Orimulsion: Myths and Realities of Bitumen in Water Spill Responses

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Abstract

A considerable amount of work has been undertaken over the past 10 - 11 years investigating, evaluating and testing Orimulsion fate/ behaviour, ecotoxicological properties and different aspects of spill response. It is a myth that there is "no response" to an Orimulsion spill. As with oil in general, there is not a single overall panacea or spill response. The strategy with Orimulsion has been to develop a good understanding of Orimulsion spill behaviour and to develop tools in the spill response armoury in terms of detection / monitoring, containment, clean up and spill modelling.

Although Orimulsion may be regarded as an innovation, in terms of spill response there are still many similarities to the challenges posed by some of the oils that come under the heading "conventional oil". In many areas work is continuing with Orimulsion in order to fine-tune, optimise and improve our knowledge. This should also be the case with "conventional oils". The following paper hopefully clarifies many of the myths and the realities concerning Orimulsion spills, and hopefully puts it into context.

1. Introduction

It is a fairly common misconception that Orimulsion is something that is both "new" and "unknown". Whilst it is true that in comparison to, say coal or HFO, Orimulsion is a relatively recent addition to the market place it should not be forgotten that over 30 million tonnes of Orimulsion have been safely shipped worldwide in the 11 years that it has been commercially available. Over this time there has also been a considerable amount of R& D undertaken and a vast amount of information gathered on this single product. This has involved close co-operation and collaboration with experts throughout the world and has cost, literally, millions of pounds. Nevertheless work is still ongoing to actively try and improve our knowledge, understanding and capability to deal with possible Orimulsion spills.

Although Orimulsion may be regarded as an innovation, in terms of spill response there are still many similarities with what one would call "conventional oils". Many of the concerns that people have had about Orimulsion relate to their (mis) perception of what Orimulsion actually is. This is also often set against a simplification regarding conventional oil spills. Often oil is regarded as something that is "known" – a purely surface phenomenon which conveniently sits on the surface of the water where it can be easily contained and recovered. **__All__** oil spills are different, and that oil containment and recovery are by no means always straight-forward.

2. What is Orimulsion?

The practical application of emulsion and emulsion technology is considerable and includes foodstuffs, pharmaceutical preparations, cosmetics, agricultural sprays and bitumenous products of which Orimulsion is one.

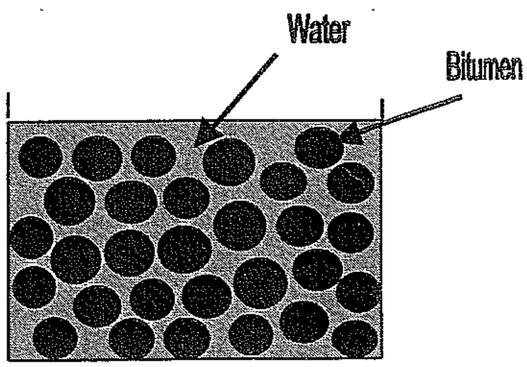
Orimulsion is a bitumen-in-water emulsion comprising 70% natural bitumen (from the Orinoco region of NE Venezuela) dispersed in fresh water. It is manufactured in Venezuela and transported in double-hulled vessels to customers worldwide for use as a power station fuel or in the heavy industry sector. The manufacture and marketing of Orimulsion is undertaken by PDVSA Bitor and its marketing affiliates.

One commonly asked question is why make an emulsion in the first place? The simple reason is that the natural bitumen is solid/ semi-solid at ambient temperatures. The addition of water acts as a carrier that enables the bitumen to be transported and handled as a liquid fuel at ambient temperatures.

The surfactant package that is used to stabilise Orimulsion comprises a commercially available alcohol ethoxylate (AE) surfactant together with a small amount of monoethanolamine (MEA). The total amount of surfactant is < 2000ppm. The AE is similar to those used in baby shampoo and other down the sink applications, and monoethanolamine is a common ingredient and intermediary in the pharmaceutical industry.

Figure 1: Orimulsion

70% Natural Bitumen Dispersed In 30% Water
Average Droplet Size 15 Microns
Stabilised with < 2000ppm Surfactant Package



It is important to remember that in Orimulsion the water is the continuous phase of the emulsion (CF mousse which is a water-in-oil emulsion) as this has important implications in terms of its fate and behaviour

3. Fate and Behaviour

As with any spill, regardless of whether it is oil, HFO or Orimulsion, the precise fate and behaviour will be a function of variables including the size of the spill and prevailing environmental conditions. All spills have a sub-surface component and in some cases this is not just a water-soluble fraction, the bulk oil may also either disperse or sit below the surface of the water.

