DISPERSANT BASICS

Mechanism, Chemistry, and Physics of Dispersants in Oil Spill Response

Presentation to NRC Committee on Understanding Oil Spill Dispersants: Efficacy and Effects
March 15, 2004

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EXXONMOBIL INVOLVEMENT IN DISPERSANT DEVELOPMENT

- Industry/World Leader for Over 30 Years
- 10's of Millions $ Spent Developing New Products
- 1967: First Product Specifically Formulated for the Marine Environment
  - COREXIT 7664 (Weak, water-based product which is no longer produced)
- 1972: First "Self-Mix" Concentrate
  - COREXIT 9527
  - First product to allow aircraft application
- 1992: First Product Effective on Heavy, Weathered, and Emulsified Oils
  - COREXIT 9500
- COREXIT Products are the Principal U.S. Dispersants
  - 2 of Only 11 Products to Pass the Demanding Effectiveness Approval Test
  - Over 6000 Drums in Stockpiles
- Current Supplier is Nalco Energy Chemicals
  - Unique Re-supply Capability

Response Options

Recovery

Burning

Dispersants

Shoreline Cleaning

WHAT ARE DISPERSANTS?

- Dispersants are Liquid Solutions of Detergent-Like Surfactants Dissolved or Suspended in Solvent
- The Surfactants Have Two Ends: One Attracted to Oil and Another Attracted to Water

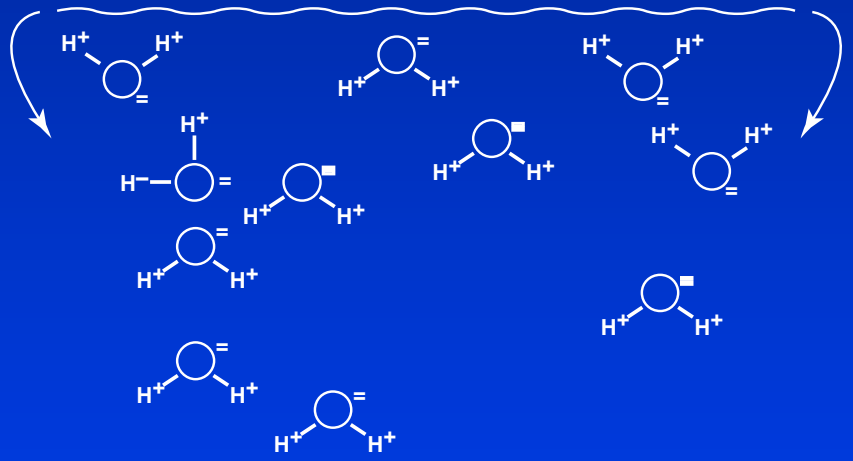
Water-Compatible (Hydrophilic)

Oil-Compatible (Lipo-or Oleo-philic)

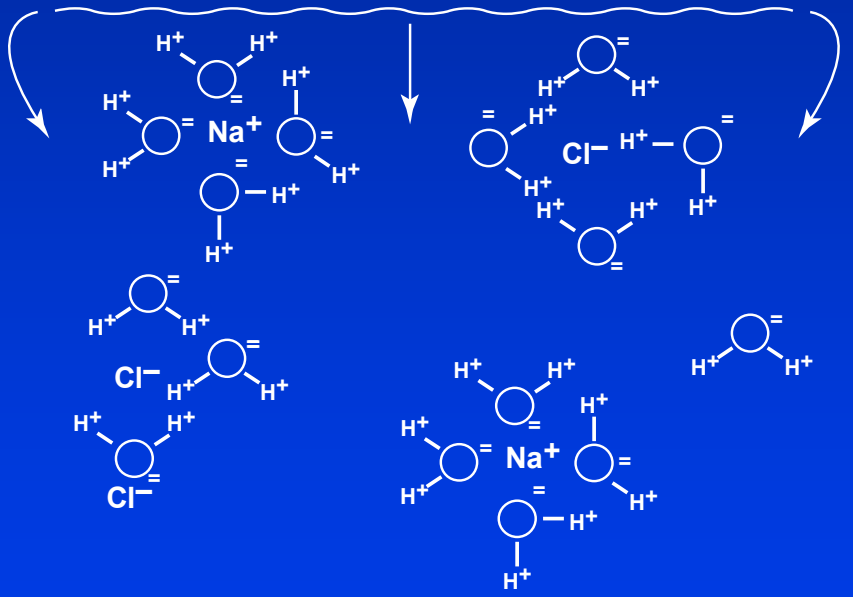
- The Solvent Enables the Surfactants (Active Ingredients) to Be Applied and Helps Get Them Through the Oil Film to the Water Interface (water, hydrocarbon, glycols)
- At the Interface the Surfactants Reduce the Surface Tension Allowing the Oil to Enter the Water as Tiny Droplets Which are Degraded by Natural Bacteria

WATER STRUCTURE

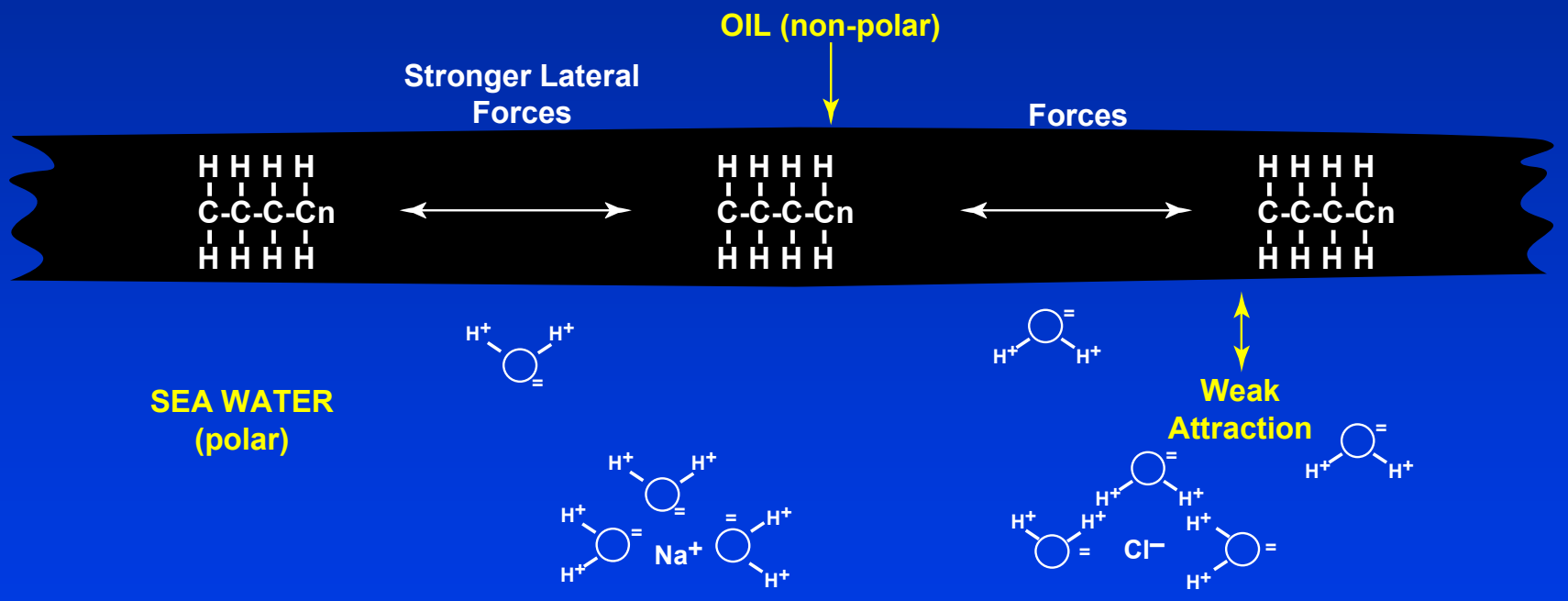
FRESH WATER
Surface Tension Caused By Attractive Forces



SEA WATER
Stronger Internal Attractive Forces



OIL IS GENERALLY INCOMPATIBLE WITH SEA WATER AND "RELAXES" THE SURFACE



SURFACE ACTIVE AGENTS CAN MAKE OIL COMPATIBLE WITH WATER BECAUSE OF SOLUBLE ENDS

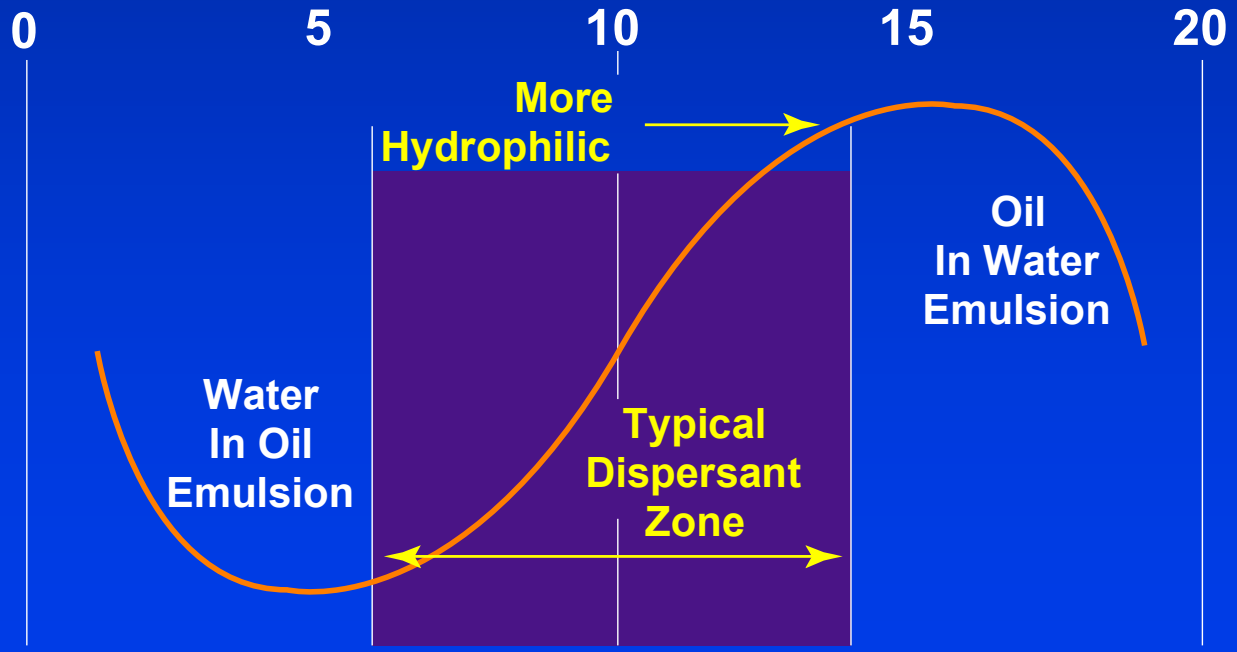
Oil Loving
"Lipophilic"

