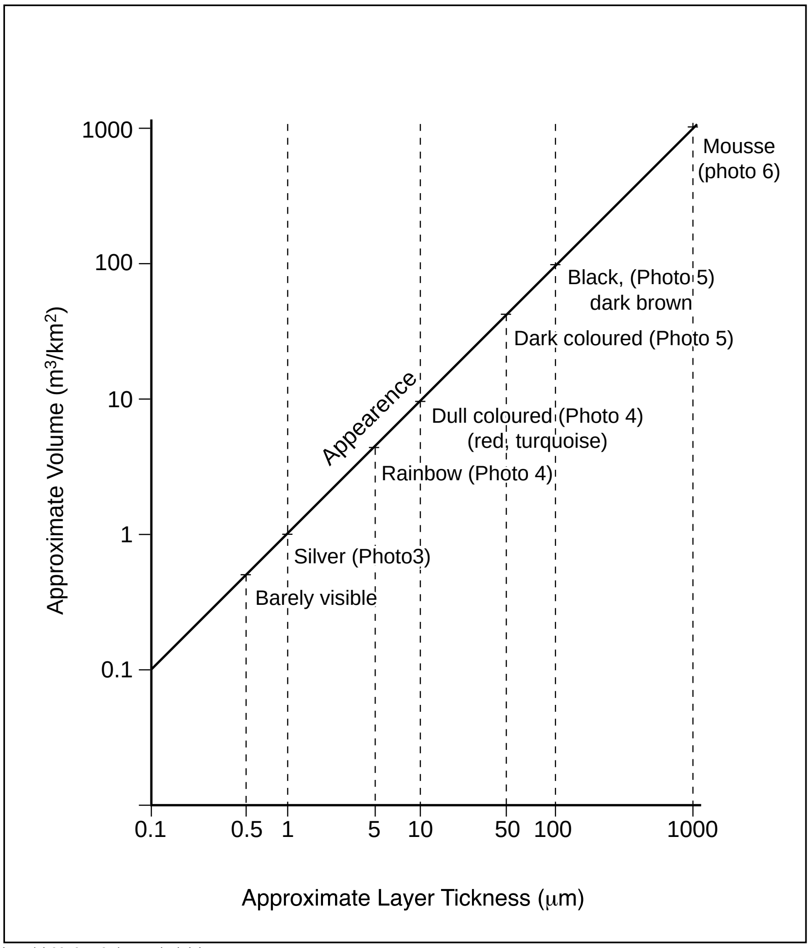
The correlation has been extended beyond the limited range of light wavelength interference in the 'rainbow' region (0.15 microns to 3 microns) to greater than 100 microns (>0.1 mm) as an average for spilled oil, and greater than 1000 µm (>1 mm) as an average for emulsified oil.

0.1 millimetre has traditionally been taken as the average thickness of non-emulsified oil slicks. However, it is now widely appreciated that oil film thickness in slicks of oil from large accidental releases varies over an enormous range, from 1 micron to several millimetres and that emulsified oil thickness can be up to several centimetres. While the average thicknesses of 100 microns for oil and 1000 microns for emulsified oil may be a good 'rule of thumb' for estimating the volume of large areas of oil, it cannot be used as an addition to the correlation to be used in the same way as the colours in the 'rainbow' region.

The designation of 'black/dark brown' for the "Oil Type" designated as 'crude and fuel oil' could be misleading if taken to mean that crude oils appear as black films and fuel oils appear as brown films, because the opposite is generally true. Presumably, this description was introduced to differentiate between the generally darker colour spilled oil compared to the lighter colour of emulsified oil.

6.6 CONCAWE 1988

The 1988 CONCAWE publication “A field guide to the application of dispersants to oil spills contained the most extensive correlation to that date (Figure 8).



boss/ch661044.01/tegner/vol-tick.eps

Figure 8. Appearance of oil (CONCAWE, 1988).

Photographs were used to explain the text on the graph (see Figure 9).