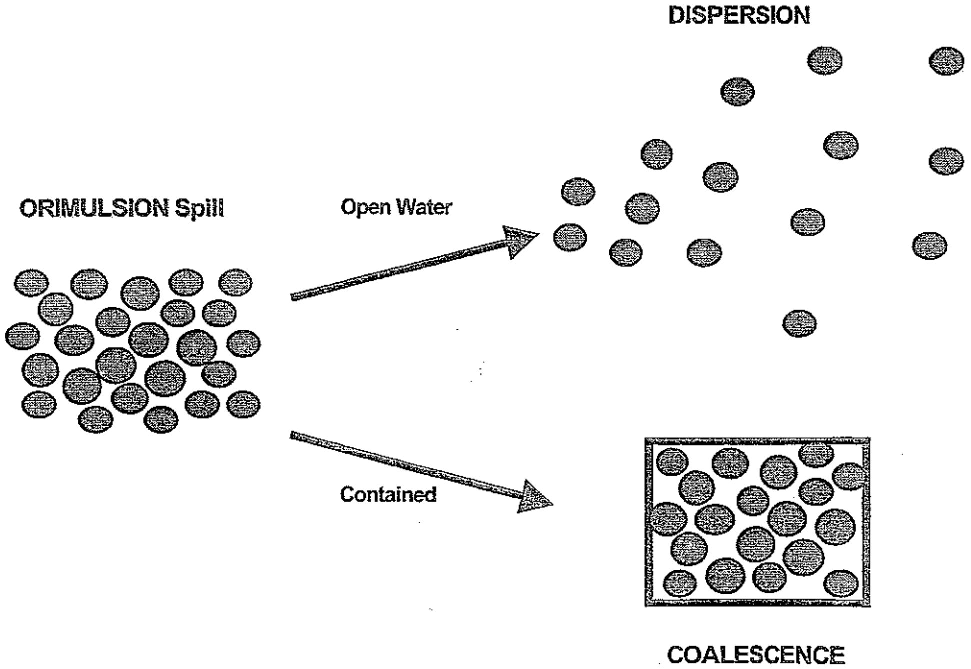
In the case of Orimulsion the micron sized bitumen droplets are already pre-dispersed in water and on contact with water they naturally and rapidly disperse. The effect is very similar to when emulsion paint is cleaned from paint brushes. In fresh water Orimulsion would totally disperse but in saline water some coalescence can occur. If coalescence occurs to a significant extent then this can lead to the formation of some tar balls or patches of bitumen (1, 2).

What causes coalescence and surface bitumen formation? In salt water the effectiveness of the surfactant is less than it is in the neat emulsion (note – less effective not ineffective). In the early stages of the spill as the droplets are diluting and dispersing some droplet collisions can occur and some of these collisions can lead to coalescence. If this process is repeated enough times then some tar balls or lumps of bitumen can be produced. Of course, as the individual droplets disperse and dilute immediately following the spill then they become far enough away from other droplets so that collisions and coalescence and hence bitumen formation will not occur.

As a rule of thumb dispersion would be expected to be total in fresh water and this may also be the case in saline water (small spills, continuous releases /leaks). However it is also possible in saline water that some coalescence and bitumen may form and in experiments to date, in open water 90% would tend to disperse and around 10% may coalesce and form surface bitumen. The important thing is the equilibrium between those droplets that disperse and those that coalesce and this will be discussed below.

It can be appreciated from the foregoing text that one of the difficulties in evaluating the fate and behaviour of a dispersed product is how to best go about this. It needs an approach that is both carefully controlled and relates to what would happen in reality. If Orimulsion is released in open water where it is allowed to disperse then it can, and will predominantly do so. However, if this natural dispersion is prevented then coalescence is promoted.

Figure 2: Naturally Dispersing and Artificially Contained Orimulsion



For this reason great care has to be taken when investigating Orimulsion behaviour in the laboratory. If Orimulsion is just simply put in a beaker then of course natural dispersion is prevented and the equilibrium is shifted towards coalescence. However, this is not a reflection of what would happen in reality and the results become an artefact of the experiment.

Such experiments can be useful to understand the relative importance of some variables but gaining absolutes is often not possible. However, there are some laboratory test protocols that are used to measure dispersant effectiveness on oil spills, that can also be applied to Orimulsion. The IFP test is a particularly useful tool as it allows a degree of dilution during the course of the experiment. By simultaneously measuring droplet size data/ coalescence rates and assessing the effectiveness of dispersion as a function of several variables (concentration, salinity) valuable information has been gathered and added to the data base.

Larger scale tests have also been undertaken – up to 2 tonnes has been released in the North Sea and hundreds of litres released in experiments in Nelson Dock in Liverpool and more recently off the coast of Venezuela. These have all provided valuable data but rather than providing **the** answer they provide **an** answer to the experimental conditions prevailing. Given that there are some variables that are beyond our control (the weather conditions) then it is better to work in a controlled environment where many variables can be controlled and investigated to give a more rounded and thorough understanding.

In summary, the natural tendency for Orimulsion is to disperse, although some tar balls or patches of bitumen may form under some circumstances. This natural dispersion is what responders try to achieve when chemically dispersing oil spills and will be considered in more detail below.

4. Spill Response

The following sections provide some very brief detail on some of the key tools in the Orimulsion spill response armoury and make reference to both the surface and sub-surface where appropriate and to containment and clean up / recovery where this is feasible.