Water Loving
"Hydrophilic"

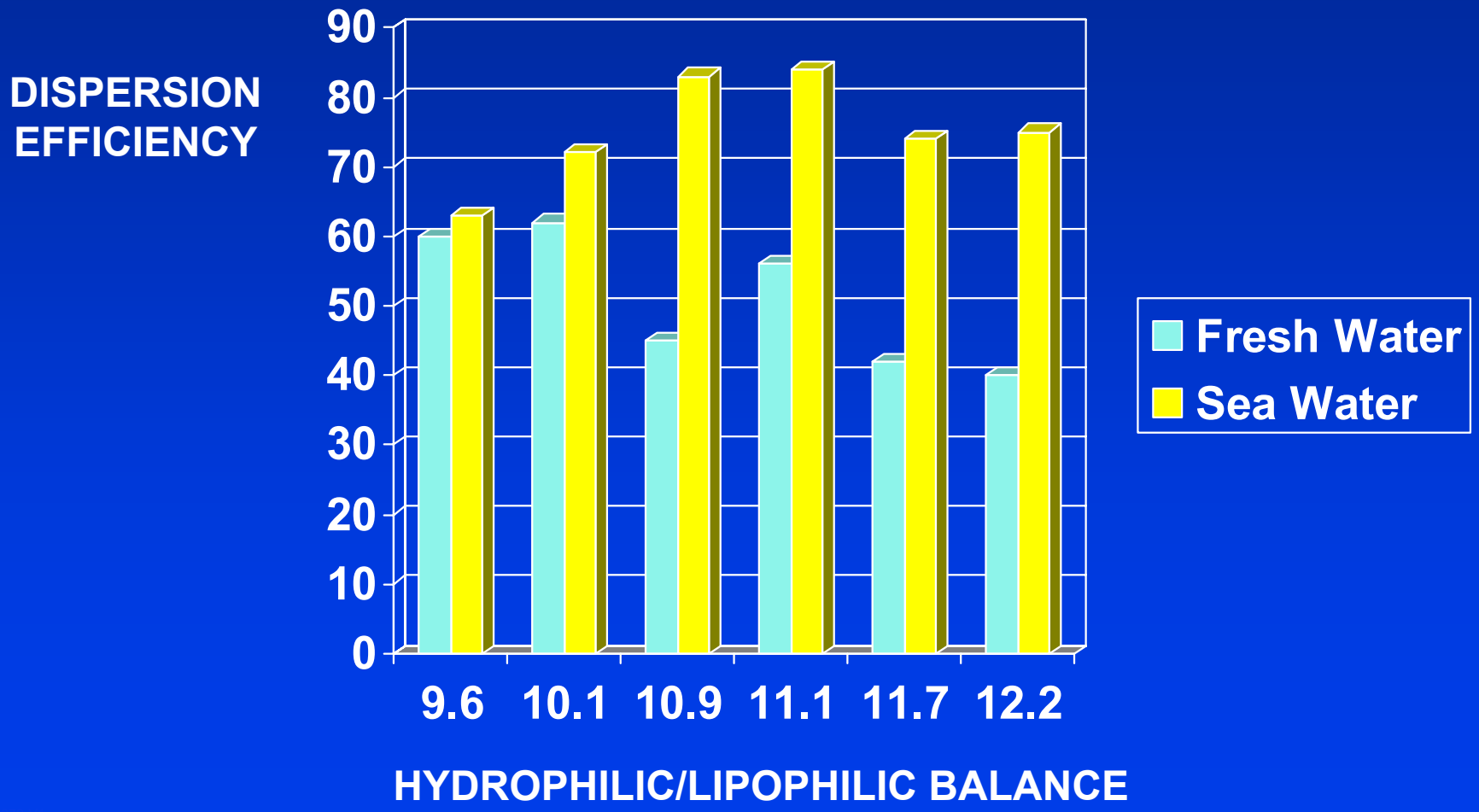
SURFACTANT BLENDS CAN BE CUSTOMIZED FOR VARIOUS APPLICATIONS

HLB = Hydrophilic/Lipophilic Balance

HLB SCALE



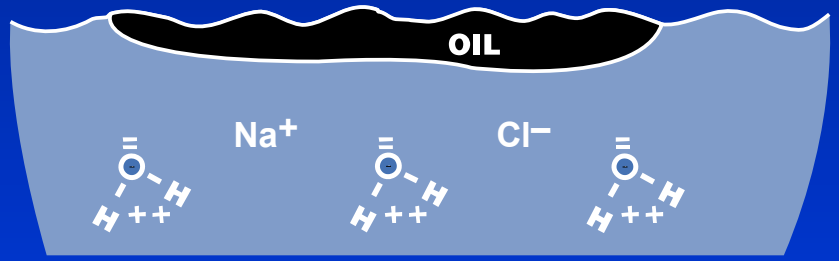
EFFECT OF SURFACTANT HLB ON DISPERSION EFFICIENCY



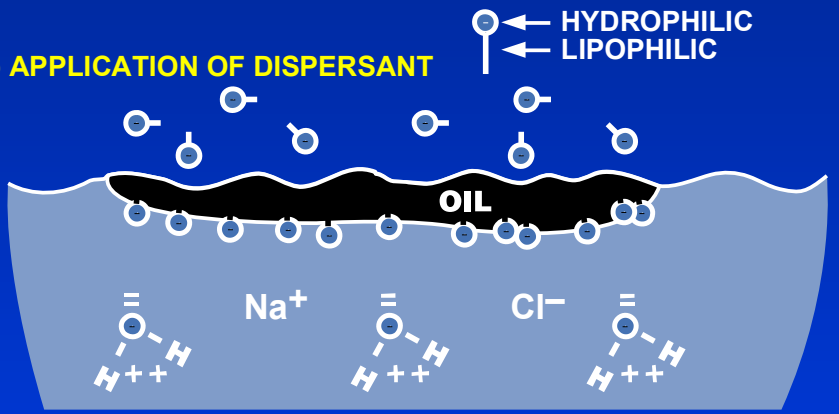
HOW DISPERSANTS WORK

THE GOAL: REDUCE OIL CONC. TO LESS THAN IMPACT LEVELS AS RAPIDLY AS POSSIBLE

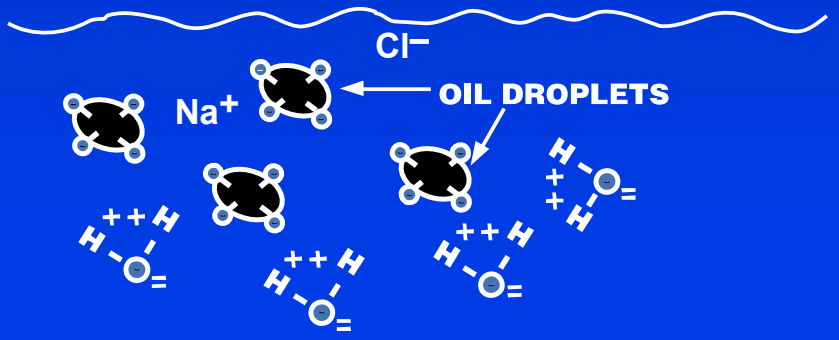
1) OIL/WATER INCOMPATIBILITY



2) APPLICATION OF DISPERSANT

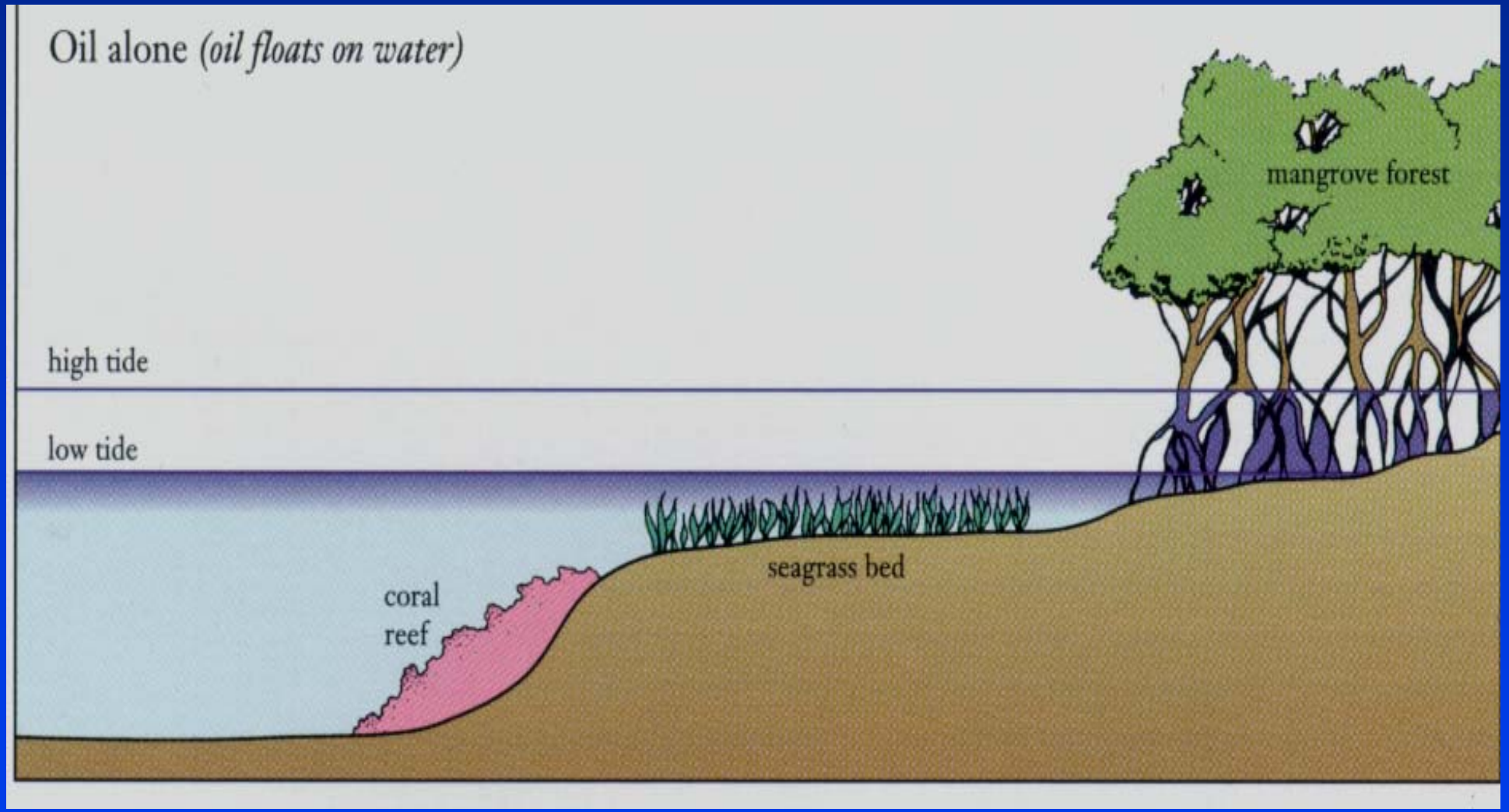


3) OIL SLICK DISPERSES INTO DROPLETS WITH MINIMAL ENERGY

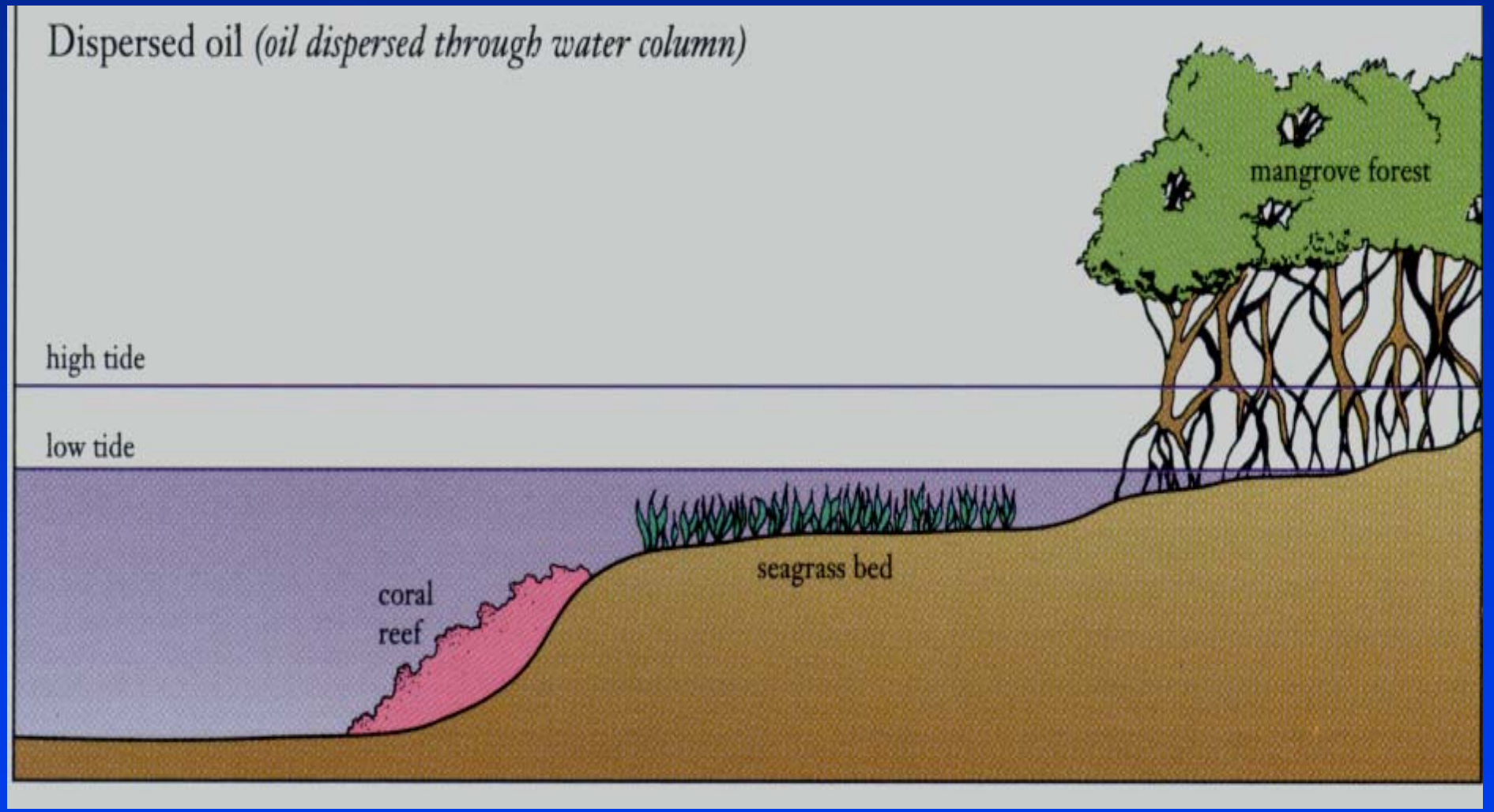


Surfaces of Droplets Repel Each Other... No Coalescence

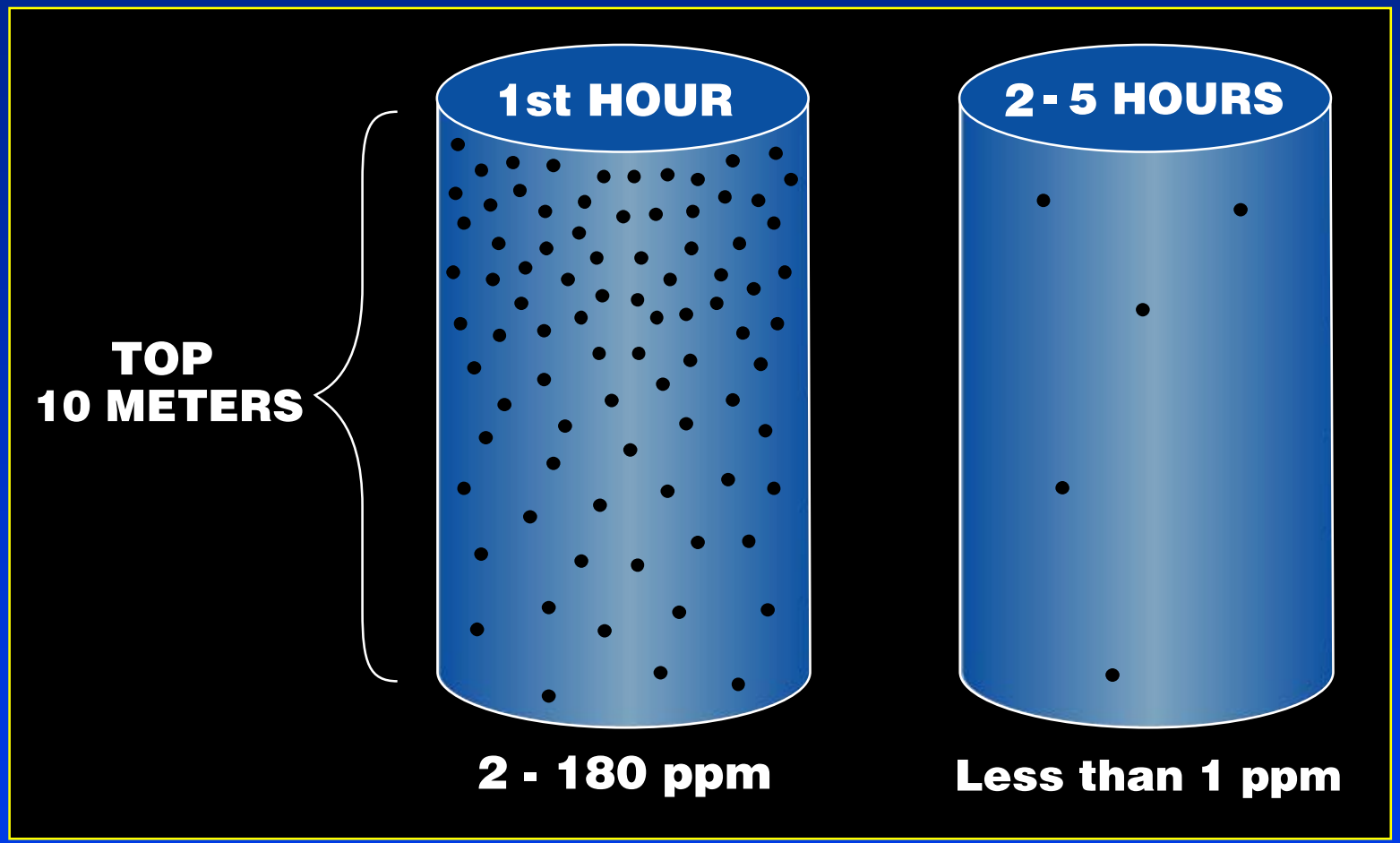
FLOATING OIL DOES NOT IMPACT CORAL OR SEA GRASSES BUT CAN KILL MANGROVES



DISPERSED OIL IMPACTS CORAL AND SEA GRASSES BUT SPARES THE MANGROVES

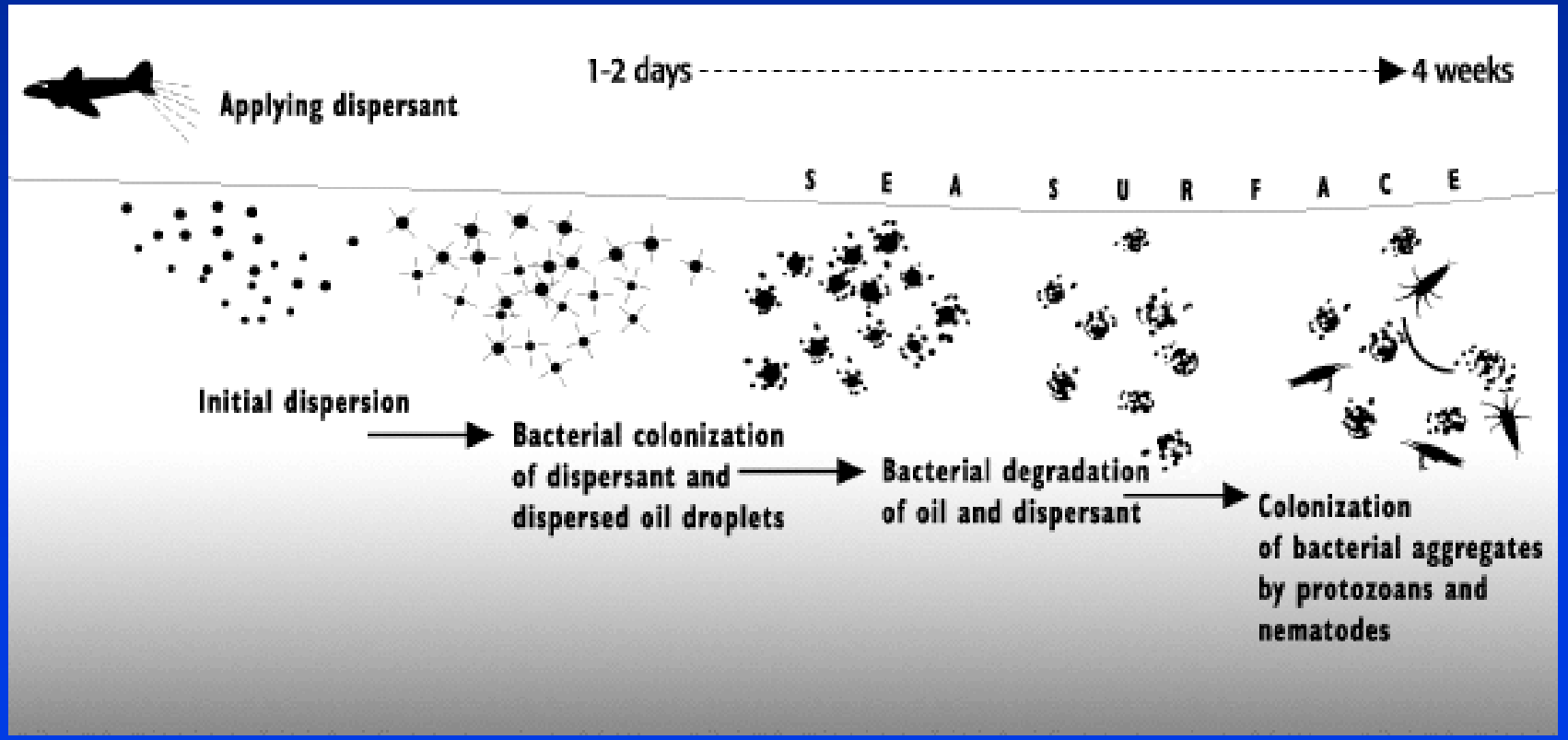


DISPERSION EFFECT



- Water Currents Distribute Oil Over Wide Area

TYPICAL FATE OF DISPERSED OIL DROPLETS