It should be noted that the photographs are only used as examples of the visual appearance of different oil thicknesses and it is known that no actual measurements were made of the thickness of the oil slicks in the photographs. Thus the relationship between thickness and appearance given in Figure 8 cannot be taken as definitive or corroborated with actual measurements.

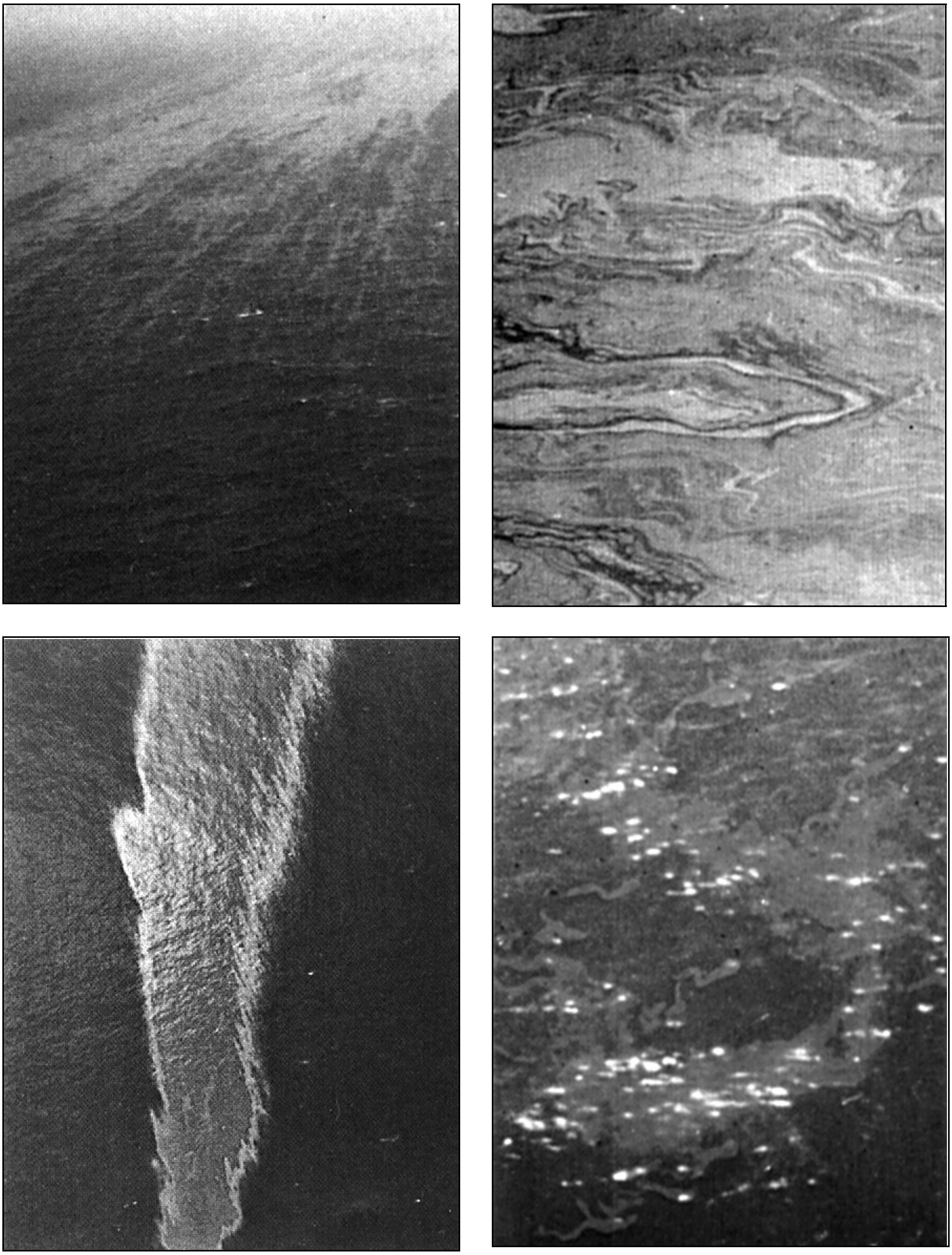


Figure 9 Photographs of different oil thicknesses.