4.1 Ecoxicological impacts

In addition to understanding the physical properties and impacts of a spill it is also important to have a detailed knowledge of ecotoxicological properties of the oil. This is particularly important in order to determine the most appropriate spill response strategy. If an oil had a very low toxicity, but had potential to cause significant shoreline damage and fatalities to wildlife then dispersion in this circumstance would be the least damaging to the environment as a whole. If a material was particularly toxic then this would need to be taken into consideration, and in this case dispersion may not be the preferred option.

Orimulsion, and its components, have been tested extensively by organisations such as the Danish Water Quality Institute, Zeneca, Environment Canada and Golder Associates. The latter have prepared a very useful summary report that makes reference to most of these studies (3). For the purposes of this paper let's consider the bitumen and surfactant components of Orimulsion separately.

As mentioned previously Orimulsion is manufactured from natural bitumen that is present in the vast reserves of the Orinoco belt in Venezuela. It contains very few of the water soluble and toxic BTEX and PAH compounds that can abound in crude oils and HFO. It should also be noted that HFO can very quite considerably depending on its origin and on the processing and diluent used in its production.

Although the bitumen that is used in Orimulsion is largely chemically inert, there have been questions asked regarding the effects of dispersed bitumen droplets on aquaculture. Tests have been undertaken by Canadian Fisheries (4) on dispersion of Orimulsion using filter-feeders

The AE and MEA are both biodegradable and do not produce any metabolites of concern. The AE has a toxicity typical of alcohol ethoxylates and the MEA has a very low toxicity indeed.

4.2 Detection /Monitoring

This is a particularly important part of the response strategy given the physical properties of Orimulsion. As with oils that have been chemically dispersed it is important to actually monitor that Orimulsion has dispersed and diluted. AEA Technology and Steptech Instruments have shown that sub-surface Orimulsion can be detected using the same fluorometers that were successfully used to monitor dispersed oil following the Sea Empress spill. Bitor has also sponsored preliminary work investigating the potential use of sonar as a means of remote underwater detection and monitoring (similar equipment has been considered for tracking sub-sea releases during exploration / production activities for oil). Initial trials by the Danish consultancy Flemingco and Reson a/s have been encouraging but further larger scale work is required.

4.3 Containment

Any boom, regardless of what is being contained, can only be used under certain conditions. If the sea-state is rough sea state or if there is just moderate current flow then this may be sufficient to make booming impractical and ineffective. Where (at the source of the spill? downstream?) and when booming is an option should be reviewed on a case by case basis. In the case of Orimulsion (and some other oils such as the Group V oils) it is necessary to consider the surface and sub-surface.

If any coalescence does occur and any tar balls or patches are formed then this surface bitumen can be contained using conventional booms. Sub-surface emulsion can be contained using deep-skirted booms. Several types of deep-skirted booms (typically 3m deep) have been tested and are commercially available. Jackson netting and then "modified" Jackson net boom were successfully tested in the early 1990s and lengths of "modified" Jackson net boom are currently located in some Orimulsion user sites. Since that time other manufacturers, particularly in the USA, have developed newer generations of deep skirted boom. One example is the company Containment Systems, based in Florida, who commercially supply Orimulsion Containment Boom and have equipped several terminals in Italy.

4.4 Clean up (surface and sub-surface)

Although bitumen (tar balls, lumps, patches) may not always form in open water, if any surface bitumen is formed then it can be considered to be similar to HFO or very weathered crude oil. The difficulties of handling such high viscosity material can be partly offset by the fact that water that is co-recovered will actually provide lubrication and slippage and assist in the bitumen transfer process. Also, by keeping surfaces water-wet bitumen adhesion can be minimised. The use of recovery "socks" made of netting have been used successfully to collect and recover floating bitumen tar balls and offer a simple "non-mechanical " way of dealing with viscous oils in some circumstances (see also below). Bitor is continuing to work with skimmer manufacturers but as the Erika spill has highlighted Orimulsion is certainly not unique in posing challenges in this respect. In the case of conventional oils the difficulty can be significant due to the characteristics of the oil but also because a much greater proportion of a spill would normally be expected to be on the water surface.

Bitor has been working to develop equipment that can clean up sub-surface emulsion if a spill occurs close to the shore, particularly in an enclosed harbour or terminal (for example, during loading / unloading operations). The initial phase of work started off in the laboratories of Intevep (the research arm of Petroleos de Venezuela) and culminated in some very successful tests of the Forced Adhesion and Flotation (FAF) principle off the coast in Venezuela in October 1996. Since then other tests have been undertaken and the "FAF" concept has been extended and developed to produce the "PNP" Orimulsion refloater. Whereas the original emphasis of the "FAF" had mainly been on the effect of the high speed centrifugal pump and air injection, with less emphasis on splash re-flotation, it was subsequently discovered that the latter process was as important and more simple and less costly to employ. The "PNP" Orimulsion refloater comprises a floating submerged or non-submerged centrifugal pump, which sucks from beneath the water surface and with great force discharges vertically up against a splash cover, from where the water splashes back to the surface. In trials to date it has been possible to obtain recovery efficiencies of > 90%. Whilst it is recognised that such high efficiencies would not always be achievable the results do at least demonstrate that a potentially valuable option has been developed for at least some spill situations. The PNP Orimulsion refloater has now been commercialised by the Canadian company Environment Recovery Equipment Inc (ERE) as a spill response tool for harbour / dockside spills (5). The device uses ERE's Heavy Oil and Bitumen Skimmer to recover the re-floated bitumen and it is transferred directly into removable bags or cassettes to minimise the amount of handling required. Bitor has worked closely with ERE Inc throughout this process and significant contributions have been made by Intevep and FlemmingCo, a Danish consultancy