COREXIT PRODUCTS

Why I'm Talking About Corexits -- The Good Stuff is Confidential (Info from USEPA National Product Listing)

- TECHNICAL PRODUCT BULLETIN #D-7 USEPA
- I.NAME, BRAND, OR TRADEMARK JD-2000™
  Type of Product: Dispersant
- IX.PHYSICAL PROPERTIES
  1. Flash Point (SW1010): 212 F
  2. Pour Point (ASTM D97): -36 F
  3. Viscosity (ASTM D445): 65.2 cst
  4. Specific Gravity 60/60 (ASTM D287): 0.99
  5. pH (EPA 150.1): 7.54
  6. Surface Active Agents: Confidential
  7. Solvents: Confidential
  8. Additives: None
  9. Solubility in Water: Dispersible in fresh and salt water. Miscible in oil, water, and solvents.

Corexit Info Also Confidential

- TECHNICAL PRODUCT BULLETIN #D-4 USEPA
- I.NAME, BRAND COREXIT 9500 (EC9500A)
  Type of Product: Dispersant
- VIII.PHYSICAL PROPERTIES
  1.Flash Point: 176F (SETA closed cup; ASTM D3278)
  2.Pour Point: -70F (ASTM D97)
  3.Viscosity: 55 cSt (at 68F)
  4.Specific Gravity: 0.949 (at 60F, ASTM D1963)
  5.pH: 6.4
  6.Chemical Name and Percentage by Weight of the Total Formulation: CONFIDENTIAL
