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The Appearance and Visibility of Thin Oil Films on Water

National Environmental Research Center
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U.S. Environmental Protection Agency
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THE APPEARANCE AND VISIBILITY OF THIN OIL FILMS ON WATER

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NATIONAL ENVIRONMENTAL RESEARCH CENTER
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ABSTRACT

When oil films of controlled thickness (up to 3000 nanometers) were formed upon water surfaces in the laboratory, an inherent and orderly thickness-appearance relationship was confirmed — a relationship that is independent of oil type and water type. The laboratory studies also investigated the effects of viewing conditions upon the ase with which these thin films were visible.

Out-of-doors observations were made; these and the observations reported by other sources corresponded with the laboratory results. The visibility of a thin oil film depends not only upon its thickness-dependent inherent appearance, but also upon conditions external to the film: the nature of illumination and sky conditions, sun angle, color and depth of water, color of bottom, and viewing angle.

Color photographs illustrate the points discussed.

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1. CONCLUSIONS

1. Oil films up to approximately 3000 nanometers (3 microns) thick show characteristic inherent color effects that are governed by interference phenomena.

2. Within this range (up to 3000 nanometers), these inherent color effects have, in theory and in fact, an orderly relationship to film thickness and are independent of the type of oil forming the film.

3. A table such as that published by the American Petroleum Institute and included in this report or an equivalent table assembled from the EPA tray photographs, reliably indicates film thickness in this range.

4. The visibility of an oil film is not constant but depends upon conditions of observation as well as upon its inherent characteristics. Optimum conditions include the absence of direct sunlight, a white overcast, a high viewing angle (approaching vertical), and low background brightness from the underlying water.

5. As viewing conditions deviate from the optimum, the visibility of a given film is lessened.

6. Under sufficiently adverse conditions, visibility becomes low or nil for films less than 3 microns thick.

7. For films too thin to show color, an adjacent area of bare water for comparison is usually necessary to discern the higher reflectivity of the film. This is not usually required for films that show definite color.

8. For films too thin to show color, waves or chop tend to obscure the higher reflectivity of the film.

2. INTRODUCTION

2.1 Reasons for this Investigation

Present Federal regulations (Ref. 1) prohibit harmful discharges of oil. Harmful discharges are stated by the regulation to be those which:

> "....cause a film or sheen upon or discoloration of the surface of the water...."

The prohibition applies not only to oil per se, but also to oil mixed with water. The latter includes, for example, oily ballast or bilge water from a vessel, and waste water from an offshore drilling platform.

The term "sheen" is defined in the regulation as:

> "an iridescent appearance on the surface of the water",

and the American Heritage Dictionary definition of "iridescence" is:

> "producing a display of lustrous, rainbow-like colors".

For convenience, this regulation will be referred to as the "sheen regulation".

2.1.1 Visibility as a Criterion

The sheen regulation, if read literally, prohibits the existence of an oil film, sheen, or discoloration; proof of existence depends upon detectability. In the absence of devices on the water surface for chemical or physical sampling and analysis, potential detection is by remote sensing devices. These devices usually respond to the electromagnetic spectrum, from the ultraviolet through the visible and infrared, and into the microwave region.

In this context, the human eye is a remote sensing device, responding to the visible spectrum in the 400 nanometer (nm) to 750 nm wavelength band (Fig.1). Compared with other presently developed remote sensing systems, the eye has greater sensitivity, it is standard equipment with observers, and it is served by a data processing center which interprets and correlates the eye's output with excellent reliability and reproducibility.

These attributes, together with the fact that the definition of "sheen" invokes the visible spectrum, leads to the stipulation that detection by eye, or visibility, is the primary criterion for the existence of a film, sheen, etc. Accordingly, this report is concerned with visual properties of thin oil films and with the visibility of oil films.

2.1.2 Problem and Scope

Limiting cases of visibility involve very thin films which produce rainbow-like colors and films which are even thinner and show no color. Films too thick to show bright color are assumed readily visible either by virtue of their self-color (browns and blacks for crudes and residuals) or by virtue of their calming of the water. These thin films range in thickness from about 15 nm, about 1/30 the wavelength of visible light, to about 3000 nm (3 microns), about 6 times the wavelength of visible light.

The following questions developed in our examination of the sheen regulation:

(a) Once thin oil films have been formed, what are their inherent optical characteristics and what are the corresponding inherent visual effects?

(b) Do these inherent visual effects imply an inherent, or constant, visibility or are there other factors that make visibility variable? Factors to consider include oil type, illumination, and viewing position.

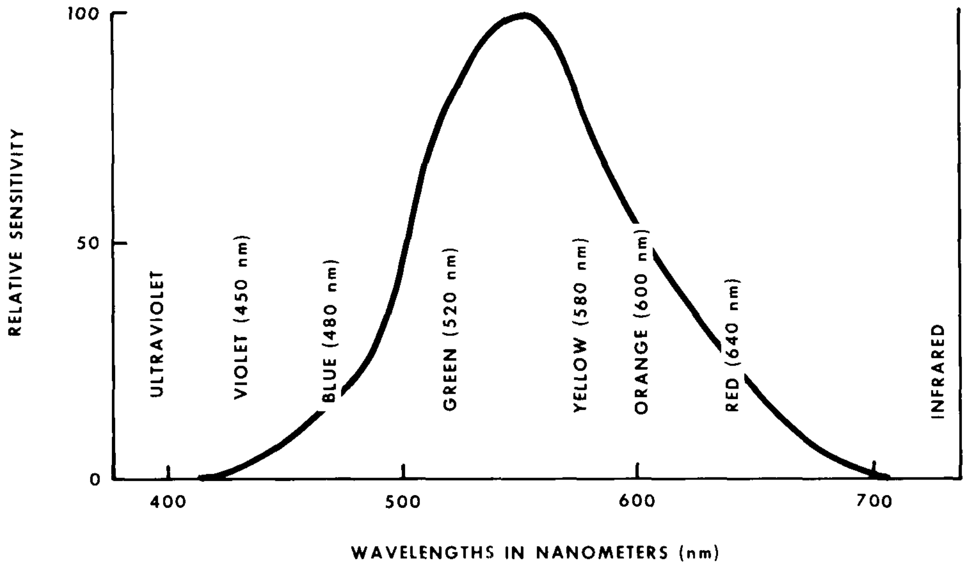


Figure 1. Relative sensitivity of the human eye to light of various wavelengths (from Ref. 7).

(c) If we can establish relationships concerning the visibility of oil films per se, can we also establish relationships between the conditions of oily water discharge and the formation of surface films?

(d) Can we then relate conditions of oily water discharge and their consequent visibility?

We undertook a two-part study. This report addresses itself to the first two questions that concern the oil film per se. The second part, concerning the latter two questions, is the subject of a separate report.

2.2 Background and Approach

2.2.1 Background Information

With the exception of some crude oils and processed products that form discrete "lenses" on the water's surface, most crudes and products spread spontaneously because of surface-active components (Ref. 2). This spreading can continue until extremely thin films are formed. The American Petroleum Institute (API) (Ref. 3) indicates a relationship between film thickness and visual effect. Table I contains this information, with thickness values in various metric units added for convenience.

In Table I, a film 38 nm thick is listed as "barely visible under most favorable light conditions". This suggests that there is a limiting thickness below which a film is not visible. It also suggests that this limiting thickness can vary with lighting conditions. The other entries indicate an orderly trend between appearance and thickness, in three main groupings:

Up to 150 nm - colorless film

300 - 1000 nm - rainbow effects (iridescence)

Greater than 1000 nm - progressively reduced iridescence.

TABLE IA *

OIL FILM THICKNESS VS. VISIBLE COLOR

Appearance	Film Thickness				
	in.	cm	μ	nm	Å Angstrom
Barely visible under most favorable light conditions	1.5×10^{-6}	3.8×10^{-6}	3.8×10^{-2}	3.8×10^{1}	3.8×10^{2}
Visible as a silvery sheen on surface	3×10^{-6}	7.6×10^{-6}	7.6×10^{-2}	7.6×10^{1}	7.6×10^{2}
First trace of color may be observed	6×10^{-6}	1.5×10^{-5}	1.5×10^{-1}	1.5×10^{2}	1.5×10^{3}
Bright bands of color are visible	12×10^{-6}	3.1×10^{-5}	3.1×10^{-1}	3.1×10^{2}	3.1×10^{3}
Colors begin to turn dull	40×10^{-6}	1.0×10^{-4}	1.0	1.0×10^{3}	1.0×10^{4}
Collors are much darker	80×10^{-6}	2.0×10^{-4}	2.0	2.0×10^{3}	2.0×10^{4}

*Tables IA and IB are based upon Ref. 3

TABLE IB

OIL FILM THICKNESS VS. SURFACE COVERAGE

Film Thickness, nm	Coverage		
	gal/acre	gal/mile^2	mg/m^2 *
3.8×10^1	0.04	25	38
7.6×10^1	0.08	50	76
1.5×10^2	0.16	100	150
3.1×10^2	0.32	200	310
1.0×10^3	1.08	666	1000 (1 gm)
2.0×10^3	2.16	1332	2000 (2 gm)

*Computed values assuming film specific gravity = 1.0

The API report (Ref. 3) does not indicate the type or types of oil used or the range of lighting investigated. The General Research Corporation (Ref. 4) reports an appearance - thickness relationship (Fig. 2) based upon a Santa Barbara crude that agrees substantially with the API data. This agreement suggests, but does not establish, that appearance is not dependent upon the type of oil.

Neither set of data mentions the effect of other variables such as water depth, bottom characteristics, or viewing angle upon visibility. Experience, however, has shown that visibility is best under an overcast sky (Ref. 5 and 6). We thus start out with the central notion that appearance is related to thickness, but not oil type, and that visibility is variable. The identity and influence of other factors affecting visibility was not known.

Additionally, we found that the existing verbal descriptions used in the appearance relationships were vague enough that different observers could classify the same film into different appearance categories.

2.2.2 Approach

In view of the foregoing, we set out to form oil films of known thickness under laboratory conditions and to vary factors of interest in a controlled manner. These factors, besides film thickness, included type of oil, surface state of the water, water salinity, water opacity and character of bottom. Along with these controlled experiments, random or contrived observations out-of-doors were made to correlate the laboratory observations with those in the outdoor environment.

To avoid the inescapable difficulty of describing in words the complicated visual effects, color photography was selected for primary documentation.

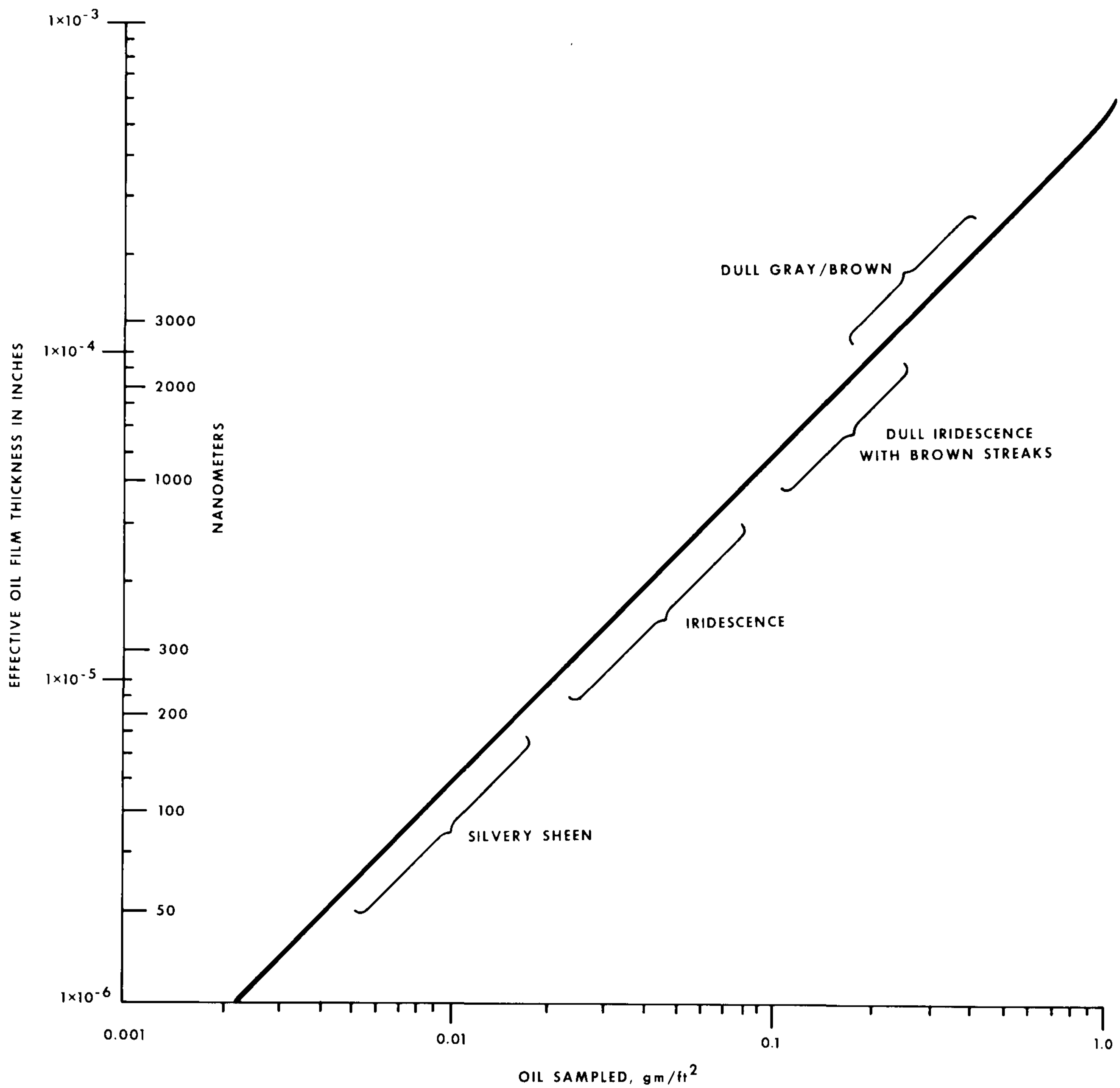


Figure 2. Oil film appearance and effective thickness vs. coverage (from Ref. 4).