It should also be noted that Bitor is working closely with experts such as Environment Canada and Cedre in different aspects of shoreline clean up. A considerable amount of work has been undertaken (6) and more studies are scheduled to further improve our knowledge and understanding.

4.5 Modelling

Spill modelling is an important tool in the Contingency Planning process according to the OPRC legislation. It will be appreciated by now that modelling of just surface oil is not appropriate for Orimulsion. However, there are spill models that are capable of tracking surface and sub-surface components and Bitor has worked closely with Applied Science Associates, Inc to "generically upgrade" their SIMAP model to ensure that it is capable of tracking the fate, behaviour and ecotoxicological impacts of Orimulsion should a spill occur. This work was undertaken during 1999 – 2000 to ensure that it included the most up to date information and of course as more data is generated this will also be added to the Orimulsion data base.

The intention would be to take this "generic upgrade" of the SIMAP model and use this as the starting point for any local site specific modelling. This may well involve working with local people who will be able to add their knowledge, data and expertise to ensure that the model takes into account the local environment.

5. Discussion

People have a natural tendency to be conservative and to fear what is perceived as the unknown. It is unfortunate that this has been the case with Orimulsion. The fact that in relative terms it has only recently been available, and the fact that it is a trade named product has drawn specific attention to it. There is now a much greater appreciation of what Orimulsion actually is (a clean burn fuel that is burned meeting all national / international environmental standards in countries such as a Denmark, Italy, Canada and Japan), and how it behaves in a spills context.

It is also fair to say that there is a wider recognition that no two spills are the same – there are different circumstances associated with each one. This could be the size of the spill, the weather but also particularly important is actually the oil itself. Oil is often not the simple surface phenomenon that can simply be contained and recovered either due to the properties of the oil itself or due to restrictions imposed by the environment, or a combination of both. The recent Erika spill perhaps highlighted some of the difficulties and challenges faced in recovering highly viscous oils. As well as focussing minds on maritime safety in general, the spill also demonstrated that further work would be useful in developing / modifying equipment and techniques for dealing with heavier products in general.

All spills have a sub-surface component and in some cases this is not just a water soluble fraction, the bulk oil may also either disperse or sit below the surface of the water. The properties of Gulfaks crude oil combined with the extreme weather that prevailed at the time of the Braer spill off the Shetlands is an extreme case where the oil, predominantly, dispersed naturally. Waxy oils can produce floating or even sub-surface tar balls and what about all of the Group V oils which by their very definition have a density greater than water? Deep sea drilling has also yielded the possibility of deep-sea spill releases that would also have some similarities to an Orimulsion spill.

There is recognition within the concept of Net Environmental Benefit that there is a need to consider the whole environmental picture and not just single impacts. In many cases oils are chemically dispersed to minimise the overall environmental impact. The devastation caused by oil reaching the shoreline or smothering and killing marine wildlife are well known, which is why dispersion can actually minimise overall environmental impacts. Orimulsion is already pre-dispersed and what is being dispersed does not contain the same levels of BTEX and PAHs associated with crude and HFO. Given the physical properties of bitumen, and its low toxicity, this is also likely to be the least damaging option to the environment. However, as with any spill, this should be determined on a case by case basis.

In terms of overall environmental impacts, an extensive study was undertaken in 1999 by the Danish Water Quality Institute (VKI) / Danish Hydraulic Institute (DHI) that compared the risks associated with the transport of Orimulsion and HFO (7). The risk assessment part of the study was undertaken by DNV Technica, and the subsequent modelling and spill impacts were investigated by the VKI/ DHI. The risk of spillage was found to be low due to the standard of equipment (exclusive use of double hulled vessels) and operational practices. In the event of a spill one of the most significant conclusions was that "For all scenarios, the modelling of the risk to aquatic organsims showed that a spill of HFO results in considerably higher risks over a much greater area than a spill of Orimulsion-400".

6. Conclusions

A considerable amount of work has been undertaken over the past 10 - 11 years investigating and studying Orimulsion fate and behaviour, ecotoxicological properties and different aspects of spill response.