  7.Surface Active Agents: CONFIDENTIAL
  8.Solvents: CONFIDENTIAL
  9.Additives: None
  10.Solubility: Soluble in fresh water, but dispersable in sea water

COREXIT 9527

- Developed in 1972
- Contains Over 60% Surfactants Plus Ethylene Glycol Monobutyl Ether (Butoxy Ethanol)
- COREXIT 9527 Remains the Most Widely Approved and Stockpiled Dispersant in the World
- Not Designed for Direct Application to Shorelines
  - COREXIT 9580 Beach Cleaner Developed for That Application
- Successfully Used on Many Spills
- Can Break Emulsions
- Not Very Effective on Weathered or Heavy Oils

KEY FOCUS OF 90'S PROGRAM: EFFECTIVENESS ON HEAVY, WEATHERED, AND EMULSIFIED OILS

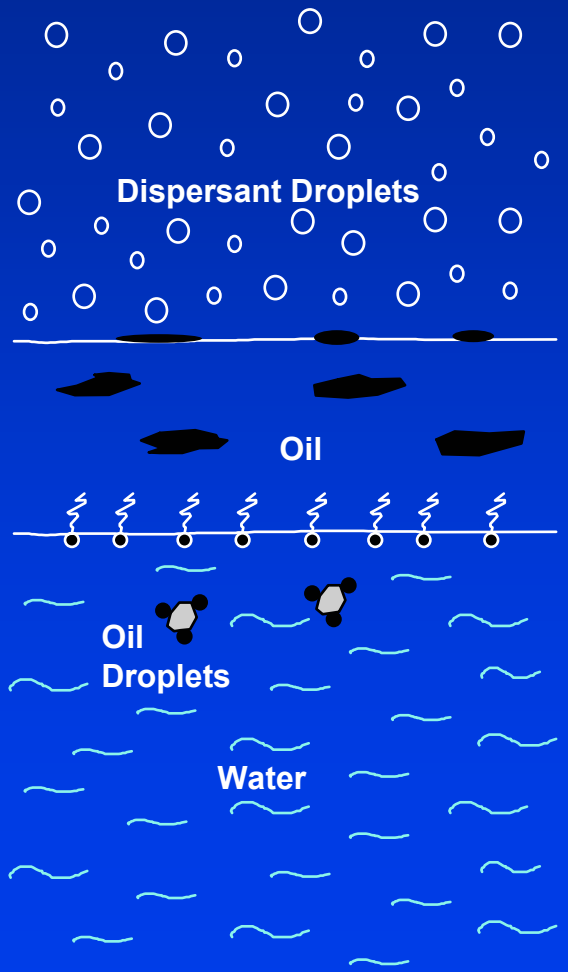
- Relatively Short "Window of Opportunity"
- Since Heavy Oil is Involved in Over Half the Spills, This Has Limited Consideration of Dispersants in Many Cases.
- Available Models (e.g., NOAA and Sintef) Predicted Very Short (a Few Hours) Windows of Effectiveness Based on Testing With Conventional Products.