3. THEORY

3.1 Applicable Phenomena

The appearance of a thin oil film on water is associated with that part of the incident light that is reflected from the water-air interface or from the oil-air and oil-water interfaces. Where the oil film displays colors, these colors are the result of interference between reflections from the two oil interfaces.

3.2 Reflectivity

Reflectivity is defined as that fraction of light (intensity) incident upon a surface that is reflected. Reflectivity is a function of the angle of incidence (from the normal) and the refractive indices of the media.

The Fresnel equation applies to reflection from the surface of a transparent medium in air:

$$R = \frac{1}{2}\left(\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)}\right) \qquad (1)$$

In this equation, the relationship between i and r is expressed by Snell's Law:

$$\frac{\sin i}{\sin r} = \frac{\mu_r}{\mu_i} \qquad (2)$$

In these equations:

$R = \frac{\text{light reflected}}{\text{light incident}}$

i = angle of incidence (see Fig. 3)

r = angle of refraction (see Fig. 3)

μ_i = refractive index of air, taken as 1.0

μ_r = refractive index of denser transparent medium

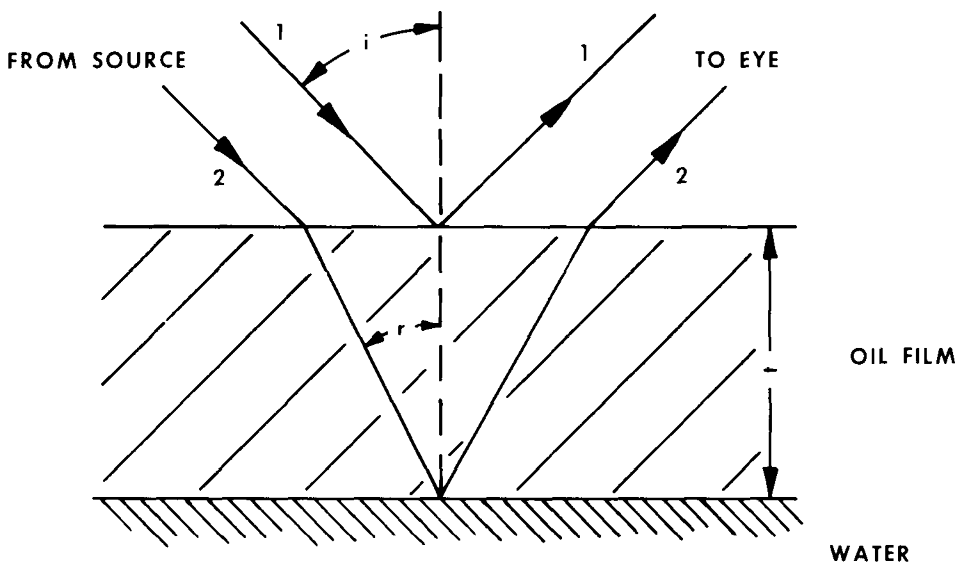


Figure 3. Reflection and refraction of light by a thin film (from Ref. 7)

We calculated the values of reflectivity from equation (1), noting that angle of incidence is measured from the normal and using the standard value of μ for water of 1.33 and an average value for oil of 1.5.

i	R(oil)	R(water)
30^{o}	0.041	0.021
60^{o}	0.090	0.060
75^{o}	0.16	0.21

The tabulated values imply that

(a) Even without color, an oil film should be distinguishable from a water surface because of its higher reflectivity if it is observed at a near vertical viewing angle.

(b) As viewing angle (angle of incidence) becomes less vertical, reflectivity of oil compared to water decreases until water has a higher reflectivity than oil. This latter case represents glare.

(c) Except for very high angles of incidence (approaching a horizontal viewing angle) only a small fraction of incident light is reflected. The rest is transmitted into the water or oil medium.

3.3 Interference

Normal illumination, or "white" light, contains all wavelengths in the visible spectrum, and each wavelength represents a color to the eye. Light has wave-like properties similar to an AC voltage or current. Two light rays of the same wavelength can reinforce each other, cancel each other, or have some intermediate additive effect, depending upon whether they are in phase, 180^{o} (½ wavelength) out of phase, or with an intermediate phase relationship. Optically, effects from these phase relationships are termed interference.

Rainbow effects (iridescence) from an oil film on water are due to interference; a given film thickness will produce different phase relationships among the various colors contained in white light. Whether a given wavelength or color is reinforced or cancelled out depends upon its relationship to the film thickness.

Any two rays of light, of the same wavelength, λ, emanating from the same point of a broad, uniform source will be in phase. Suppose ray 1 is reflected from the top surface, and ray 2 is reflected from the bottom surface of an oil film on water. Additionally, since the oil film has a higher refractive index than that of water, ray 2 will undergo a phase shift upon reflection of 180^o, or ½ wavelength. Figure 3 (Ref. 7) schematically shows the longer optical path of light ray 2 compared with that of ray 1. The difference in optical path length, ΔL, is

$$\Delta L = 2t\ (\mu^2 - \sin^2 i)^{\frac{1}{2}} \qquad (3)$$

where

t = film thickness

μ = refractive index of oil forming the film

i = angle of light incidence (the same as viewing angle) measured from the normal to the surface.

For any given wavelength of light, the interference effects depend upon the number of wavelengths in ΔL, taking into account the 180^o phase change (½ wavelength) that occurs at the oil-water interface.

If ΔL contains a whole number of wavelengths, maximum <u>destructive interference</u> will occur; that is ray 1 and ray 2 are out of phase, and will cancel each other. Mathematically, this condition is,

$$\Delta L = x\lambda \quad (x = 1,2,3,4,\text{ etc}) \qquad (4)$$

If ΔL contains an odd number of half wavelengths, maximum <u>constructive interference</u> will occur; that is, ray 1 and ray 2 are in phase, and they reinforce each other. Mathematically, this condition is,

$$\Delta L = x\frac{\lambda}{2} \quad (x = 1,3,5,7,\text{ etc}) \qquad (5)$$

Intermediate conditions will give partial interference.

Transposing equations 4 and 5 allows calculation of the wavelengths that give maximum effects.

For destructive interference:

$$\lambda = \frac{\Delta L}{x} \qquad (x = 1,2,3,4, \text{ etc.}) \qquad (4a)$$

For constructive interference:

$$\lambda = \frac{2\Delta L}{x} \qquad (x = 1,3,5,7, \text{ etc.}) \qquad (5a)$$

Since normal illumination contains all wavelengths, a given film thickness will selectively reinforce some wavelengths and cancel others, changing the color composition of the total light reaching the eye and giving the effect of visual color. For illustration, assume an oil film, refractive index = 1.5, viewed at an angle of 45°. In Table II are the calculated wavelengths <u>within the visible</u> at which interference will occur for different film thicknesses. Wavelengths between 408 and 816 nm are considered to be in the visible, or close enough to influence the visual effect (see Fig. 1).

The approximate resulting color, listed in Table II, is obtained through the following type of reasoning; 300 nm film is used as the example:

Constructive Interference:	at 544 nm (yellow-green)
Destructive Interference:	at 408 nm (violet) and at 816 nm (red)
Net results:	Original white light plus green, and minus red and violet results in a net green light.

The color sequence deduced as a function of thickness is, in fact, the sequence found experimentally. Examination of the photographs confirms this.

Thus far we have established that films thinner than 150 nm should display no color since wavelengths subject to interference are in the ultraviolet, outside the visible. Between 75 and 150 nm, there is some slight influence in the violet/blue end of the visible. As a speculation, this may contribute to the "silvery sheen" effect, which we interpret as a film that shows no distinguishable color but which does

TABLE II

THEORETICALLY IMPLIED COLOR VS. WAVELENGTH

Film Thickness, nm	ΔL nm	Constructive Interference at nm	Destructive Interference at nm	Resulting Color Approx.
75	204	408	(none)	Slight bluish
150	408	816	408	warm tone
200	545	(none)	545	purple
250	677	451	677	blue/blue green
300	816	544	816,408	green

have a pearl-like or metallic luster. We also see that films in the 200-300 nm range should display a variety of colors of high purity since in this range there is only one, or at most two wavelengths that show strong constructive interference.

As film thickness increases, a greater and greater number of wavelengths exhibit strong interference. Table III is a list of wavelengths subject to constructive and destructive interference versus film thickness. With an increasing number of wavelengths (colors) that are intensified or depressed by a film, the net color becomes a blend of colors distributed through the visible spectrum, so that the apparent color becomes less and less pure. In the extreme, such as with a 3000 nm film, so many colors are involved that the result approaches the "whiteness" of a complete spectrum, and the effects become a weakening alteration of light grey and dark grey bands instead of a repeating sequence of pure colors.

We can now summarize a theoretically deduced trend of appearance versus film thickness;

Thickness less than 150 nm:

no color apparent

Thickness of 150 nm:

warm tone apparent

Thickness of 200 to 900 nm:

variety of colors, including purple, magenta blue, green, yellow, showing considerable purity, with a net rainbow-like effect

Thickness greater than 900 nm:

colors showing progressively less purity, degrading toward grey as thickness increases.

TABLE III

WAVELENGTHS SUBJECT TO INTERFERENCE VS. THICKNESS

Film Thickness (nm)	Wavelengths for Constructive Interference (nm)	Wavelengths for Destructive Interference (nm)
300	544	408,816
600	652,465	816,544,408
900	699,544,445	816,612,490,408
1200	725,593,502,435	816,652,544,466,408
1500	742,528,544,480,429	816,680,583,510,453,408
1800	753,653,516,616,466,426	816,699,612,544,490,445, 408
2100	762,672,601,544,497,457, 423	816,714,634,571,519,476, 439,408
2400	768,687,622,568,522,484, 450,421	816,725,653,593,544,502, 466,435,408
2700	733,699,639,588,544,506, 474,445,420	816,734,668,612,565,525, 490,459,432,408
3000	777,710,653,604,563,526, 495,466,441,418	816,741,679,627,582,543, 509,479,453,429,408

3.4 Fluorescence Not Significant

Fluorescence is the absorption of light at a wavelength appropriate to the structure of the absorbing substance with prompt re-emission at a longer wavelength. Some components of petroleum, notably aromatic and other ring species, exhibit fluorescence in the UV and short visible. As a generality, absorbtion is in the 200 to 400 nm range, with re-emission in roughly the 350 to 450 nm range.

Compared with the interference effects, the contribution of fluorescence to the visual appearance is negligible because of the relatively small fraction of oil components affected, the low intensity of re-emitted light, and the low sensitivity of the eye in this spectral region.