It is a myth that there is "no response" to an Orimulsion spill. As with oil in general, there is not a single overall panacea or spill response. The strategy with Orimulsion has been to develop a good understanding of Orimulsion spill behaviour and to develop tools in the spill response armoury in terms of detection / monitoring, containment, clean up and spill modelling. The key is to try and develop options and alternatives but of course it needs to be flexible depending on the spill in question and on the local sensitivities and conditions prevailing at the time.

It is also a myth that oil should be regarded as a "known" and Orimulsion is an "unknown". It is fair to say that there is a greater recognition now that oils can, and do, behave differently to one another. Whilst Orimulsion is an innovation many of the properties and challenges in terms spill response are not unique. There are similarities and differences to conventional generic oil spill response. Research and Development work is continuing with Orimulsion in order to optimise, fine-tune and improve knowledge and understanding and this should also be encouraged within the industry as a whole (particularly at the "heavier" end of the range).

As a final remark, it goes without saying that Bitor places a considerable emphasis on spill prevention. This is illustrated in the company's Environmental Policy that seeks to ensure that operations and vessels (exclusive use of modern, double-hulled ships) are as safe and reliable as possible.

7. References

1. "Orimulsion Spill Response Manual (Volume 1)", February 1999 – PDVSA Bitor

2. "Orimulsion", paper at the 1997 International Oil Spill Conference - Matthew Sommerville , Tim Lunel, Nick Bailey (AEA Technology), Dave Oland, Chris Miles (OSRL) and Paul Gunter, Thomas Waldhoff (Bitor Europe Ltd)

3. "Summary of the Environmental Fate and Effects of Orimulsion-400", dated November 1998 – Golder Associates Inc.

4. "Effects of an Emulsified Bitumen Fuel and Physiological Energetics of Sea Scallops", dated November 1999 Shelley L et al Department and Oceans Marine Environmental Sciences Division, Canada.

5. "Oriliminator ERE PNP Refloater: Options for Terminals for the Recovery of Spilled Orimulsion and No. 5 Oils", brochure prepared by ERE Inc.

6. "Orimulsion Spill Response Manual Volume II – Protection & Cleanup of Marine Shorelines", dated March 1999 prepared by Owens Coastal Consultants / Environment Canada.

7. "Orimulsion 400 and Heavy Fuel Oil: Assessment of risks for marine accidents and the environment during transport to Asnaes Power Plant", dated October 1999 – VKI in collaboration with DHI and DNV.

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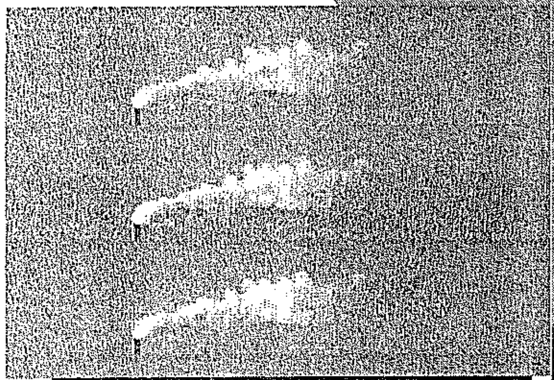
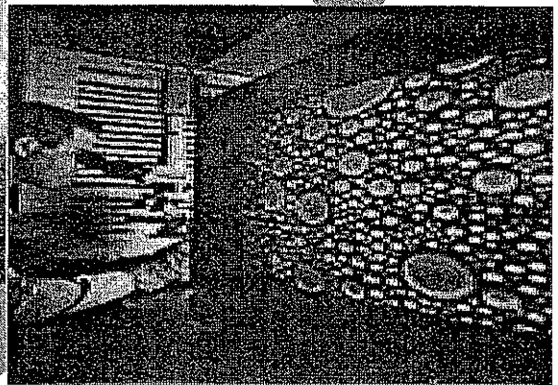
INTERSPILL 2000 - Session 5

Orimulsion: Myths and Realities of Bitumen-in-Water Spill Responses





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Orimulsion-400

- What is Orimulsion ?
- Orimulsion Fate and Behaviour
- Spill Response
  - Ecotoxicological properties
  - Detection / Monitoring
  - Containment
  - Clean up
  - Spill Modelling
- Conclusions