COREXIT 9500

- Formulated in 1992 Specifically for Weathered Oils
- Same Surfactants as COREXIT 9527
- New Solvents are the Key to its Capabilities
- Acknowledged Broadly as the Dispersant With the Widest Window of Opportunity; Effectiveness on Emulsions, Bunker #5, and Weathered Crudes Demonstrated in Large-Scale North Sea Test by AEA
- Applied in U.K. on CAPTAIN Spill; Effective Even Though Applied at Low DOR (1:80-100)
- Already Used on U.S. Spills (e.g., Red Seagull)

THE KEY: MORE OIL-COMPATIBLE SOLVENTS

(The Old Solvent Was Being Extracted Before Delivering the Surfactant to the Interface in Heavy Oil)



	COREXIT 9527	COREXIT 9500
SURFACTANTS	Same	
SOLVENTS		
– Simple Glycol Ether	✓	
– Complex Glycol Ether		✓
– Parafin Solvent		✓
Solvent Solubility in Water	Infinite	Very Low

HEALTH & SAFETY CONSIDERATIONS

DISPERSANTS

CONCAWE

“Oil Spill dispersants are not hazardous to humans”

- **But must be handled properly**
- **Proper protective equipment and clothing required**

MAFF (UK)

“...No evidence that properly stored and properly used modern dispersants are harmful to man or the environment”

“Risks to bystanders and terrestrial wildlife will be negligible providing dispersants are used correctly”

SURFACTANTS

- **Non Ionic: essentially non toxic (> 100g/kg)**
  - Sorbitan mono oleates -- preferred for most dispersants
  - Alkyl/Phenoxy polyethoxy ethanols
  - Ethoxylated alkyl phenols
- **Anionic: slightly toxic to moderately toxic (1-10g/kg)**
  - Alkyl sodium sulfates
  - Sulfonates
  - Sulfonated petroleum oils
- **Cationic: moderately to very toxic (10-100 mg/kg)**
  - Alkyl and/or aryl substituted ammonium chloride, bromide or sulfate
  - Alkyl substituted “quats”

Cationic Surfactants are Not Used In Dispersants

POTENTIAL EFFECTS OF SOLVENTS

- Eye Irritation
- Dermatitis
- Nose and Throat Irritation
- Glycol Ethers: Liver and Kidney Damage

General Protective Procedures

- Conduct specific product hazard communication/hazard control training
  - Review MSDS
- Minimize contact where possible
  - Wear personal protective equipment (nitrile gloves, Saranex™ suit, chemical goggles)
  - Position upwind or sidewind of application
  - Promptly wash affected skin
  - Decontaminate clothing

Common Sense!


LEAN CARI

DISPERSANT EFFECTIVENESS

FACTORS AFFECTING EFFECTIVENESS

Oil Type/Properties

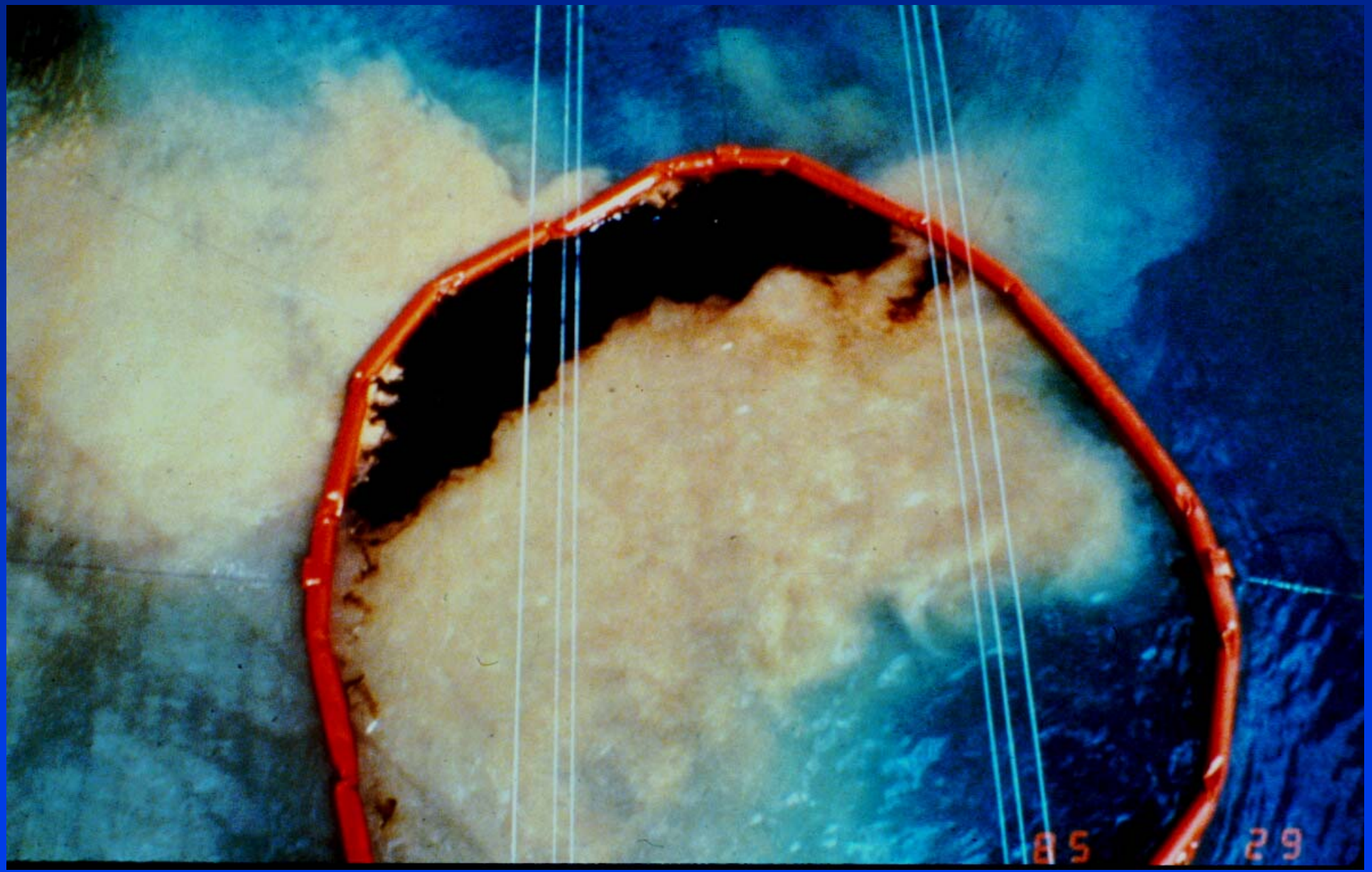
- Viscosity
- API Gravity
- Wax Content/Pour Point
- Emulsifiers