It is possible that fluorescence may contribute to (but not dominate) the luster of the "silvery sheen" effect. Fluorescence may also contribute to photographic recording of a thin film out-of-doors because the photographic emulsion has higher sensitivity to this spectral region than has the human eye.

4. EXPERIMENTAL

4.1. General

4.1.1. Preparing and Photographing Laboratory Oil Films

The two main aspects of laboratory experimental procedure were physical and photographic. Physical procedure included the equipment and techniques used to prepare the oil films in small trays in the laboratory; photographic procedure included equipment and lighting for producing the photographic record. Although both procedures are basically simple, some difficulties were encountered in the physical procedure. A sufficiently detailed account is given so that others who may wish to perform similar or related experiments will be able to proceed with the fewest possible problems.

4.1.2. Other Observations

Besides photographing oil films in the laboratory, a variety of observations were made in the laboratory and out-of-doors, but were not usually photographed. These were done to guide and interpret the laboratory procedures, to establish the correspondence of laboratory and non-laboratory effects, and to generalize and order the results. These observations included:

(a) An extensive series of small-pan observations in the laboratory to verify the similarity of effects produced by different oils on distilled and sea water.

(b) Daily observation of a weathered oil-on-water film in a 4 x 6 foot tray, out of doors, for several weeks. The effect of viewing angle and outdoor illumination -- sky and cloud conditions, intensity of light, sun angle -- were observed.

(c) A number of out-of-doors observations of small-pan oil films. These films were identifical with those formed in the laboratory. These established the identity of results as seen and photographed with laboratory lighting and as seen under ideal outdoor lighting. For example, the greater brilliance and intensity of iridescence illuminated by white clouds (ideal) was clearly evident when compared with illumination by clear blue sky.

(d) Occasional visits to nearby oil spills. Some photographs of these observations are included to illustrate certain points.

4.2 Physical Procedure

The basic setup was simple. For each film formed, a tray approximately 9 x 12 inches was lined with clear plastic, a liter of the desired water was added and allowed to calm, then a measured volume of oil was expelled from a syringe onto the water surface.

4.2.1 Plastic Liner

The thin, clear plastic film liner served two purposes. First, it could be thrown away after one use, and a fresh liner could be used for the next oil film. This precluded the need for scrupulous cleaning of the pan between successive films. Perhaps more important, it provided a container with reproducible surface properties and avoided possible effects of variation in tray cleaning. The liner was carefully handled to avoid contact with the hands or other source of contamination. To smooth the sheet into the pan, fresh Kim-Wipes (lintless paper towels) were used.

Second, the clear liner made it possible to vary the background brightness when white, grey or black paper was inserted between the liner and the tray bottom (see Section 4.2.2.6, Background).

Some plastic sheet materials strongly inhibited the spreading of oil. A&P Clear Freezer Wrap was satisfactory from this standpoint. One roll of polyethylene gave good results. Other rolls (different sources) inhibited spreading.

4.2.2 Measurement of Film Thickness

If a known volume of oil spreads uniformly to cover a known area, then the film thickness can be computed.

$$t = \frac{\text{volume}}{\text{area}} \qquad (6)$$

If volume is expressed in microliters ($1\ \mu l = 10^{-3}\ cm^3$) and if area is expressed in square meters ($1\ m^2 = 10^4\ cm^2$), then the oil film thickness in nanometers ($1\ nm = 10^{-9} m = 10^{-3}$ micron) is:

$$t(nm) = \frac{\mu l\ oil}{m^2} \qquad (7)$$

4.2.2.1 Water Surface Area

Area was deduced by measuring the depth of a known volume of water (1 ± .01 liters) in the tray. Corrections were applied to compensate for the sloping sides and rounded bottom edges of the pan. A check was made by measuring pan dimensions at the water line, correcting for rounded corners.

The two determinations checked within 5%. Allowing for the fact that the plastic liner did not completely follow the tray contour, we estimated the total uncertainty in area at 10%. The surface area so determined was:

$$A = 0.068 \pm 0.0034\ m^2$$

For convenience in computing nominal film thickness, a nominal area was used:

$$A = 1/15\ m^2 = 0.067\ m^2$$

4.2.2.2 Oil Volume

A Hamilton microliter syringe (25 μl capacity, 1/2 μl graduations) was used to meter oil volumes up to 20 μl. For larger volumes, up to 200 μl (0.2 ml), a normal 1 ml syringe, graduated in 0.01 ml, was used.

If the syringe was in continuous use with the same oil, it was not cleaned between successive uses. At the end of continuous use, or when changing oil, the syringe was flushed several times with carbon tetrachloride, after which the plunger was removed and rinsed with acetone. The barrel was attached to a vacuum line, acetone was drawn through by vacuum to rinse, and the barrel was then dried with air aspirated by the vacuum. A clean syringe was first flushed five or six times with the oil to be used.

The estimated overall accuracy of delivered oil volume is ± 0.5 μl for the 25 μl syringe, and ± 10 μl for the 1 ml syringe.

This takes into consideration inaccuracies in scale reading, dribbling, and small droplets that occasionally remained attached to the delivery end of the needle.

4.2.2.3 Accuracy of Film Thickness

In nearly all cases, the oil spread over the entire water surface, and thus the nominal film thickness was 15 nm per microliter of oil. Uncertainties in oil film thickness owing to the oil volume measurement are:

Nominal Oil Volume	Nominal Oil Thickness, nanometers	Uncertainty, nanometers
1 - 20	15 - 300	± 7.5
50 - 200	750 - 3000	± 15.7

Additional uncertainty owed to surface area is: ± 5%.

Resulting total uncertainty is as follows:

Nominal Oil Thickness nanometers	Total Absolute Error nanometers	Percent of Nominal
15	± 8.3	± 55
38	± 9.4	± 20.5
300	± 22.5	± 7.5
750	± 187.5	± 15.7
300	± 300.0	± 10.0

4.2.2.4 Oils Used

The need to pick up and deliver oil through the fine needle of a microliter syringe limited the choice to low viscosity types. Those used were:

Mediterranean Crudes (dark brown)
- Light Arabian
- Agha Jari (Iranian)

Domestic Crude (Dark brown)
- South Louisiana

Distillate (Clear with light yellow to red tint)
No. 2 Fuel Oil

Samples were withdrawn from full or nearly full drums and placed in polyethylene bottles. Small ullage in the nearly full drums implied they had never been or were infrequently opened. Thus, there had been negligible loss of volatile components, and the samples were representative of the parent stock.

4.2.2.5 Water Used

Distilled water (with and without background dye: see Section 4.2.2.6) and visually clean, coastal sea water (salinity 26 ppt) were used as substrates for several hundred oil films. Since the spreading of the test oils was apparently identical on all these waters, no further characterization of water was made.

Because of this identity in behavior, distilled water, with or without dye, was used for the films photographed for this report. The properties of distilled water are less variable then those of tap, river, estuarian, or sea water. The advantage is clear should there be future need to compare results obtained at different laboratories or at different times.

4.2.2.6 Background Brightness

Background brightness was varied to represent a range of real life bottom and water conditions. In shallow, clear water over a light sand bottom, most of the light incident on the water surface penetrates to the bottom and is reflected back through the water surface with little absorption. At the other extreme, the water is so deep, or the bottom so dark, that almost all the incident light is absorbed below the water surface and the water looks almost black. The former gives a high background brightness; the latter, a low background brightness.

In a shallow pan with clear water, the high brightness situation was simulated by white paper (or white tray bottom) under the plastic liner. Black paper under the liner gave a medium high, rather than a low, background brightness owing to reflection from the surface of the plastic liner itself.

Low background brightness was obtained by dyeing the water. Sheaffer Permanent Jet Black ink (2½ ml per liter) gave an intense dark color that completely obscured a white tray bottom. The ink did not inhibit oil spreading on distilled water; it did inhibit spreading on sea water. On undyed water, however, representing true field conditions, oil spreading on distilled water and sea water are equivalent (Section 5.2). For experimental reproducibility, distilled water is preferable (Section 4.2.2.5). Thus ink-dyed distilled water was used to simulate a low background brightness.

Other dyes tried were unsatisfactory. Liquid food coloring gave excellent opacity and did not inhibit spreading on either distilled or sea water, but gave unnatural colors. RIT fabric dye gave excellent opacity and good color, but strongly inhibited spreading on both distilled and sea water.

4.2.2.7 Surface State

Oil placed on the calm water surface spread to form a static film of nearly constant thickness and of nearly uniform color. To simulate the more realistic conditions of an active water surface, two things were done.

(a) By blowing onto the film in the middle of the tray, a hole was formed in the film, exposing a circular patch of bare water. Around the bare water, the oil film tapered in thickness from zero at the edge to the full thickness away from the edge.

(b) The tray, containing the water and oil film, was agitated by a laboratory shaker table. Horizontal orbital motion of the shaker table generated waves about ½-inch to 1-inch trough-to-crest.

Besides providing glittering reflections from the irregular surface, the waves produced variations in film thickness. The film is compressed at the crest and stretched thin in the trough, similar to the effects of sound propagation in a fluid where the medium is compressed at the node and rarified at the antinode.

The sequence of operations was:

(a) Observe static film as laid on calm water

(b) Observe film with hole blown in it

(c) After calming, start shaker table and observe film

(d) Observe film after stopping shaker table and while allowing surface to calm.

4.3 Photographic Procedure

No special photographic equipment was needed except supplementary devices for critical focusing at object: image ratios of about 6:1. The lighting was arranged to give optimum conditions -- a bright white uniform source with an area large enough so that its image, reflected by the water surface into the lens, would substantially fill the negative area. This simulated illumination by a uniform white sky.

A schematic, Figure 4, shows the general arrangement used. Details are in the following sections.

4.3.1 Camera and Objective

A 35 mm Leica IIIb body was mounted on the rear plate of a Leica sliding focusing attachment. A 9-cm Leica Elmar f:4 objective with lens shade was mounted on the front plate. The sliding focusing attachment provided ground glass viewing and critical focusing with a 10X magnifier. The attachment added 11.8 mm to the normal lens flange to focal plane distance, acting as an extension tube or bellows for closer-than-normal focusing. The 9-cm focal length, compared to the normal 5-cm objective, increased the object-lens distance to about 60 cm (24 in.) for more convenient working at the reduction ratio of 6 or 7 to 1.

4.3.2 Lighting

A No. 2 photoflood lamp (color temperature 3400^{o}K) or a 500 watt 3200K lamp (color temperature 3200^{o}K) in a 12-inch aluminum reflector with diffusing screen provided good illumination. For maximum light and to fill the negative area with its image, the diffuser was close to the water