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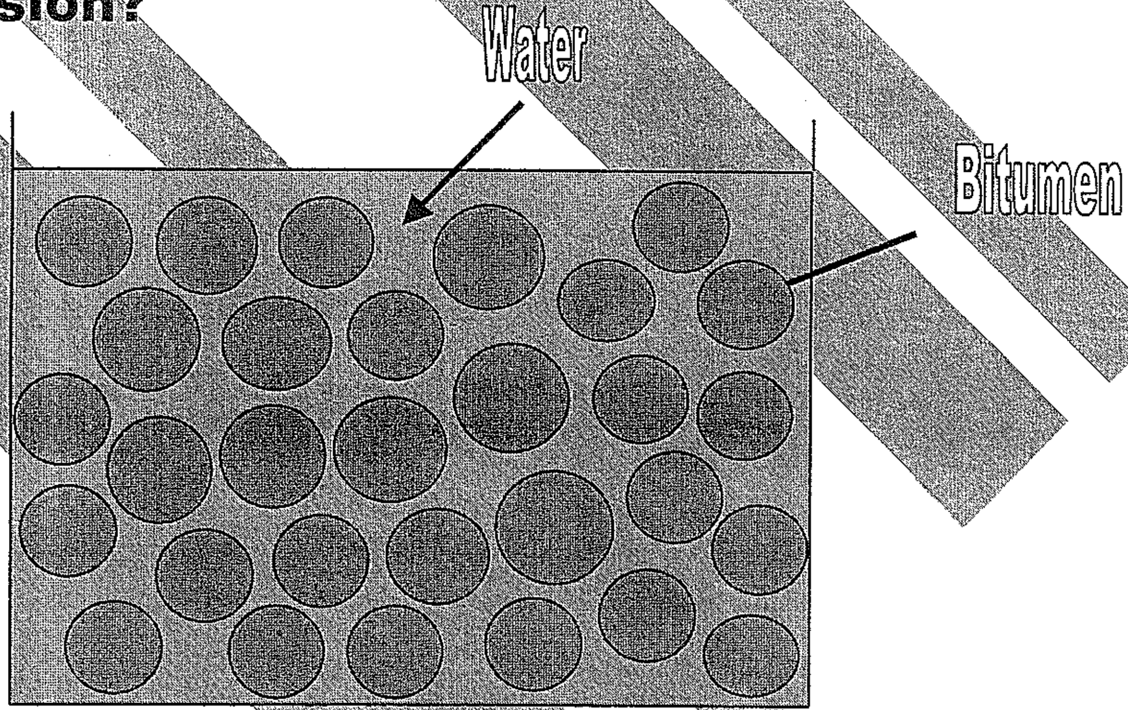
What is Orimulsion?



70% Natural Bitumen Dispersed In 30% Water
Average Droplet Size 15 Microns
Stabilised With 1225ppm AE / 300ppm MEA

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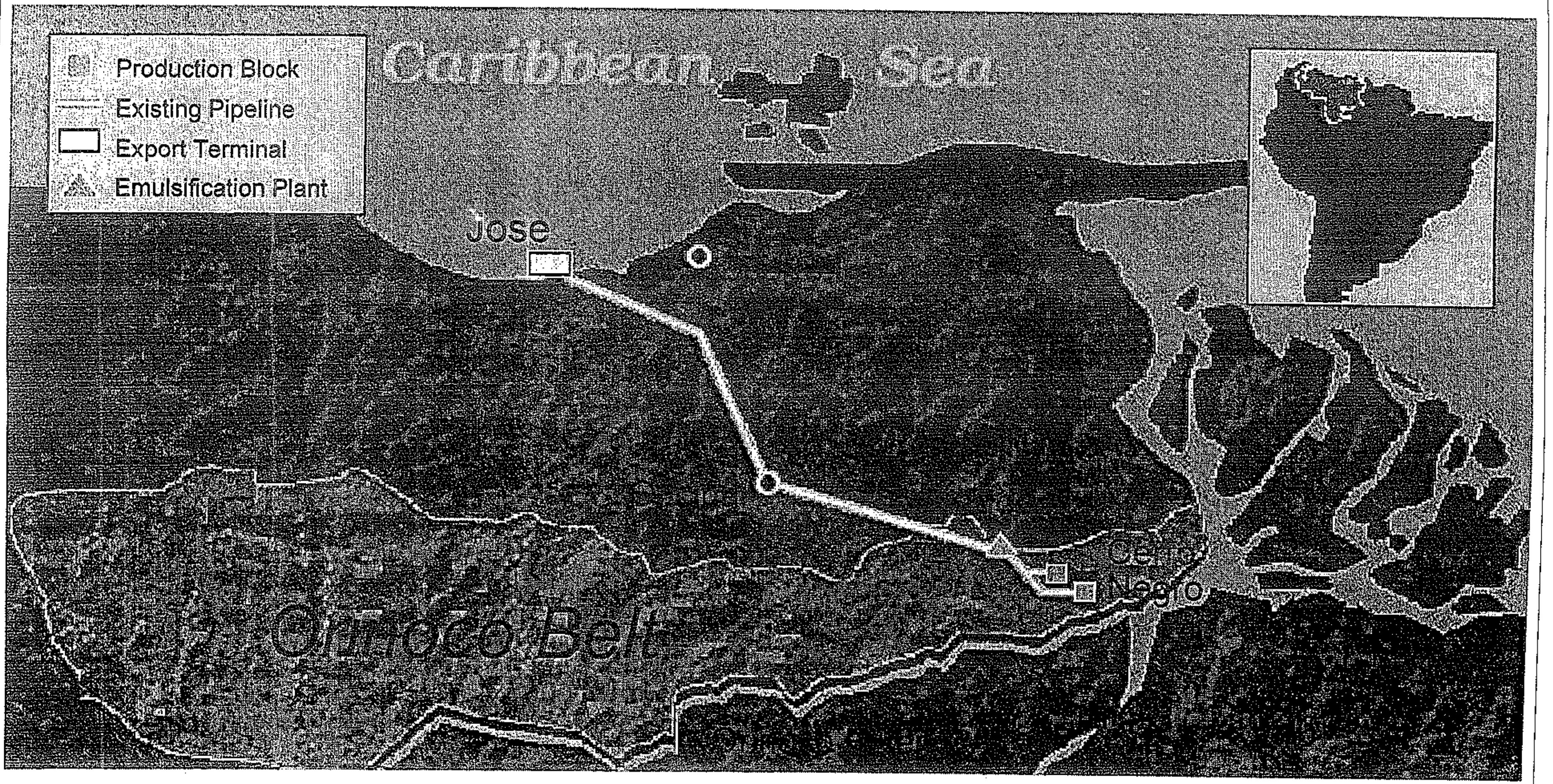
Geographic Location Orinoco Belt, Venezuela