The information in Figure 8 has been summarised in table form as Table 5 to aid comparison with the other correlations.

Table 5. Appearance of oil, (CONCAWE, 1988).

Approximate thickness (µm)	Approximate volume (m^3/km^2)	Appearance / Colour
0.5	0.5	Barely visible
1	1	Silvery (Photo 3)
5	5	Rainbow (Photo 4)
10	10	Dull coloured (Photo 4) (red, turquoise)
50	50	Dark colours (Photo 5)
100	100	Black, (Photo 5) dark brown
1000	1000	Mousse (Photo 6)

There is a major difference between this and the earlier correlations by Hornstein that had be corroborated with laboratory measurements; there is an increase by a factor of ten in the oil film thickness where colours are said to be caused by interference patterns, compared to earlier work - Table 6 compares thickness and description with the API 1963 correlation.

Table 6 Comparison of API 1963 and CONCAWE 1988 descriptions of appearance and oil film thickness.

CONCAWE 1988 Film thickness µm	API 1963 Film thickness µm	Appearance
0.5	0.038	Barely visible under most favourable light conditions. (API) Barely visible (CONCAWE)
1	0.076	Visible as a silvery sheen on surface.(API) Silvery (CONCAWE)
-	0.15	First traces of colour may be observed, (API)
5	0.31	Bright bands of colour are visible. (API) Rainbow. (CONCAWE)
10	1.0	Colours begin to turn dull. (API) Dull coloured. (CONCAWE)
50	2.0	Colours are much darker. (API) Dark colours (CONCAWE)

The 1988 CONCAWE oil film thickness / colour and appearance correlation, in the region from 0.5 µm to 50 µm does **not** agree with previous correlations or theoretical considerations. The two categories above this region, 100 µm (0.1 mm) for black oil and 1000 µm (1 mm) for water-in-oil emulsion or 'mousse', are similar to the 1981 ITOPF additions to the correlation, but the > (greater than) symbol has been omitted.

Although this CONCAWE correlation is presentation in a visually attractive way, it is not an original work and the earlier references have been misquoted to produce a correlation that is obviously wrong.

6.7 Bonn Agreement 1993

The 1993 Bonn Agreement Manual - Oil Pollution at Sea (Bonn Agreement, 1993) has the following correlation:

Table 5 A Guide to the relationship between the Appearance, Thickness and Volume of Floating Oil (Bonn Agreement, 1993).

Code	Approximate thickness (µm)	Approximate volume (m^3/km^2)	Appearance / Colour
1	0.02	0.02	Silvery
2	0.1	0.1	Grey
3	0.3	0.3	Rainbow
4	1.0	1	Blue
5	5.0	5	Blue/brown
6	15-25	15-25	Brown/black
7	>100	>100	Dark brown/black
	see note		Brown/orange mousse

Note: A brown/orange mousse shows the presence of water-in-oil emulsion. While the thickness is usually 1-4 mm, it may be even higher. The percentage of oil in the emulsion can only be assessed with samples. The presence of mousse, however, shows a very high quantity of oil which would, in the case of discharges dealt with in this Manual, correspond to an exceptionally large discharge.

The accompanying text states that "... up to Code 5 were derived from the results of sea exercises with controlled oil discharges. Beyond that the relationship emerges from experience of ITOPF and oil spill survey teams." The ITOPF 1981 reference is quoted.

Codes 1, 2 and 3 are derived from earlier work, such as the API manual and Hornstein's work for the US EPA and are correctly quoted. Code 7 and the description of emulsion have been taken from the 1981 ITOPF reference.

The expansion of the colour code is in the region of 1 μm to 25 μm oil film thickness. This has been categorised as three 'new' bands;

1.0 μm	Blue
5 μm	Blue/brown
15 - 25 μm	Brown/black

The source of this new correlation is not precisely identified, apart from the reference to 'oil spill survey teams', presumably from actual incidents and at the joint exercises undertaken by the Bonn Agreement countries.