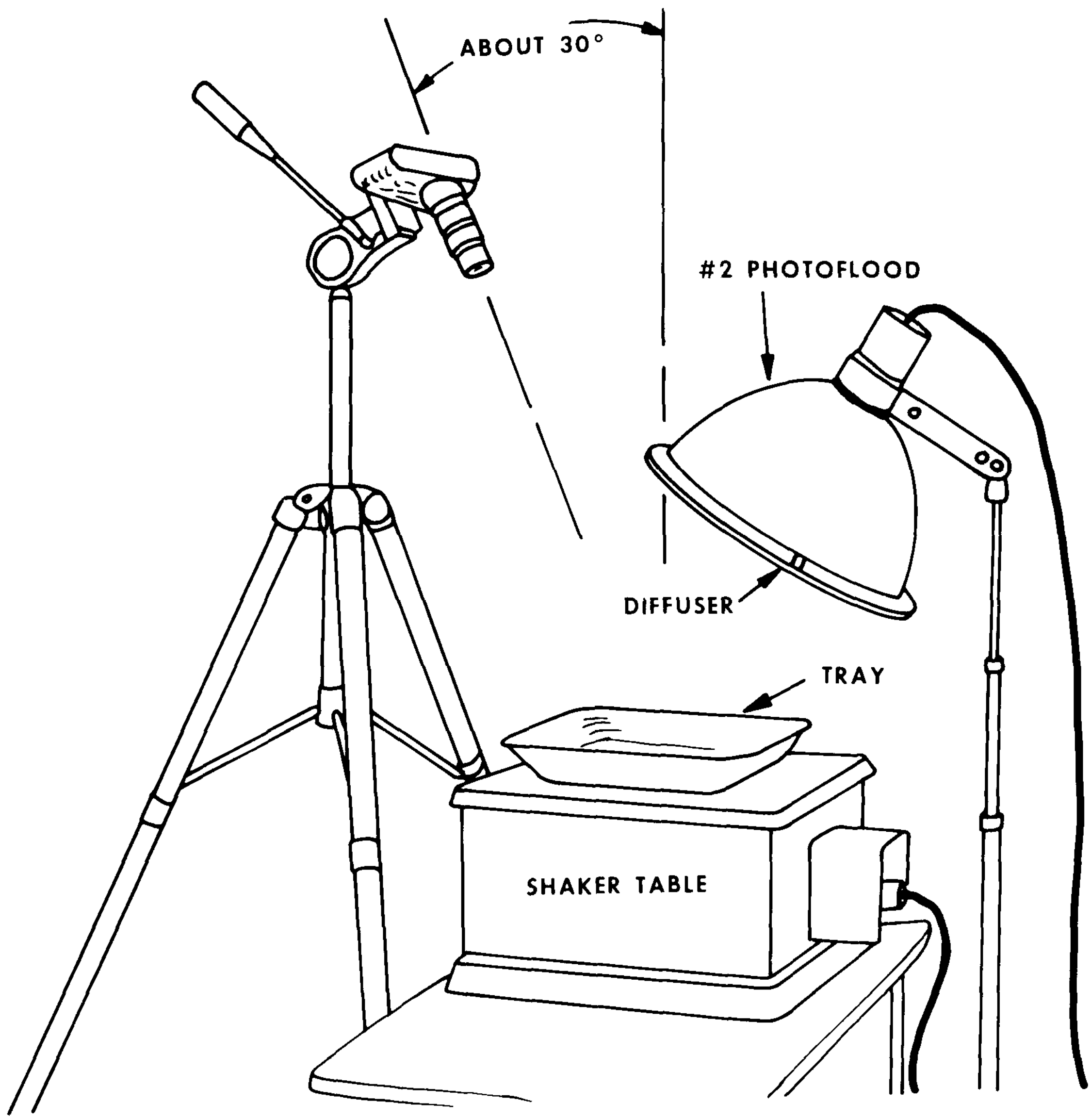


Figure 4. Arrangement for photography oil film in tray.

surface, about 12 inches. The "earth from space" effect in the photographs clearly illustrates the lamp placement; the circular light source covers the height of the photograph, but does not quite cover the full width of the format.

Illumination at the water surface varied from about 4000 lumen/ft^2 at the center to about 3000 at the edges. Intensity at the center was about half that of a normal sunlit outdoor scene; variation over the field represented a one-half stop exposure variation.

4.3.3.1 Film and Exposure

For the laboratory photographs, High Speed Ektachrome (ASA 125 with 3200K lamp) was used at first; later on, Kodachrome II Professional, Type A (ASA 40 with 3400K lamp) was adopted. The higher contrast and greater apparent saturation gave transparencies that seemed closer to the visual impression. Most of the out-of-door photographs were on High Speed Ektachrome, daylight type.

Exposure for the tray photographs, as indicated by an incident light exposure meter, was 1/100 sec. at a marked aperture of F:6.3. Effective aperture (correction for close-up focusing) was f:8.

4.3.3.2 Processing

The exposed film was given to a local dealer for normal processing by Kodak. There were no special arrangements. Results were satisfactory. Slight variations in overall tone were found (slight green cast vs. slight blue cast) among rolls processed at different times, but these differences were insignificant for the purpose at hand.

5. RESULTS

5.1 General

This section presents the results obtained from laboratory observations and includes photographs of oil films formed in small trays. Additional photographs of oil films taken in the field are included to show the correspondence between effects in the laboratory and in the field.

5.2 Spreading on Different Waters

The degree of spreading between films of Arabian and No. 2 Fuel Oil on sea water and distilled water, in 1/15 m^2 trays, was compared (Table IV).

Although in the thinnest films there are differences in spreading tendency between different oils, the spread of each oil is nearly identical for sea water and distilled water. This fact allowed the use of dyed distilled water as a controlled substrate for experimental purposes.

Photographs of water-to-water comparisons are not included in this report.

5.3 Photographs of Laboratory Oil Films

In the color photographs, the oil films range from 15 to 3000 nm (nominal) thick (Figs. 5 thru 21). Films of Light Arabian represent the entire range. Films of South Louisiana represent the range 15 to 300 nm (nominal). Agha Jari and No. 2 Fuel Oil represent two thicknesses each: 15 and 150 nm. This series used dyed water for a dark background and shows nearly pure optical effects from the surface film alone, undegraded by extraneous light from glare or background.

The four photographs in Figure 22 show the effects of background brightness on visibility.

Figures 5 through 21 each have three or four different photographs of the same oil film (one film per figure), with each photograph representing a different surface state. The arrangement of photographs is a consistent vertical sequence from top to bottom:

Film as formed
Hole blown in film
Shaker table in operation
At rest after shaker table

TABLE IV

COMPARISON OF OIL SPREAD ON SEA WATER AND DISTILLED WATER

Oil/Water	Fraction of Surface Covered oil, μl*		
	1	5	10
Light Arabian			
Sea Water, undyed	0.8	1.0	1.0
Distilled water, undyed	0.8	0.9	1.0
Distilled water, dyed	0.8	1.0	1.0
No. 2 Fuel Oil			
Sea water, undyed	0.5	0.8	0.9
Distilled water, dyed	0.5		1.0

*Film thickness = μlx15 for coverage = 1.0

If one of the spaces within the sequence is blank, there is no photograph of that particular surface state.

5.3.1 Effect of Film Thickness

Figures 5 through 12 record the changing appearance of Light Arabian oil films as thickness increases from 15 nm to 3000 nm. The main points are:

(a) Films less than about 150 nm show no color, but are brighter when compared with bare water because of the higher reflectivity of the oil film. There is no color for these thicknesses because interference occurs only at wavelengths shorter than those in the visible spectrum.

(b) At about 150 nm, a bronze tint is seen in the calm film, as laid. Surface activity introduces an additional purple tint owing to local thickening.

(c) From 300 to 750 nm, strong color and brilliant rainbow coloring (iridescence) prevails, the latter when surface activity causes thickness variations.

(d) At 1500 nm, brilliance is lost from the rainbow, and at 3000 nm, considerable dulling is evident. As film thickness increases beyond this, iridescence will disappear completely except where there is pronounced local thinning, and the film will assume the color of the bulk oil.

5.3.2 Effect of Oil Type

Figures 13 through 17 similarly show the appearance of South Louisiana films from 15 nm to 300 nm. Once nearly complete coverage is obtained at 38 nm (2.5 µl), the appearance of these films is nearly identical with their Arabian counterparts. As a further comparison, 150 nm films of Agha Jari and No. 2 Fuel Oil (Figs. 19 and 21) are similar in appearance to the Arabian and South Louisiana.

Differences are found in the thinnest films, formed by 1 µl of oil. Arabian and Agha Jari spread uniformly to give thin films, about 15 nm thick, with reflectivity somewhat higher than that of the water.

The South Louisiana and No. 2 Fuel Oil (1 μl) (Figures 13 and 18) give incomplete films with a Swiss cheese appearance of decidedly higher reflectivity than do the other two oils. Note, however, that the greater reflectivity is associated with a lower surface coverage and, thus, a film thickness greather than that obtained with full coverage. In fact, these films of low coverage do indeed appear similar in brightness to the 38 or 75 nm films of Arabian.

Thus, even when spreading characteristics of an oil do vary, owing to type, composition, or other factors, the appearance of the film, in terms of brightness or color, is appropriate to the actual local thickness, in accord with theory.

5.3.3 Effect of Surface State

5.3.3.1 Blown Holes (Films with tapered edges)

The main purpose in exposing the bare water was to demonstrate that even very thin films, 15 and 38 nm, displayed a reflectivity greater than water. In fact, comparing these photographs with those of the fully spread films (Arabian and Agha Jari, Figs. 6 and 20), it is evident that the detection, or visibility, of thin colorless films depends on the ability to make such a comparision. The eye is unable to make quantitative estimates of brightness without comparing an unknown to a reference or standard. This is a significant aspect of visibility and detectability.

With films thick enough to show iridescence, 300 nm and thicker, the tapered edges show the sequence of the interference colors as thickness increases. This sequence is bronze, purple, blue and green; as the film becomes thicker, the sequence repeats (Figures 10, 11, and 12.).

From the discussion of theory and the application of equation 3 (Section 3), one would expect this sequence to repeat for approximately each 300 nm increment of thickness. Counting sets of bands in the 300 to 3000 nm films shows this to be true, allowing for an occasional extra band due to ripples. In the 1500 and 3000 nm films, one can also see that, with an increase in thickness and in the number of wavelengths subject to interference (Table III) some colors drop out of the sequence and the intensity or purity of color degrades.

Figure 12b is an enlargement showing the 3000 nm film in greater deail. The changing appearance with each 300 nm increment, although sometimes subtle, can be seen. The major changes reflect the groupings in Table I; the first two sets of bands are bright, the next three degrade to brick-red and turquoise, and ultimately color is lost and the bands are light-dark. This one photograph in itself summarizes the thickness-appearance relation.

5.3.3.2 Waves (Shaker Table)

Where a thin, colorless film covers the entire field of view, (Fig. 5 and 6) waves or chop on the water produce a glitter of reflected light spots that make it hard to identify these films. A difference in reflectivity between a film and the adjacent bare water can be obscured by the brightness differences in the glitter pattern.

The relative reluctance of South Louisiana and No. 2 Fuel Oil to spread tends to be preserved under wave conditions. Because of the incomplete coverage, bare water can be seen and the colorless film can be discerned. The lower spreading tendency affects the films up to 150 nm, and the local thickening gives the appearance of a nominally thicker film.

The wave condition also illustrates well the progressive dulling of iridescence as film thickness increases beyond 1000 nm.

5.3.3.3 Calm After Waves

There frequently occurs, in actuality, the condition of calm after waves; during the lifetime of a film it can be exposed to changing weather and sea conditions. Three effects of wave actions were noted in the laboratory when the surface came to rest after wave making on the shaker table.

(a) The tendency of wave action to work a compressed deposit into a larger, thinner film is illustrated in Figs. 13 and 18, where the initial "Swiss cheese" films of South Louisiana and No. 2 Fuel Oil have been worked into a more continuous film. This "working out" was observed in experiments on the open sea (Ref. 8).

(b) A weathering effect is quite noticeable with the 150 nm films. Loss from the Arabian film, Fig. 8, has been enough to decrease the apparent film thickness to about 75 nm as evidenced by the change from the original yellow color to a colorless reflecting film. The South Louisiana film, Fig. 16 does not show this effect markedly. This may be because of a difference in duration of exposure to wave conditions, or it may represent a true difference owed to differences in solubility and volatility of light components. The Agha Jari film, Fig. 21, shows an intermediate effect. The No. 2 Fuel Oil film shows a notably different phenomenon. The loss of components from the film, and perhaps their partial solution in the water, changed the interfacial properties so as to inhibit spreading. Examination of the original color slide shows that the deposit had become an array of small discrete flecks of oil separated by apparently open water that gives the film a grainy appearance.

In the paragraph above, material loss from the film was attributed to volatilization and solubility. A third possibility is that some of the oil became stuck to the tray liner during agitation; this was, in fact, observed with thicker films. The behavior of No. 2 Fuel Oil, however, substantiates that even though material loss via edge-sticking may have occurred, it was not the sole mechanism. The change in spreading properties requires a selective loss of constituents; this indicates that volatility and solubility are involved, since these processes are selective with respect to molecular weight and molecular structure.

(c) A third result of wave action noticed especially with the thicker film was the creation of apparently permanent or long-lasting variations in film thickness that give rise to color variation and streaking in the quiescent film.

5.3.3.4 Background Brightness

Figures 22a, 22b, and 22c show 15 nm, 105 nm, and 300 nm films of Arabian oil. In each case, one half the tray contributes a high background brightness and the other half, a medium to medium-high background brightness. These films were gently disturbed to develop local variations in thickness. For comparison, Figure 22d shows a 300 nm film over a dark background (dyed water), at rest, after wave-making on the shaker table.

The increased visibility and brilliance owed to the low background brightness is evident. Also evident in the trays having both bright and medium backgrounds is the apparent discontinuity at the background boundary, even though the oil film is continuous over both backgrounds.