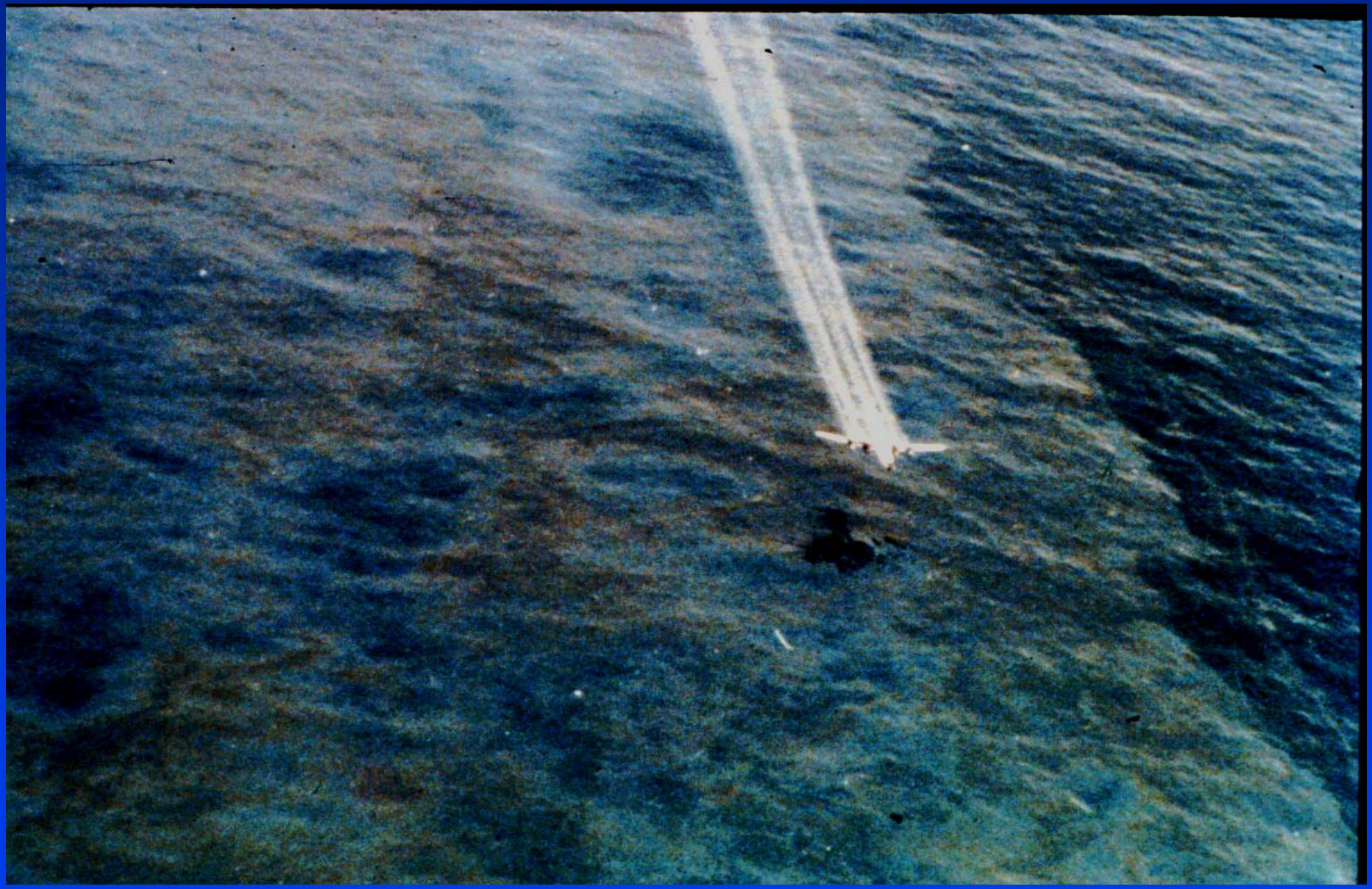
Environmental Conditions

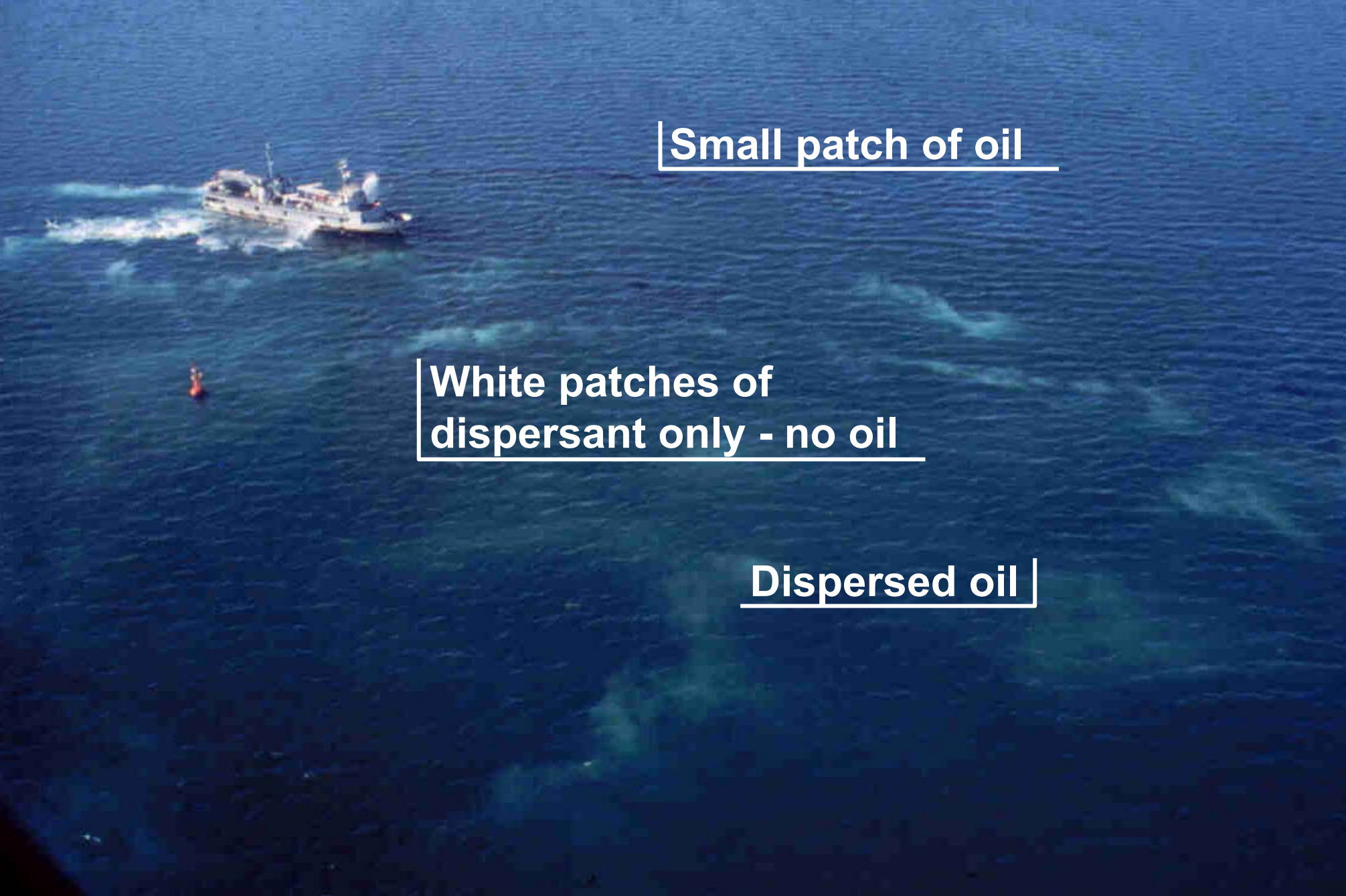
- Water Temperature
- Sea State (Mixing Energy)
- Extent of Weathering (How Long on the Sea)
- Water Salinity

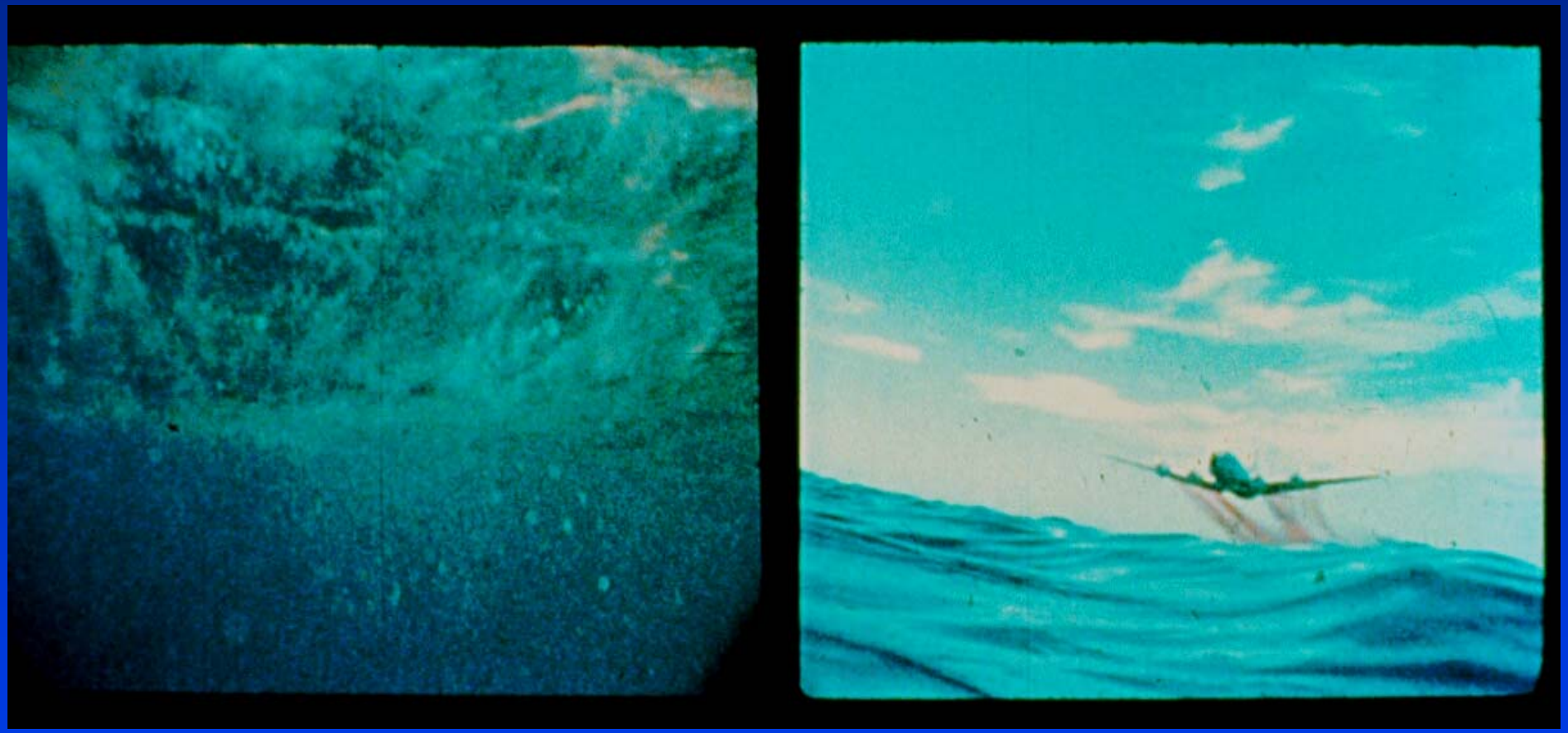
HOW TO TELL THAT DISPERSION IS OCCURRING

- Visual (For Spontaneous or Rapid Dispersion)
  - Don't Confuse Dispersion and "Herding"
- Remote Sensing (e.g., IR) to Detect Change in Film Thickness
- Sampling of the Water Column
- Fluorometry for Continuous Oil Detection in the Water Column