6.7.1 Code 4 Blue - 1 μm thick

The blue colour associated with 1 μm thick layers may be similar to the 'turquoise (rather bright blue-green)' described by Hornstein in 1973, although the colour of this 0.9 μm thick oil film was also described as a 'rich terra cotta (brick red)' (Hornstein, 1973), as a series of bands of both colours.

There is therefore a discrepancy between Hornstein's earlier, laboratory-validated work and the Bonn Agreement Code 4, although the operational significance may be slight.

6.7.2 Code 5 Blue/brown - 5 μm thick

Although there are theoretical grounds for a blue band to exist in the colour code, caused by filtering of reflected white light by brown oil (see Section 5.3), no experimental evidence has been gathered to confirm that it exists. This is the first recorded instance of the inclusion of a colour code correlation at this thickness (with the exception of the erroneous 5 microns being equivalent to rainbow colours in the 1988 CONCAWE report).

Theoretical considerations show that the effect would be a function of oil colour (and therefore oil type) **and** thickness and it is therefore unlikely to occur at 5 micron oil thickness for all oil types. However, the value of 5 microns may represent a reasonable average for all of the occasions when it has been observed.

6.7.3 Code 6 Brown/black - 15-25 μm thick

There is **no** theoretical or experimental evidence to suggest that a specific brown/black colour will be caused by oil films of 15 to 25 microns thick.

In this thickness region, it is possible that colour modification by selective light absorbance / filtering **could** occur by films of transparent or semi-transparent oils. This is most likely to give rise to colours in the blue part of the spectrum and produce blue/brown colour combinations. However, this will be oil type-specific and cannot be generalised into a correlation that can be applied to all oil types.

Practical experience from Bonn Agreement exercises (through knowledge of amount of oil released and subsequent observer reports) might indicate that this is a reasonable figure to use on the occasions that the observations have been made, but it cannot be a reliable indicator for other circumstances.

Discrimination between this and Code 7 (dark brown / black and 100 µm thick), must be difficult. It is likely that all possible oil film thicknesses, from the very thinnest up to several millimetres or several centimetres, exist within oil slicks at some time in their development.

6.7.4 Bonn Agreement Pollution Observation Log 1997

The current (1997) Bonn Agreement Pollution Observation Log contains the correlation contained in Table 6.

Table 6 Current (1997) Bonn Agreement Pollution Observation Log.

Code	Appearance / Colour	QUANTITY cbm/km^2	Thickness (µm) calculated for this report
1	Silvery	0.02	0.02
2	Grey	0.1	0.1
3	Rainbow	0.3	0.3
4	Blue	1	1
5	Blue/brown	5	5
6	Brown/black	15 - 25	15 - 25
7	Dark brown/black	> 100	> 100

Table 6 is almost identical to the 1993 version (table 5) except that the thick mousse (with footnotes) is no longer included.

7. Conclusions

A theoretical consideration of the appearance of the colour of oil films on the surface of water and a consideration of the available literature shows that the observed colour depends on several factors.

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 - 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 - 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 - 0.3 microns) is in very good agreement with all theoretical and experimental observations. However, the current Bonn Agreement Code 4 (Blue - 1 micron) is in conflict with theoretical and experimental evidence.

3. Oil films from 3 μm to around 50 μm can give rise to blue tinted reflections by filtering the white light reflected from the underlying sea surface. The effect will depend on the optical properties (colour and optical density) of the oil, plus the oil film thickness.

   The current Bonn Agreement Codes 5 (Blue/brown - 5 microns) and 6 (Brown/black - 15 to 25 microns) are not supported by theoretical considerations or measurements made in the laboratory. Calculations made on the basis of total volume of oil discharged and observer reports made at Bonn Agreement exercises may support these correlations, but were not available for this literature review.

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 (e.g. diesel fuel) 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 am 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.

8. References

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