Because only a fraction of the incident light is subject to interference, the inherent visual effect is readily diluted by extraneous light. If the incident light is nearly normal to the surface, most of the light will penetrate. Simple measurements with a photographic exposure meter indicated that about 2% to 5% of the incident light is reflected by a bare water surface, and about 5% to 10% by a surface with an oil film. This is as predicted by theory. Of the 90% that penetrates, some will be absorbed in the water column, some absorbed by the bottom, and some reflected by the bottom. After reflection, and after further attenuation, this light returns through the oil film to the observer. The amount of returned light depends on the absorbtivity of the water and the bottom and on suspended particles that can reflect light directly. This returned light, added to the interference effects, dilutes the color effects and reduces the interference effects, the contrast, and the relative brightness between oil-covered areas and bare water areas.

In its extreme, a bright background can overwhelm the optical effects of an oil film as shown in the photographs. The effect is similar to projecting a slide or movie in a darkened room and then turning on the house lights.

5.4 Field Observations

Our own and the published results of other observers substantiate the effects observed in the laboratory and add further information that expands upon the laboratory results.

5.4.1 The Appearance of Oil Films

Comparison of relationships between film thickness and visual appearance shows excellent agreement among our laboratory photographs, the API data (Table I) and the General Research Corporation data (Figure 2).

Figures 23, 24 and 25 are of oil films formed by a spill of No. 2 Diesel Fuel on fresh water, the Raritan River. Figure 23, a view from a bridge across the river, shows a colorless oil film along the right bank; Figure 24, a thicker iridescent film; and Figure 25, a film with a circle of bare water created by tossing a stone. The effect is similar to blowing a hole in the laboratory film, and demonstrates unequivocally the presence of the film.

Figure 26 shows a film of No. 2 Fuel Oil from a spill on estuarian water, the Arthur Kill. The low background brightness and overcast sky produced clear color effects similar to those in the laboratory.

5.4.2 Viewing Angle and Viewpoint

Figure 27a, colorless films of an unknown oil on estuarian water shows how a high viewing angle (bottom of photograph) gives better visibility. As distance from the viewer becomes greater, and thus the viewing angle departs more from the vertical, the oil film becomes less visible and finally is obscured by the increased glare from the surface. A similar effect is apparent in Figure 27b, a brightly iridescent film of No. 2 Fuel Oil (which can be seen better in Figure 26, taken at a high viewing angle).

Figure 28 shows the results of a 50 gallon per minute sea water discharge (Raritan Bay) containing 100 ppm South Louisiana Crude. In Figure 28a, taken from the vessel and showing the discharge, it is hard, if not impossible, to see the resulting oil film because of the poor viewing angle. On the other hand, Figure 28b, taken from a helicopter at 100 ft. altitude, clearly reveals a film described by the observer as "sheen, non-metallic, no color".

Figure 29 illustrates a reversed situation. The discharge here is 25 gallons per minute and contains 10 ppm South Louisiana. The oil discharge rate was too low to yield a large continuous film, and formed instead the discontinuous streaks and patches of thin colorless film. From the vessel, these were visible; from the helicopter, however, there was no visible result of the discharge. In this case, a close viewpoint permitted the detail to be seen, whereas at a distant viewpoint, this detail could not visually or photographically be resolved.

5.4.3 Illumination, Background Brightness and Surface States

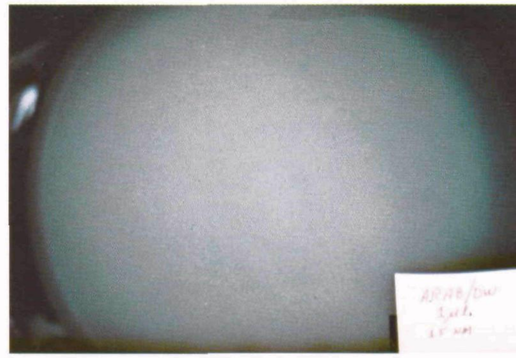
These factors are considered together because it is sometimes hard to separate them in a real situation.

References 5 and 6 emphasize that an overcast sky gives better visibility than a blue sky with sun, and our experience is certainly in accord. Interestingly, with an overcast sky, illumination need not be intense. Figure 30 is a photograph of an iridescent patch of oil on a blacktop driveway on a rainy day. Light intensity from the overcast sky was 450 lumens/ft^2, about 1/60 of the intensity on a sunny day. The primary factors are the overcast sky, giving a broad uniform light source, and the dark background.

In sunlight, best results are obtained when the area observed is shaded from direct sunlight and illuminated only by light from the sky. Figure 31 is a photograph of a colorless film viewed from our vessel, whose shadow can be observed in the foreground. In the shadow, the oil film is readily discerned. In the sunlit upper right portion, the film is not detectable owing to an adverse combination of illumination, background brightness, and surface state.

If sunlight illumination cannot be avoided, the sun should generally be at the observers back for best visibility, or at least not more than 90 degrees to either right or left. See also Reference 6.

Calm, as formed



Hole blown

Waves (shaker table)

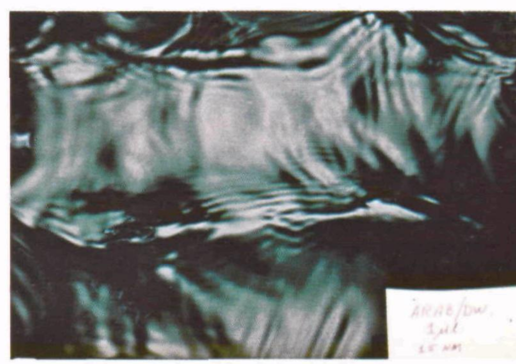
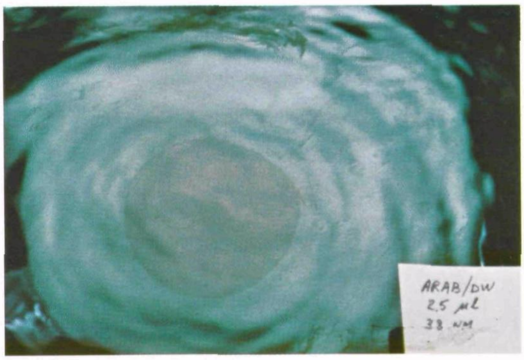


Figure 5. Light Arabian Crude (1 μl). Thickness is 15 nm.

Calm, as formed

Hole blown



Waves (shaker table)

Figure 6. Light Arabian Crude (2.5 μl). Thickness is 38 nm.

Calm, as formed

Hole blown

Waves (shaker table)

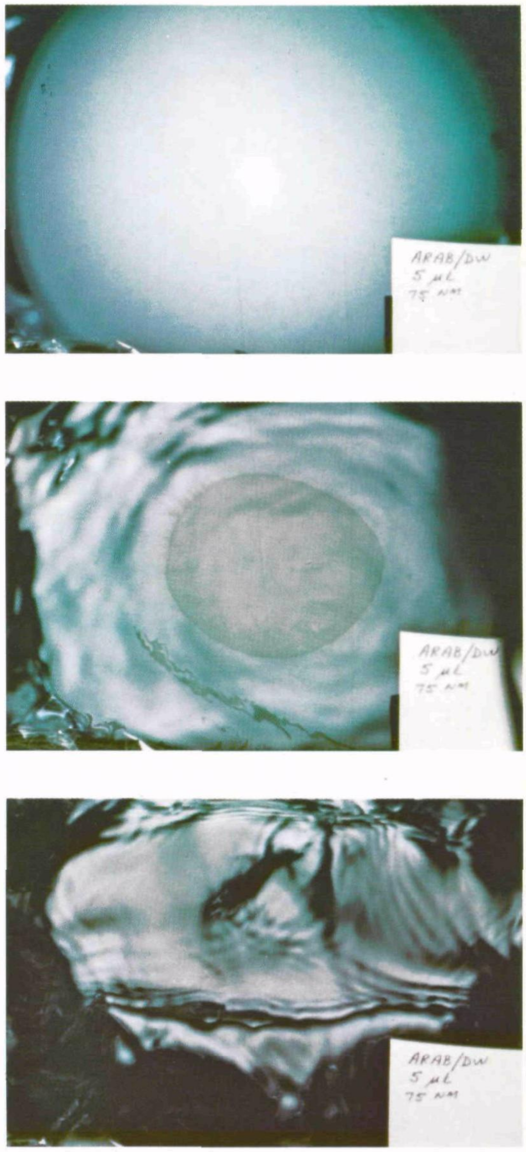


Figure 7. Light Arabian Crude (5 µl). Thickness is 75 nm.

Calm, as formed

Hole blown

Waves (shaker table)

Calm after waves

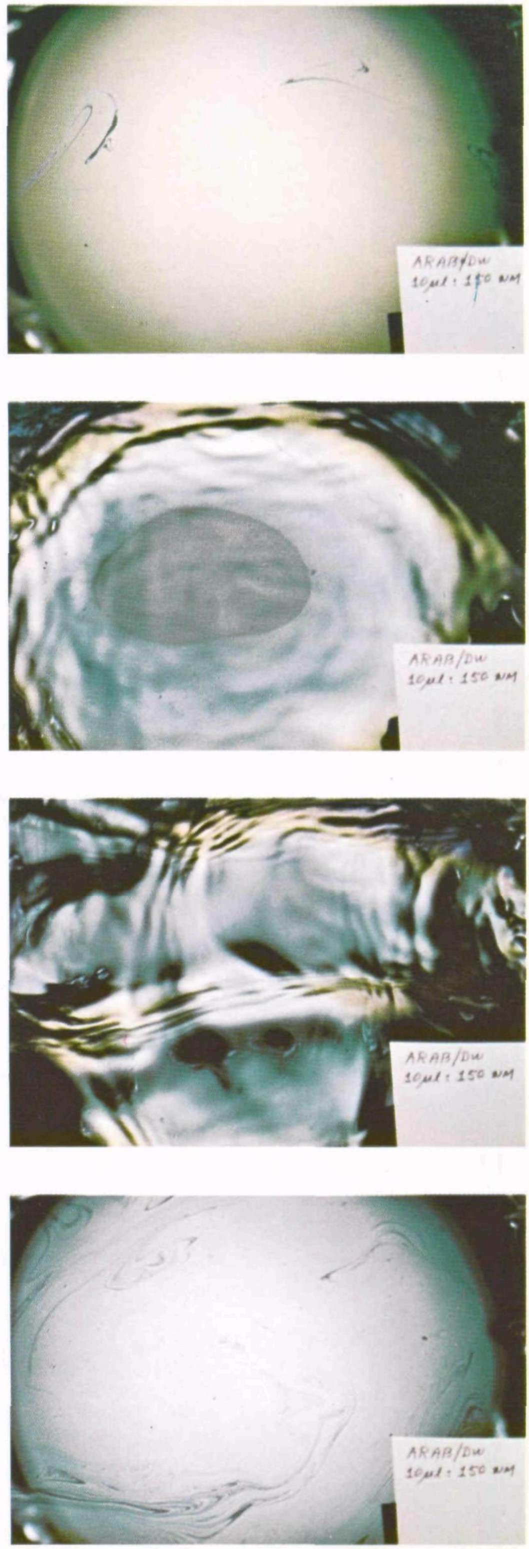
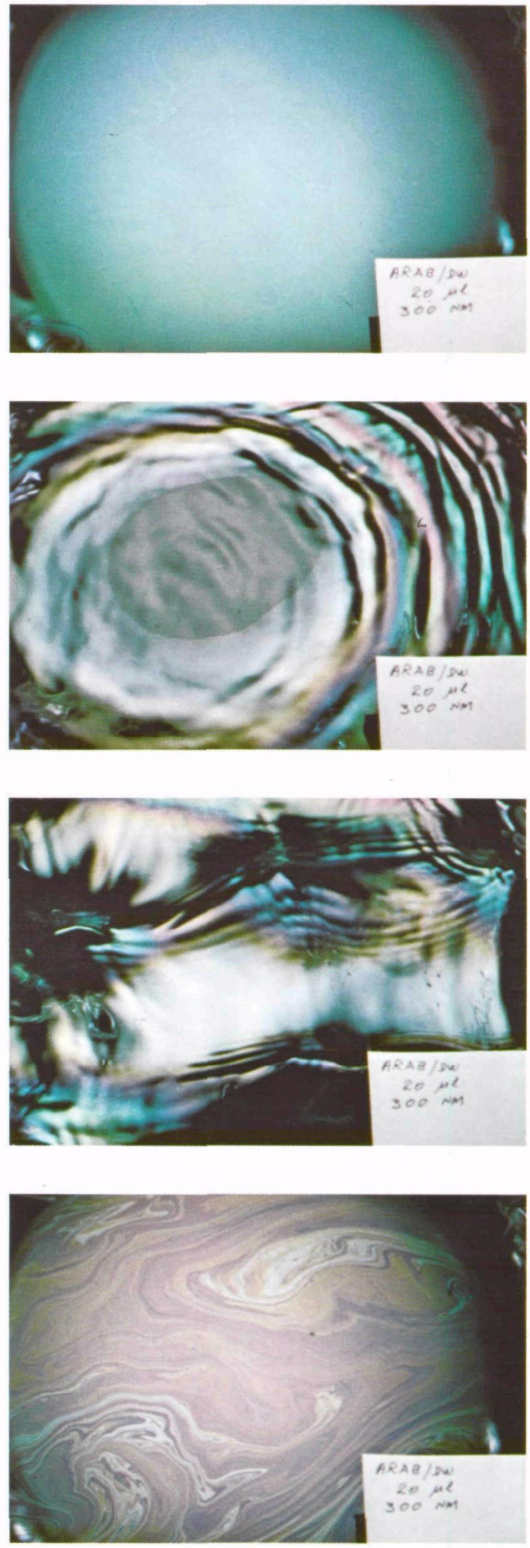


Figure 8. Light Arabian Crude (10 μl). Thickness is 150 nm.