85
29




Small patch of oil
White patches of
dispersant only - no oil
Dispersed oil



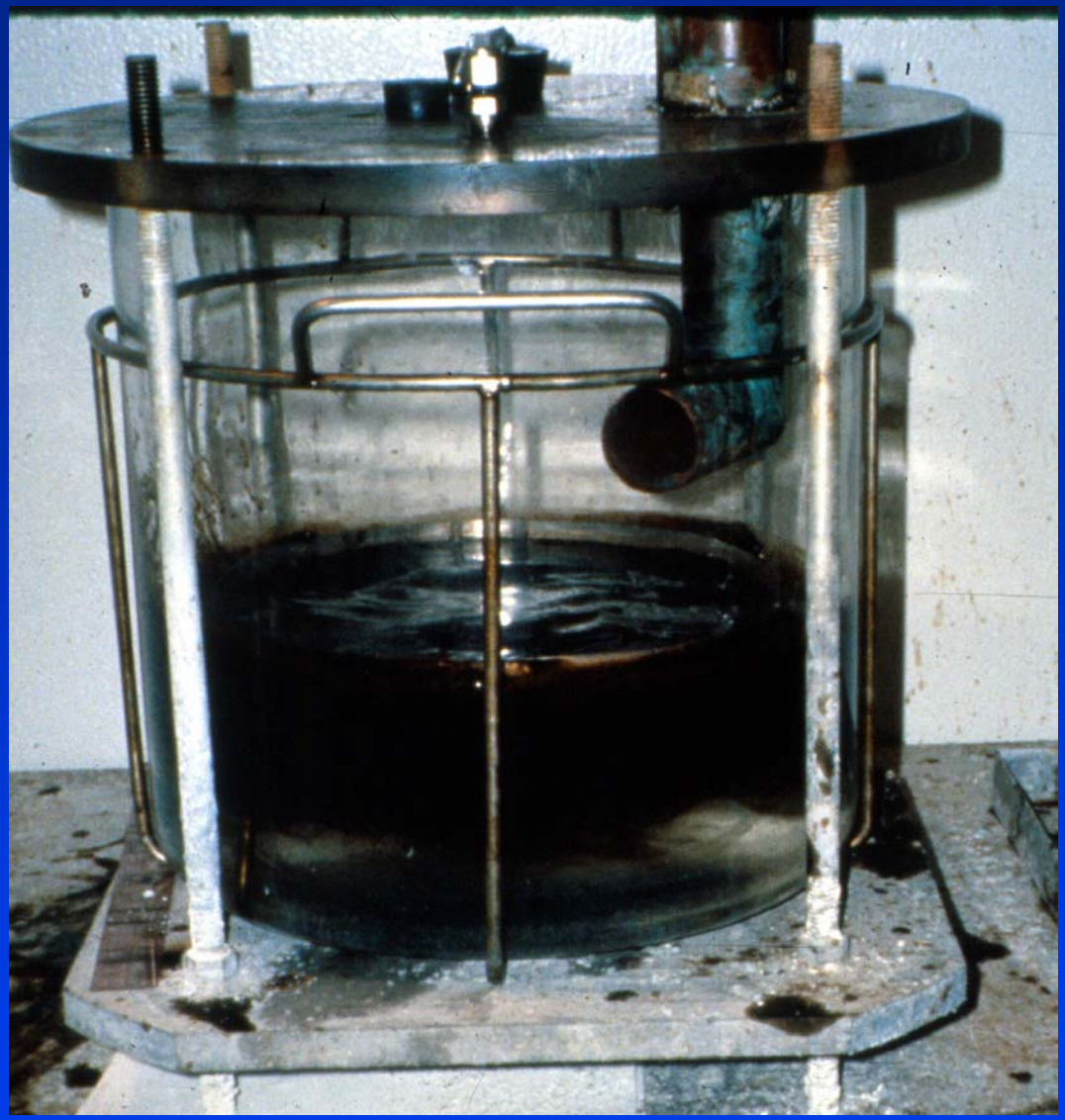
SALINITY EFFECTS

- Some Products (e.g. COREXITS) Require Some Sea Salt to be Effective
  - Seawater is 34 PPT
  - Effectiveness Drops Off Below 10 PPT
  - COREXIT 9500 Ineffective Below 3 PPT
- France is the Only Country With an Approval Process for Freshwater Dispersants. Those Approved:
  - Dasic Fresh Water
  - Disperep 8
  - Enersperse 1037
  - Inipol IPF
  - Gamlen OD 4500
  - Petrotech 25
- Canada and France Have Conducted Field Tests With Freshwater Dispersants
  - Applied in Several Actual Spills in Canada With Reported Low Effectiveness
- No Dispersants Developed Specifically for Freshwater are on the US EPA National Contingency Plan Product Schedule

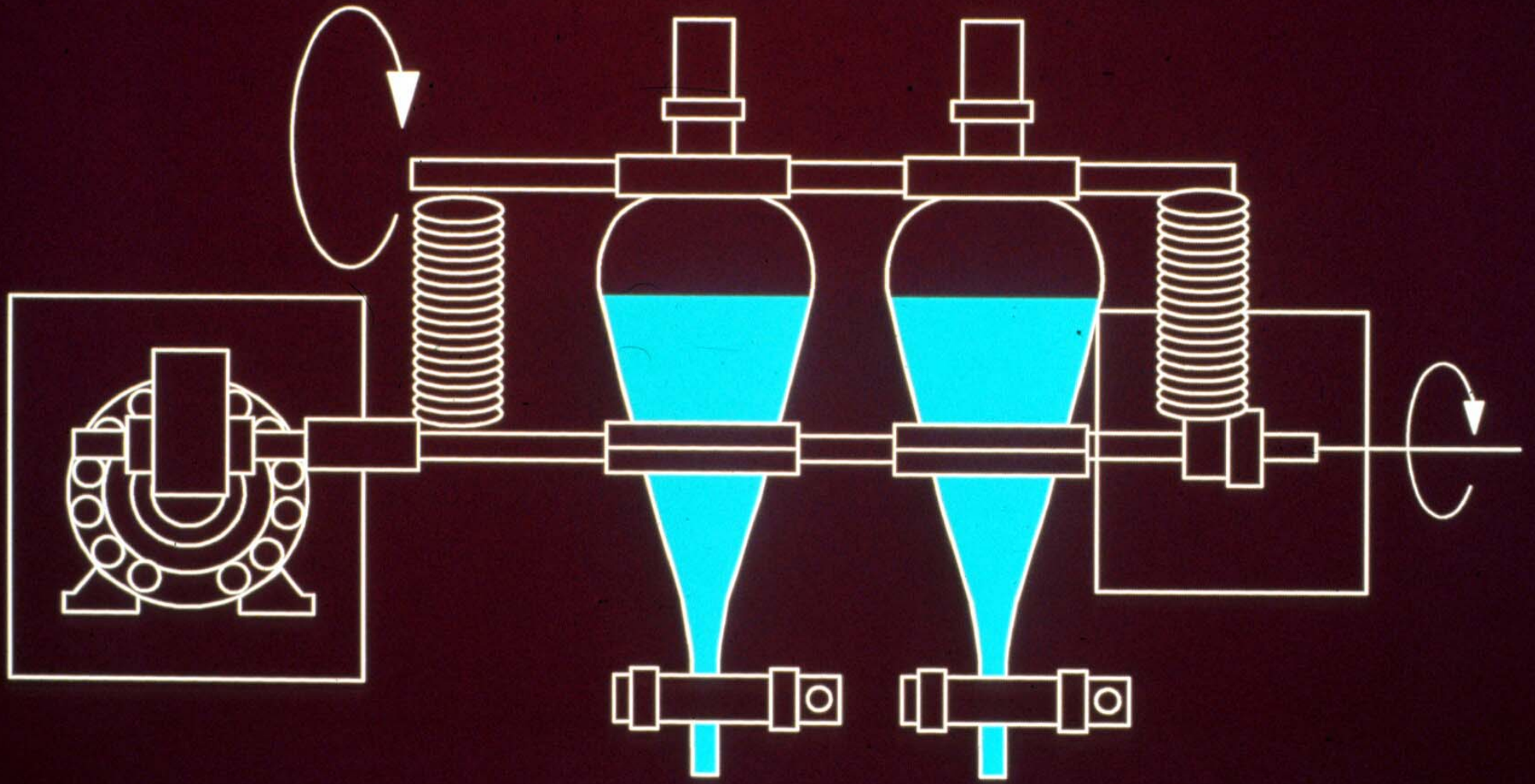
DISPERSANT EFFECTIVENESS TESTS

Test ID	Energy Source	Energy Level [a]	Water Vol. (mL)	OWR[b]	Dispersant Appl. Method	DOR[c]	Settling Time (min)	Complexity Rating[d]
MNS	High Velocity Air Stream	3	6000	1:600	Dropwise/ Premix	Variable	None	3
IFP-Dilution	Oscillating Hoop	1-2	4000-5000	1:1000 and Then Decrease	Dropwise	Variable	None	2
Flowing Cylinder	Vertical Flow of Water	1	1000	1:1200 and Then Decrease	Premix	1:25	10	2
Labofina Rotating Flask	Rotating Vessel	3	250	1:50	Dropwise	1:25	1	1
Swirling Flask	Shaker Table	1-2	120	1:1200	Premix/ Dropwise	1:10 to 1:25	10	1
EXDET (Exxon)	Wrist Action Shaker	1-3	250	Variable	Premix/ Dropwise	Variable	None	1

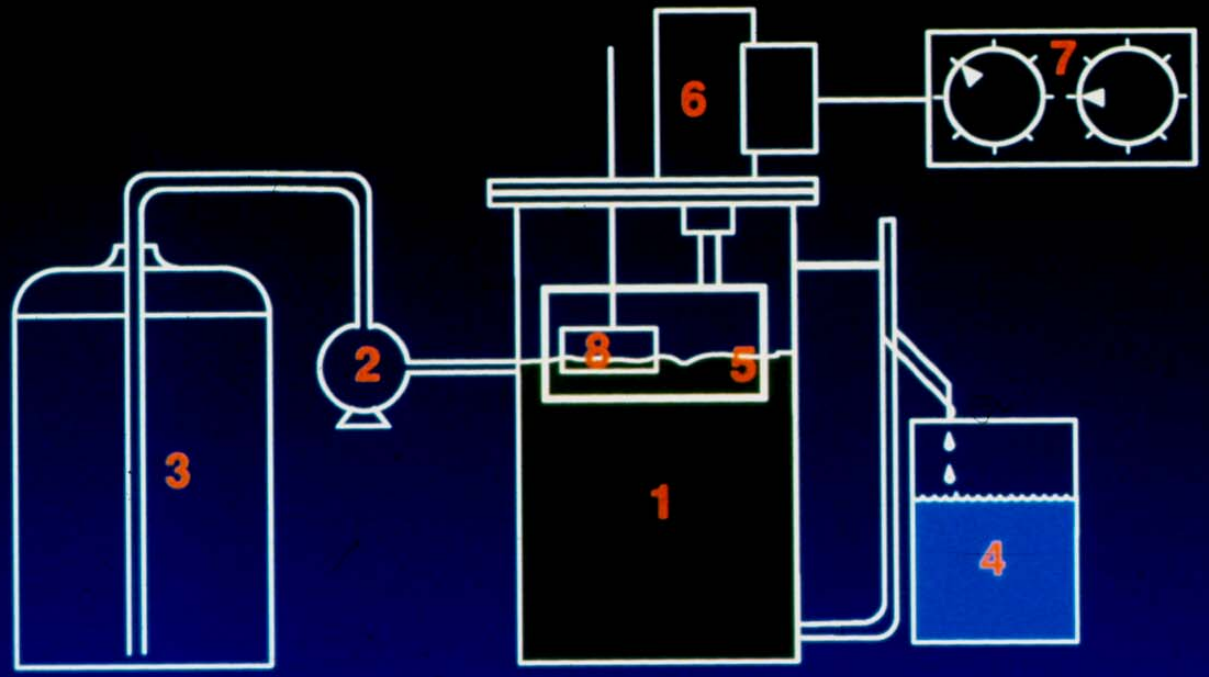
a Energy Rating: 0 = None; 4 = Highest
b OWR = Oil-to-Water Ratio (v:v)
c DOR = Dispersant-to-Oil Ratio (v:v)
d Complexity Rating: 1 = Lowest; 4 = Highest