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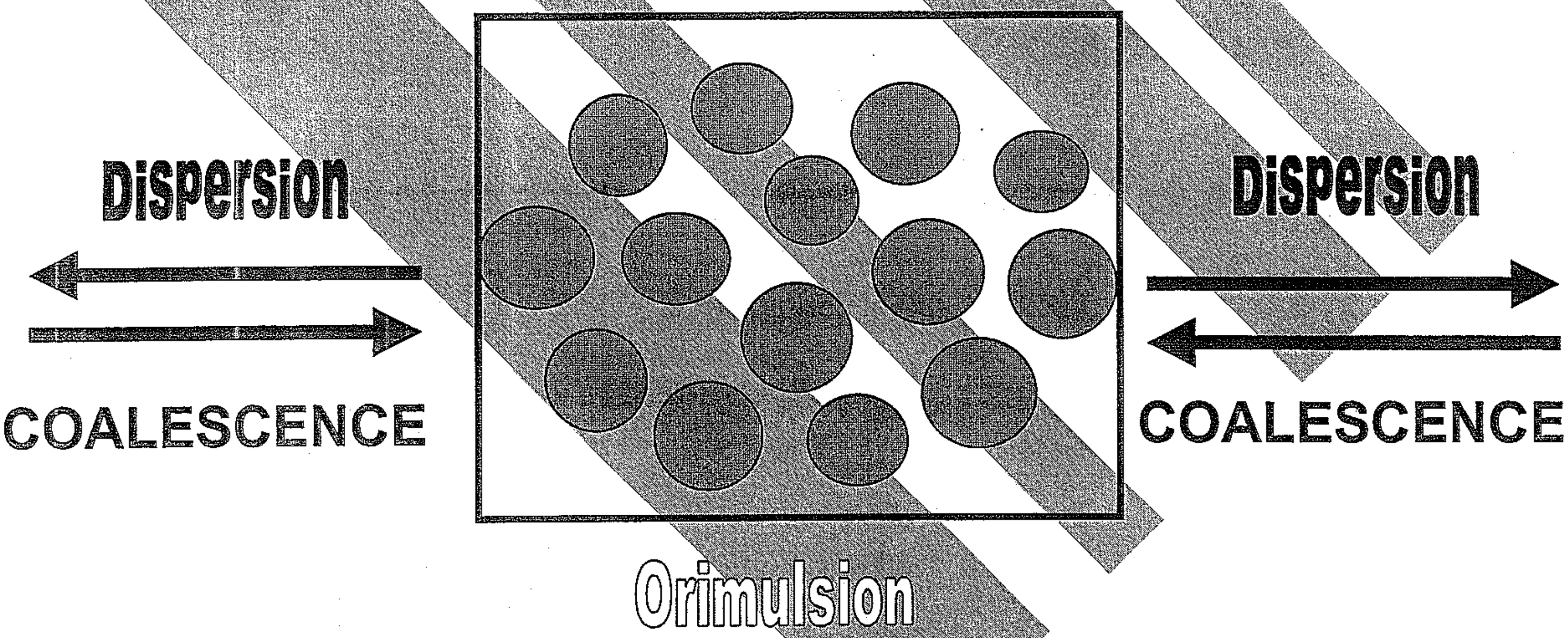
Dispersion
COALESCENCE
Orimulsion
Dispersion
COALESCENCE

Orimulsion®

Physical Spill Behaviour

As with any spill the precise behaviour is spill specific (size of spill, prevailing environmental conditions)

- On initial contact with water Orimulsion naturally self-disperses in the water column. This will be encouraged by currents.
- Some surface sheen may be observed.The sheen is very thin and can be broken up by wind / wave action.
- Some coalescence of bitumen droplets may occur under some circumstances in saline water and this may result in some surface tar balls, lumps, or patches of bitumen.

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Orimulsion Surfactant Package

⇨ **Alcohol Ethoxylates (AE)** are the most abundant class of non-ionic surfactants in terms of both production and consumption.

⇨ Most common application is in household laundry detergents i.e. “down the sink” continuous / long term discharges. “Industry standard”for NPE replacement.