Calm, as formed

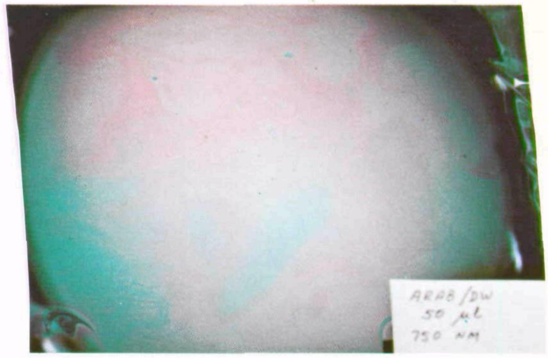
Hole blown

Waves (shaker table)

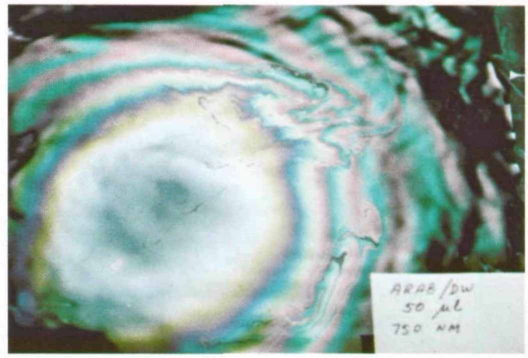
Calm after waves

Figure 9. Light Arabian Crude (20 µl). Thickness is 300 nm.

Calm, as formed



Hole blown



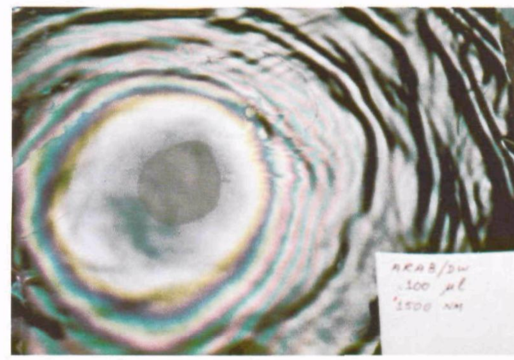
Waves (shaker table)

Calm after waves

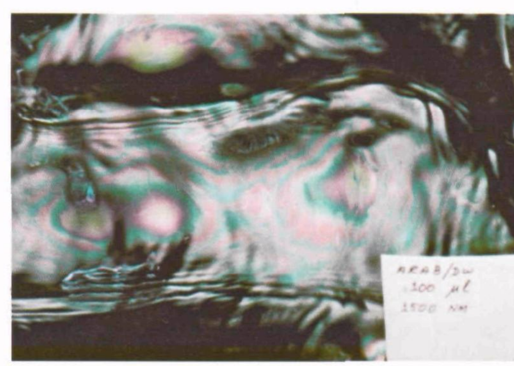
Figure 10. Light Arabian Crude (50 µl). Thickness is 750 nm.

Calm, as formed

Hole blown



Waves (shaker table)

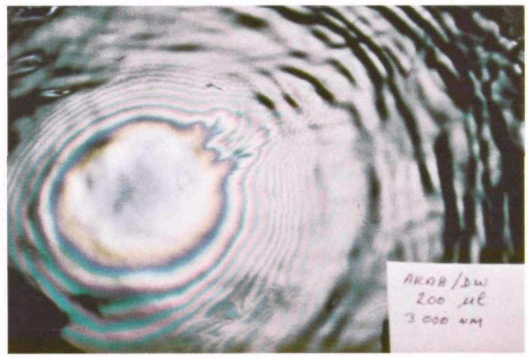


Calm after waves

Figure 11. Light Arabian Crude (100 µl). Thickness is 1500 nm.

Calm, as formed

Hole blown



Waves (shaker table)

Calm after waves

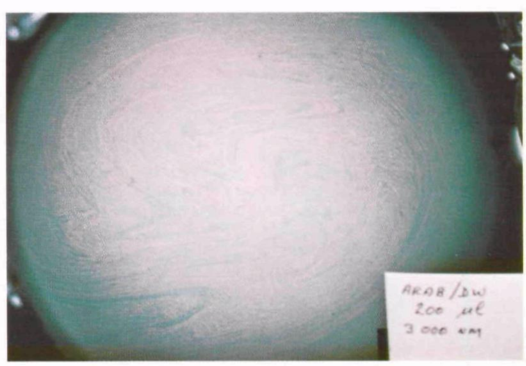


Figure 12a. Light Arabian Crude (200 µl). Thickness is 3000 nm.

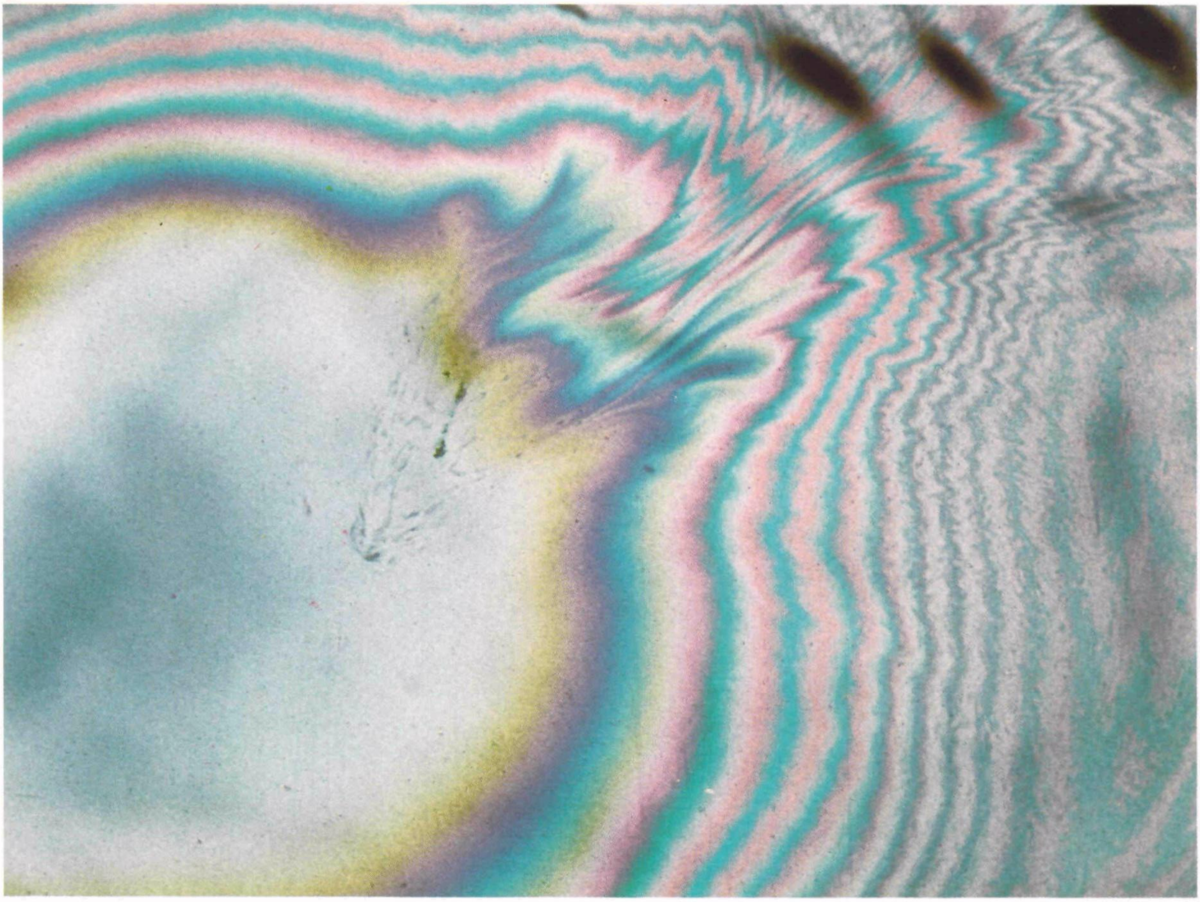
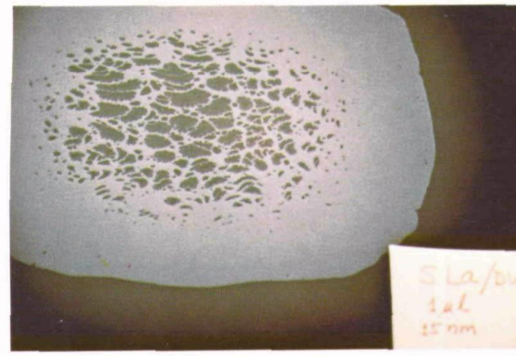


Figure 12b. Light Arabian Crude.
Enlarged view of 3000 nm film (Figure 12a).

Calm, as formed



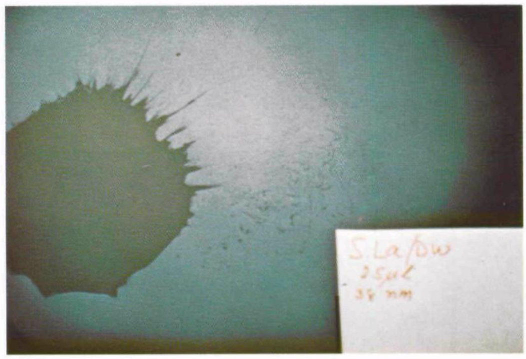
Waves (shaker table)

Calm after waves

Figure 13. South Louisiana Crude (1 µl).
Thickness would be 15 nm for full coverage.

Calm, as formed

Hole blown



Waves (shaker table)

Calm after waves

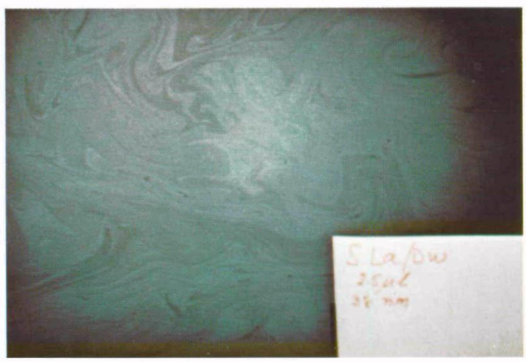
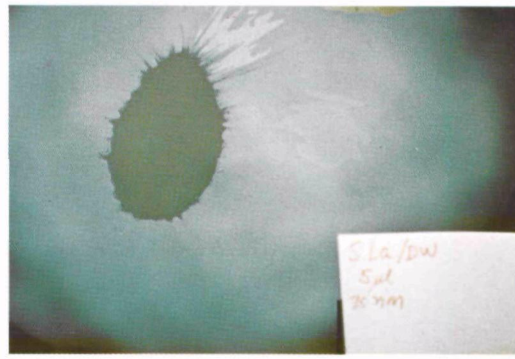


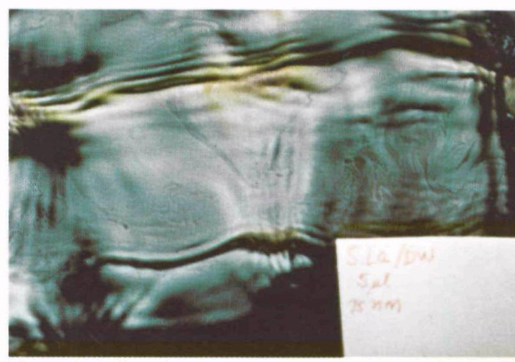
Figure 14. South Louisiana Crude (2.5 μl). Thickness is 38 nm.