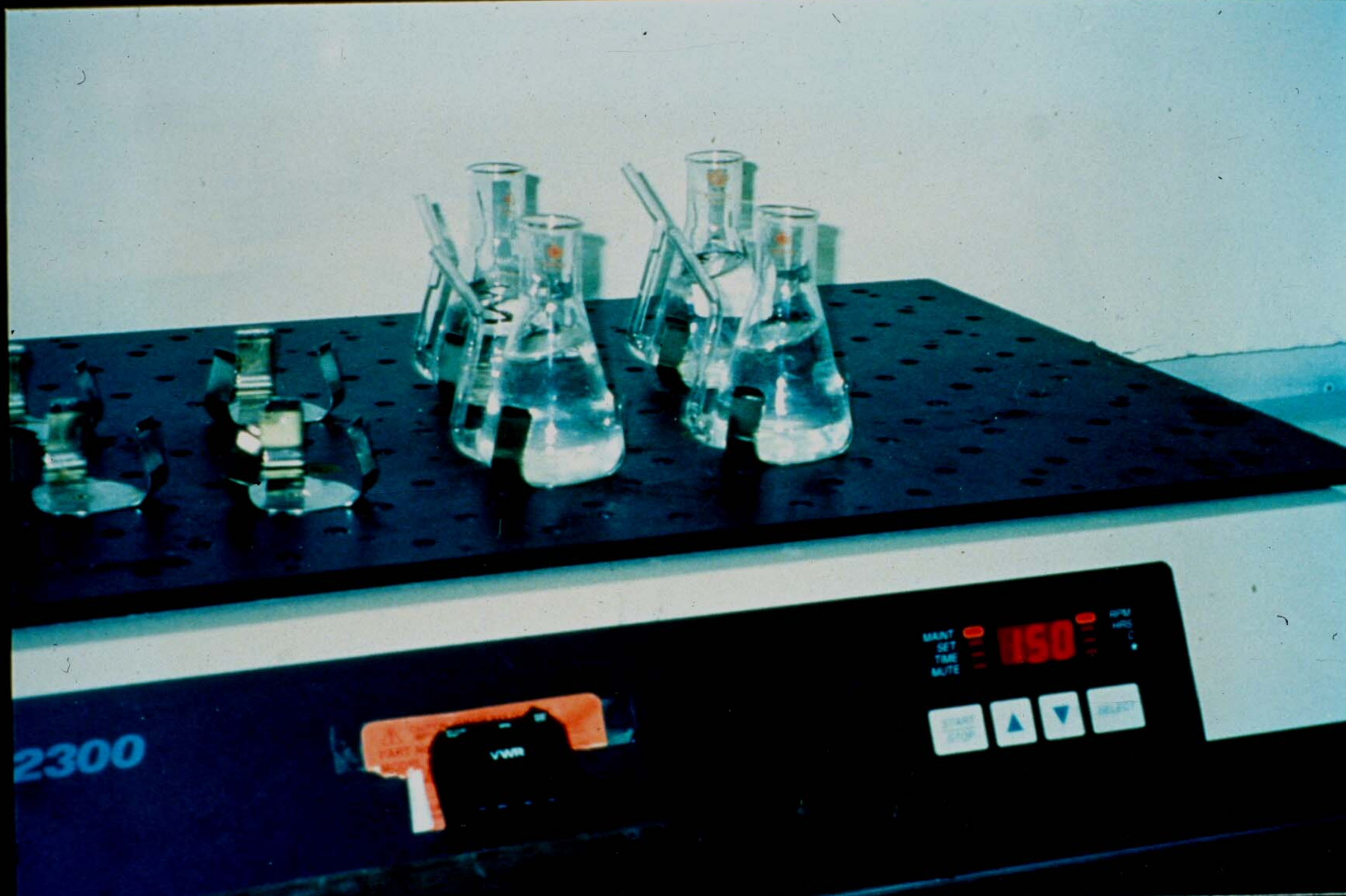
Labofina / WSL Test
(Rotating Flask Apparatus)

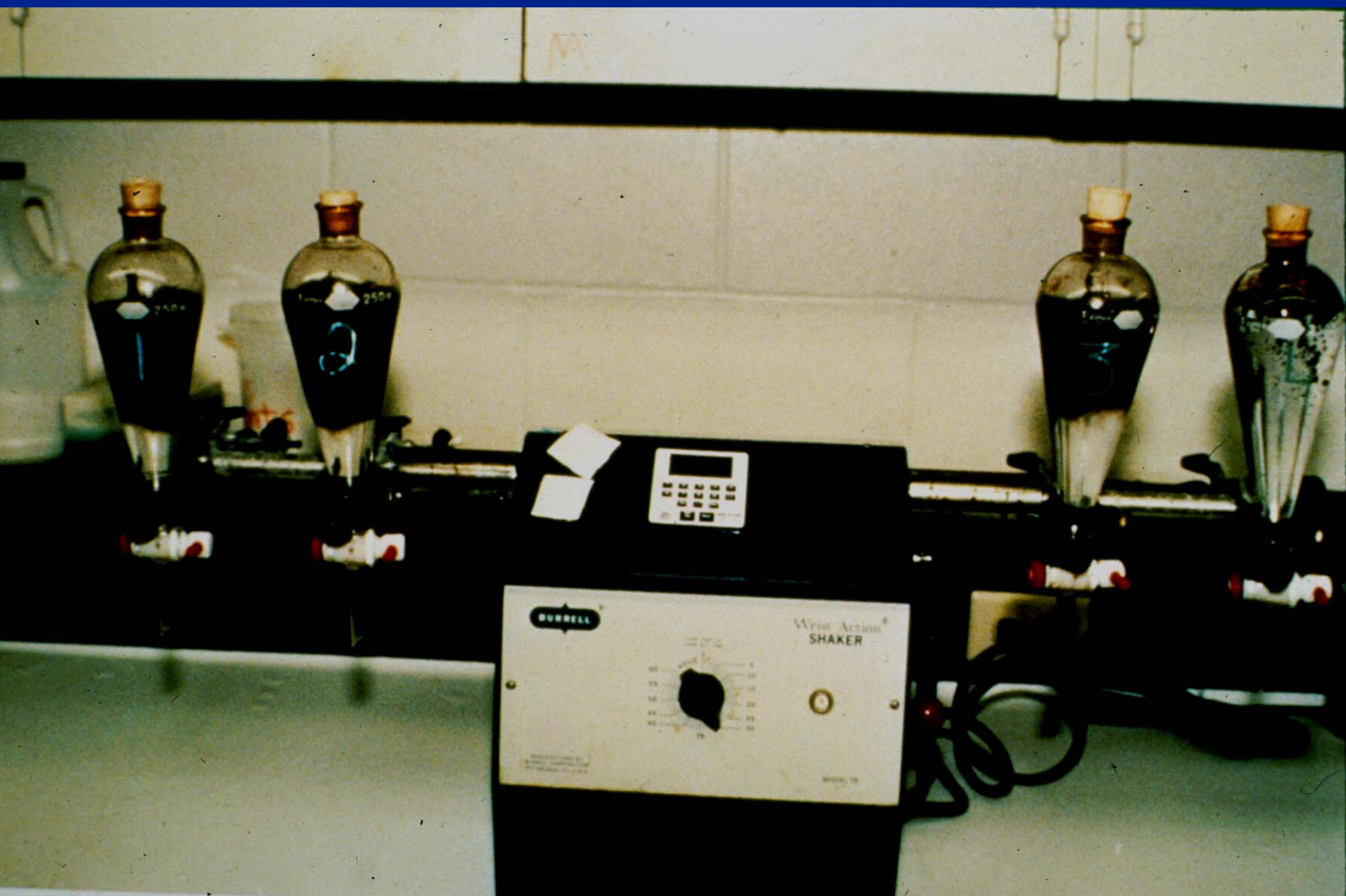


IFP - DILUTION TEST
TO EVALUATE DISPERSANT FORMULATIONS



1. Experimental Vessel
2. Peristaltic Pump
3. Storage Water
4. Sampling Container
5. Pulsed Hoop
6. Electro-Magnet
7. Timer
8. Oil Confinement Ring


MAINT
SET
TIME
MUTE
150
RPM
HRS
2300
VWR


BURRELL
Wrist Action
SHAKER

KEY POINTS

- Key Purpose of Lab Tests is for Relative Comparisons of Dispersants at Given Conditions and for National Approval/Registration
- All Tests Give Different Results for a Given Dispersant
- Most Important Factor is Degree of Energy
- Other Factors:
  - How Long Sample Settles Before Evaluating
  - Premix vs. Direct Addition
  - Ratio of Oil to Water
  - Specific Gravity of the Oil (Rise Velocity)

EFFECTIVENESS

- Considerable Laboratory Data Confirm the Effectiveness of Dispersants
  - Important: Mixing Energy and Type of Crude
- Many Field Trials:

– Canada	1975 - 81
– U.K.	1978
– U.S. East Coast	1978 - 79
– U.S. West Coast	1979
– France	1979 - 83
– Norway	1984
– U.K. and Norway	1994 - 99

- Esso Wave Basin Tests in Canada
- OHMSETT Wave Basin Tests
- Successful Application In Many Actual Spills