Calm, as formed

Hole blown



Waves (shaker table)



Calm after waves

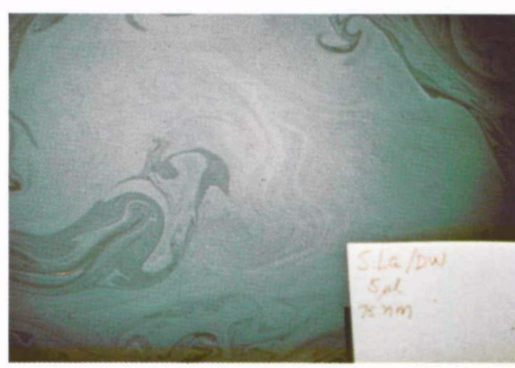
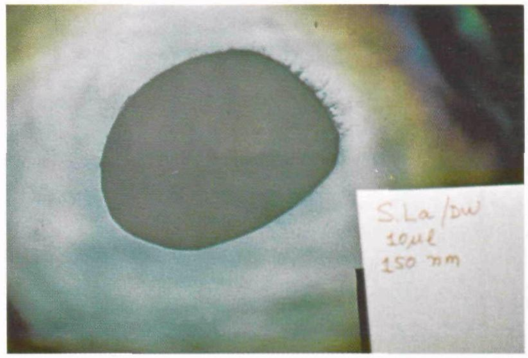


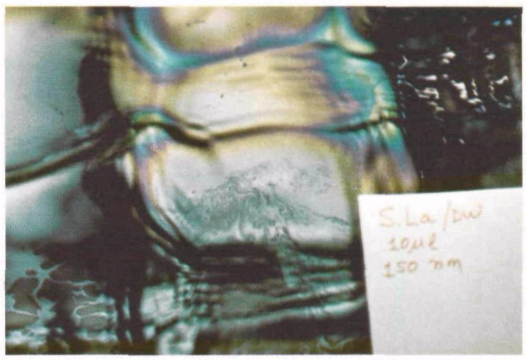
Figure 15. South Louisiana Crude (5 μl). Thickness is 75 nm.

Calm, as formed

Hole blown



Waves (shaker table)



Calm after waves

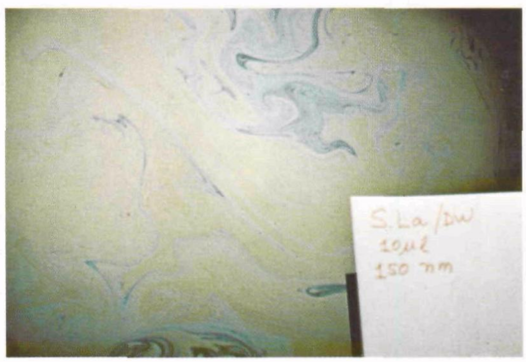
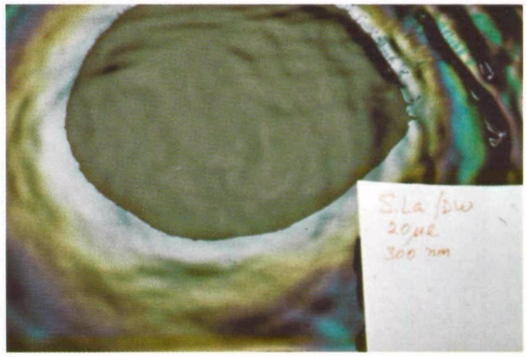


Figure 16. South Louisiana Crude (10 µl). Thickness is 150 nm.

Calm, as formed

Hole blown



Waves (shaker table)

Calm after waves

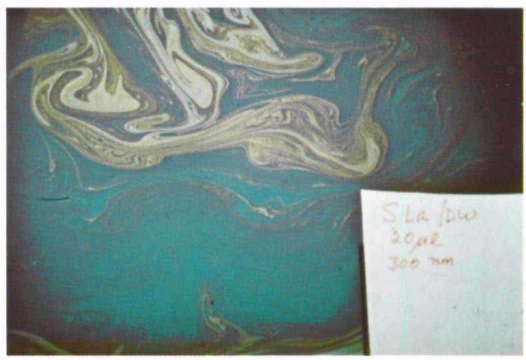
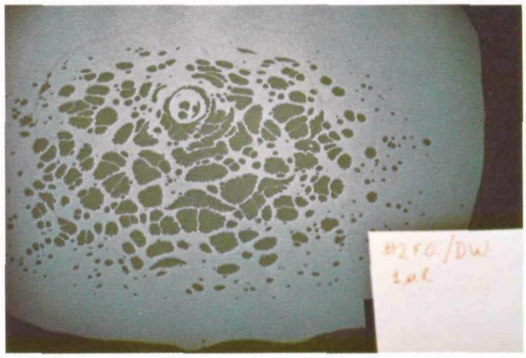


Figure 17. South Louisiana Crude (20 µl). Thickness is 300 nm.

Calm, as formed



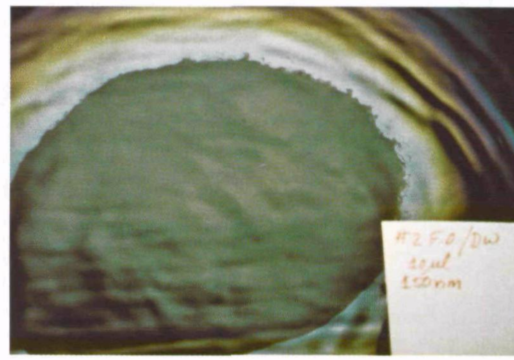
Waves (shaker table)

Calm after waves

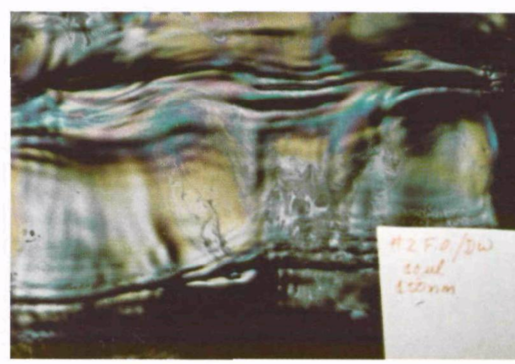
Figure 18. No. 2 Fuel Oil (1 μl).
Thickness would be 15 nm with full coverage.

Calm, as formed

Hole blown



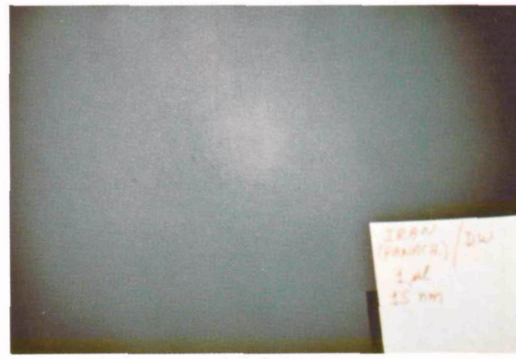
Waves (shaker table)



Calm after waves

Figure 19. No. 2 Fuel Oil (10 µl). Thickness is 150 nm.

Calm, as formed



Hole blown

Waves (shaker table)

Calm after waves

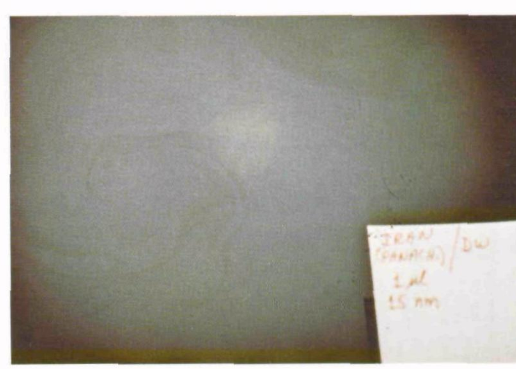
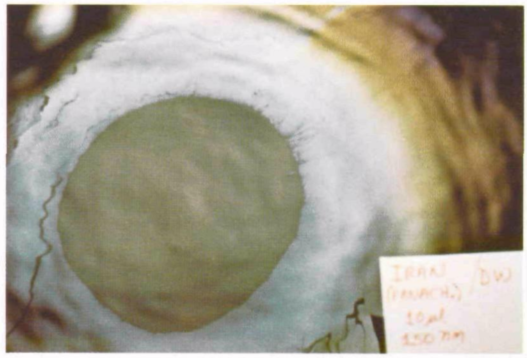


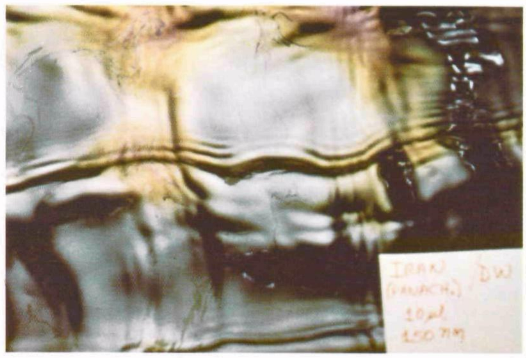
Figure 20. Agha Jari Crude (1 μl). Thickness is 15 nm.

Calm, as formed

Hole blown

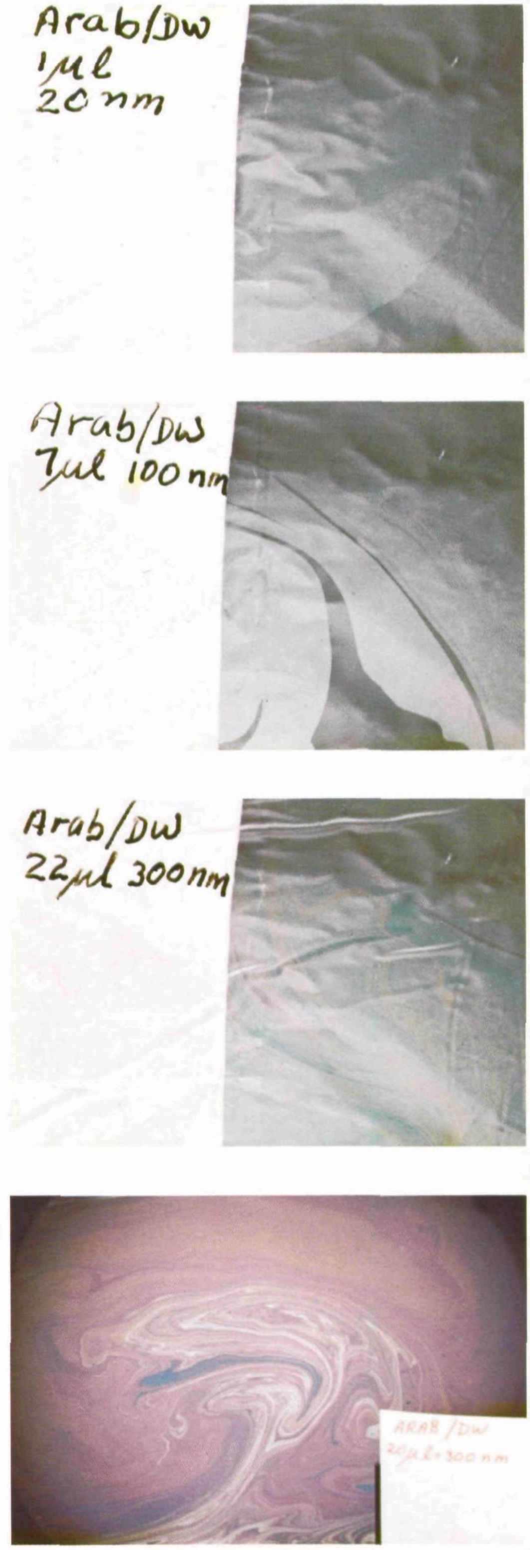


Waves (shaker table)



Calm after waves

Figure 21. Agha Jari Crude (10 µl). Thickness is 150 nm.



a. 1 μl 15 nm (if full coverage)

b. 7 μl 105 nm (if full coverage)

c. 22 μl 330 nm

d. 20 μl 300 nm

Figure 22. Effect of Background Brightness of Visibility. (a),(b),(c) Bright and Medium Background; (d) Dark Background.

Figure 23.

No. 2 Diesel Fuel on Raritan River.

Figure 24.

No. 2 Diesel Fuel on Raritan River (iridescence).

Figure 25.

No. 2 Diesel Fuel, with bare water exposed.

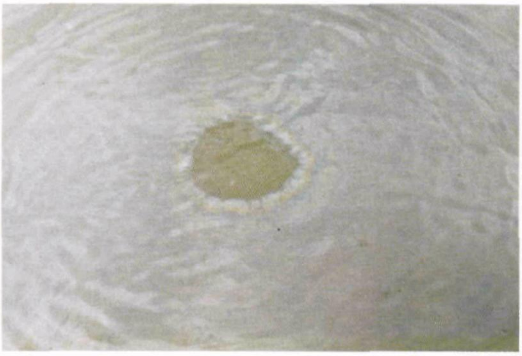


Figure 26.

No. 2 Fuel Oil on Arthur Kill (iridescence).

a. Unknown oil on Arthur Kill.

b. No. 2 Fuel Oil on Arthur Kill.

Figure 27.
Diminishing visibility as viewing angle departs from vertical.

a

b

Figure 28.

Visibility of 50 gpm, 100 ppm oil-water discharge, from the surface (a) and from the air (b).

a

b

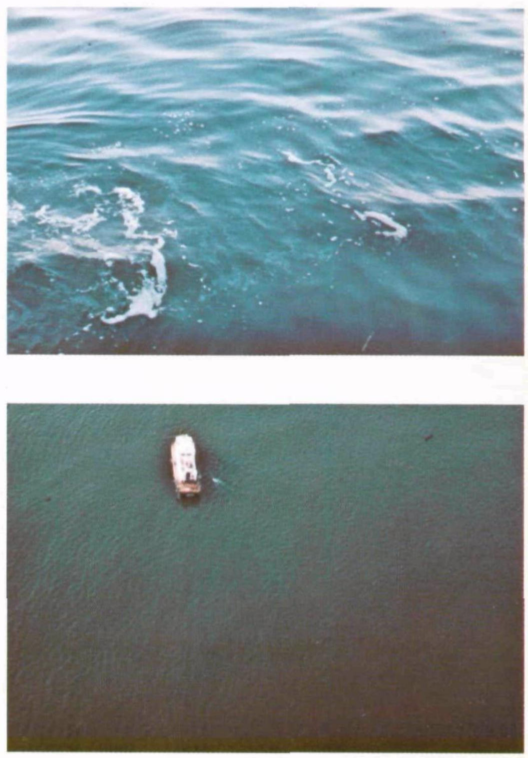


Figure 29.

Visibility of 25 gpm, 10 ppm oil-water discharge, from the surface (a) and from the air (b).

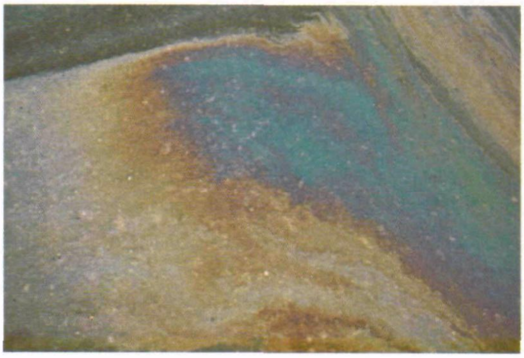


Figure 30.
Undiminished visibility of driveway oil film in low intensity light.

Figure 31.
Reduced visibility in direct sunlight compared with visibility in shadow.

6. DISCUSSION

6.1 Inherent Optical Properties and Visibility

This investigation provides direct answers to the questions that prompted it:

(a) Thin oil films have defnite optical characteristics that produce inherent visual effects with an orderly relationship between film thickness and appearance. This relationship is independent of oil type. The most evident aspect of appearance is color, with orderly variations in the number of colors present and in their purity or intensity.

(b) Visibility is not inherent or constant, but is the product of the inherent visible effects and of the various factors external to the film that can degrade or obscure the inherent effects. These factors include sky conditions, sun position, state of the water surface, character of underlying water and bottom, viewing angle, and distance between observer and film. Light intensity does not appear as a strong factor.

6.2 Results are General, not Unique

The laboratory photographs are an internally consistent set of data that shows the inherent appearance of oil films and variations in visibility that result from viewing conditions. We must now establish that these results and the conclusions based upon them are completely general. Correspondence between laboratory results and observations in actual situations is just one aspect of the generality sought.

One way to establish generality is by comparing enough observations to show that the same effects are found in a wide range of circumstances.

The appearance-thickness relationship demonstrated in our laboratory photographs corresponds closely if not identically with those of the American Petroleum Institute and the General Research Corporation. Taken as a whole, these three sets of data include laboratory and field observations, a minimum of five and probably six or more types of oil, a minimum of three different observers, a minimum of two different water types, and an unknown number of different viewing conditions. The net results, with regard to the thickness relationship, is that inherent appearance is a function of thickness and is not a function of oil type or of water type. A further implication is that our laboratory photographs show the same visual effect as do oil films in the field. This is further supported by our photographs of real films.

The effect of ambient or viewing conditions upon visibility also shows agreement between our laboratory results and field observations. Photographs in this report of real situations bear out the trends established in the laboratory, especially with respect to background (optical character of water and bottom) and surface condition. Comments of the Coast Guard and other observers upon sky condition and sun position are the same as ours. During the course of studying oily water discharges (to be reported separately), extensive observations were made from the air. These confirmed the trend indicated in the laboratory that water chop and high background brightness (because of light return from the particles in turbid water) lessen visibility, especially for colorless films.

When comparing a range of observations, we find agreement in all respects and an absence of contradiction and conclude that our photographic data and the conclusions offered can be applied to all instances of thin oil films on water.

A second approach to assess generality is to compare results with theory. Two optical phenomena are involved: the relative reflectivites of oil and water surfaces, and the interference between light reflected from the top and the bottom oil film surfaces.

Reflectivities of 2% to 5% for water and 4% to 10% for oil are obtained both from theoretical calculation and measurement. Only that small fraction of the incident light reflected by the oil film is involved in creating the optical effects of brightness and color that we see. With only 10% of the light being "processed" by the film before reaching the eye, it follows that, if even a small fraction of the "unprocessed" light is returned to the eye, the effects resulting from the film will be diluted and weakened. The observed effects of background brightness and of viewing angle (glare) upon visibility, even to the point of making a film non-visible, are in complete accord with this physical picture.

The photographs of laboratory films were made under ideal conditions; glare was eliminated by the higher viewing angle, and background minimized by dying the water. Because of this, they show with high purity the inherent visual effects produced by the oil film itself. Comparing the photographs with the effects predicted from increasing the thickness (Equation 3), one sees complete correspondence: the onset of color is at the correct thickness; the sequence in which colors appear is correct; the reduction in the number of colors with increasing thickness is appropriate to the increasing number of wavelengths in interference; the progressive dulling colors, with their eventual disappearance into greyness, is as expected.

Also apparent from Equation 3 is the fact that the visual effect of an oil film is, for practical purposes, independent of the type of oil. Thickness and refractive index are the only film properties that enter the equation. The refractive indexes of most components of oils are between 1.4 to 1.5 and the limits are 1.3 to 1.7. The maximum variance from the average value 1.5 is $\pm$ 13%, which is negligible compared with the 200:1 ratio of thickness values investigated. Once again, the photographs bear this out.

From the theoretical standpoint, we see that:

(a) The two principles of reflectivity and interference adequately explain the quantitative as well as qualitative appearance and visibility of oil films less than 3000 nm thick.

(b) No other phenomena need be invoked to explain these findings.

In summary, the data from this laboratory and from other sources agree: our data are adequately explained by the above physical principles; and these principles are fundamental and general. Therefore, the effects reported here should apply, and do apply without restriction, to all thin oil films on water.

6.3 Field Application of Results

Many of the details developed can be useful in field observations and may be especially helpful to inexperienced observers. Some aspects are discussed below.

The thickness-appearance relationship can be used with complete confidence to estimate the thickness of an oil film. This, together with an estimate of area, yields an estimate of the amount of oil in the film. For this purpose, the relationship listed in Table I is convenient. Table I is simple enough to commit to memory. We suggest that thickness in nanometers be used, since the surface coverage in milligrams per square meter is numerically the same as thickness in nanometers.

If observation conditions do not permit a fine judgment of color purity or of film brightness, a simple scale of "no color - bright color - dull color" still provides useful information on the approximate thickness.

Conversely, if careful observation is possible, one can make up a table, based upon our photographs, that is more detailed than Table I (see Section 6.4).

The series of laboratory photographs has proved useful in our laboratory as a direct illustration of actual appearance that avoids the imprecision of verbal color description. They have been useful in indoctrinating new observers and in refining the perception of more experienced people. They have been used in training courses given at this laboratory for field personnel of Federal and State organizations.

Appreciation of the factors affecting visibility should help the observer evaluate what he sees. Although some of the factors are not under his control (sky conditions and water background), to some extent he may be able to select the most favorable viewing position and angle or to otherwise influence the total set of conditions under which he must operate.

6.4 A Modified Thickness-Appearance Table

By using the guidance provided by theory and the effects shown in the photographs, especially Figure 12b, one can make more refined estimates of film thickness. In Table V, a set of colors is referred to as being characteristic of a given film thickness; remember that the range of colors represents a small range of thicknesses, more or less ending at the nominal value cited.

TABLE V

SCHEMATIC BASIS FOR THICKNESS-APPEARANCE RELATIONSHIP

Appearance	Thickness Range (nanometers)	Description
Colorless Films	Up to 150	Films reflect more light than does water, and look brighter. May need adjacent bare water for comparison. Apparent brightness increases with thickness. At about 75 nm and thicker, a pearly or metallic luster is usually apparent.
Onset of Color	Approx. 150	First color seen is a warm tone, more bronze than yellow. As film thickens, deep violet or purple appears, these colors begin the first set of rainbow bands.
Pure Rainbow Colors	150 to 900	The set of bands around 300 nm are in the sequence: bronze, purple, blue, green, in order of increasing thickness. These colors are pure and intense. The set of bands around 600 nm are slightly less intense than at 300 nm, and have a modified color sequence: yellow, magenta (reddish violet), blue, green. They are quite pure.
Dull, Impure Colors	900 to 1500	Main characteristic is reduction in number and purity of colors. Colors at 900 nm are a rich terra cotta (brick red) and turquoise (rather bright blue-green). At 1200 nm and 1500 nm these colors are progressively duller or less pure looking. These sets of bands may also contain a trace of white or pale yellow.

TABLE V (Continued)

Appearance	Thickness Range (nanometers)	Description
Light and Dark Bands with Little Color	1500 to 3000	Any color present is merely a tint in the light and dark alternating bands. At 1800 nm, the contrast between light and dark bands is strong, but weakens as thickness increases. At 3000 nm, it is apparent that interference effects are weak, and they will quickly disappear as thickness increases.

7. GLOSSARY

cm	centimeters
gm	gram
lumen/ft^2	intensity of illumination, same as foot-candle
m	meter
mg	milligram, 10^{-3} gm
ml	milliliter, 10^{-3} liter
nm	10^{-9} meters, 10^{-3} micron, 10 Å Angstrom units
Å	Å Angstrom unit, 10^{-1}nm or 10^{-8} cm
λ	wavelength in nm
μ	refractive index; also micron or 10^{-4}cm
μl	microliter, 10^{-6} liter or 10^{-3} ml

8. REFERENCES

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SELECTED WATER RESOURCES ABSTRACTS

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THE APPEARANCE AND VISIBILITY OF THIN OIL FILMS ON WATER,

Hornstein, B.

In-House Report

Environmental Protection Agency
Edison Water Quality Laboratory
National Environmental Research Center
Edison, New Jersey 08817

Environmental Protection Agency report number EPA-R2-72-039, August 1972.

Oil films of controlled thickness up to 3000 nanometers, upon water surfaces in the laboratory, confirm an inherent and orderly thickness-appearance relationship which is independent of oil type and water type. These laboratory studies also investigated the effects of viewing conditions upon the ease of visibility of these thin films.

Out-of-doors observations were made; these and the observations reported by other sources were found to correspond with the laboratory results. The visibility of a thin oil film depends not only upon its thickness-dependent inherent appearance, but also upon conditions external to the film. These include nature of illumination and sky conditions, sun angle, color and depth of water, color of bottom, and viewing angle.

Color photographs are included for illustration of the points discussed.

*Oil-water interfaces, *Thin films, *Oil, *Color, Theoretical analysis, Laboratory tests, On-site investigations, Water pollution, Oil pollution, Water pollution effects.

*Visibility, Appearance, Iridescent films, Optical interference, Reflectivity.

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