⇨ The AE used in Orimulsion is a commercially available product similar to those used in baby shampoo - it is biodegradable and the metabolites are less toxic than the parent molecule and do not bioaccumulate / are non-persistent .

Orimulsion®

Orimulsion Surfactant Package

⇨ **Monoethanolamine (MEA)**, is a known emulsion stabiliser from the cosmetics/ pharmaceutical industries.

⇨ MEA has a low toxicity, is readily degradable and does not bioaccumulate

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PAH Concentration in Fuel Oil #6 and Orimulsion

(Adapted from: Ostazeski et al., 1997. Report prepared for Volpe National Transportation Systems by Battelle Ocean Sciences, Duxbury, MA)

Compound	Concentration (µg/g)	
	#6 Fuel Oil[b]	Orimulsion
acenaphthene	2270	10.6
acenaphthylene	554	nd
anthracene	1270	nd
benzo(a)pyrene	826	3.3
benzo(e)pyrene	617	6.4
benzo[b]fluoranthene	434	2.1
benzo[g,h,i]perylene	277	1.7
benzo[k]fluoranthene	71.3	nd
benz[a]anthracene	1160	nd
biphenyl	4230	5
chrysene	1830	6.8
dibenzofuran	204	5.4
dibenz[a,h]anthracene	153	nd
fluoranthene	1070	4
fluorene	3140	13.5
indeno[1,2,3-cd]pyrene	88	nd
naphthalene	9960	15.4
perylene	260	7.8
phenanthrene	7060	68
pyrene	3050	9.6

[a] No. 6 fuel data represents the average of three individual samples; Orimulsion data from a single sample.

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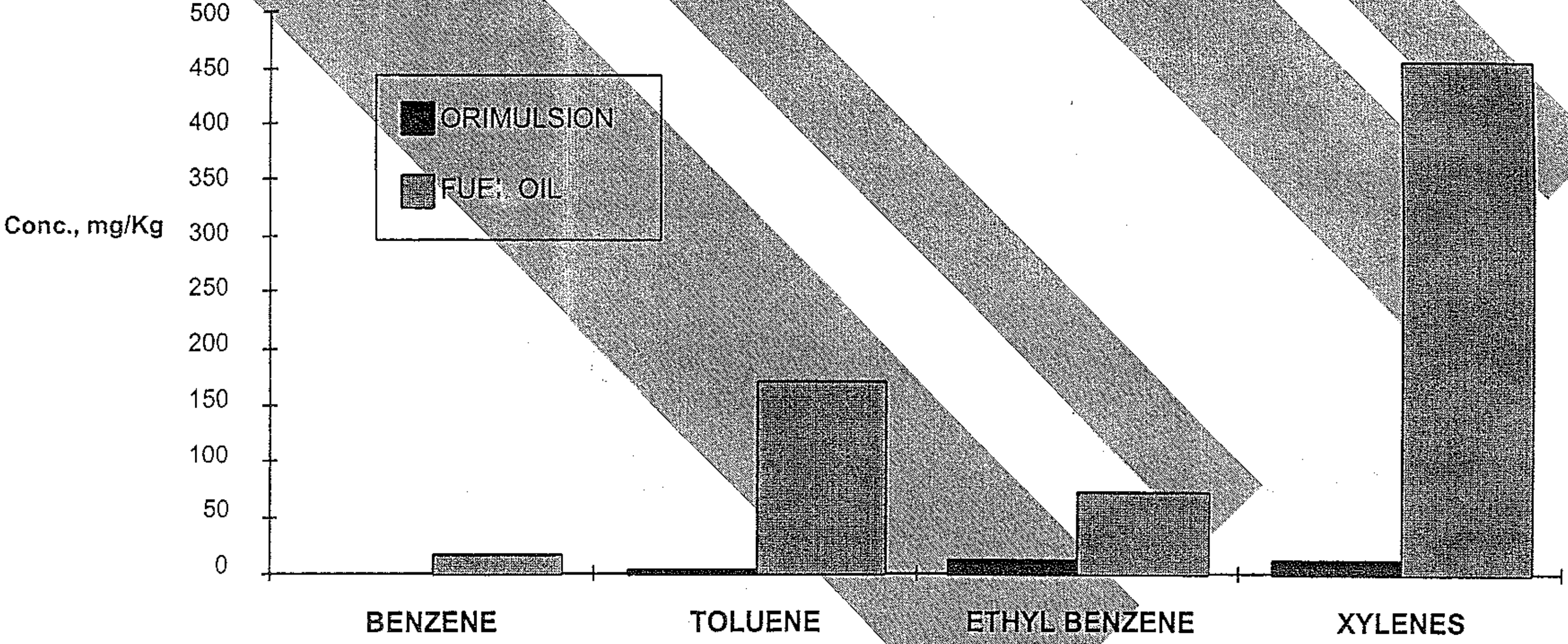
Orimulsion and Fuel Oil #6
BTEX Composition, EPA Method 8240
Source: Savannah Labs (94-95)



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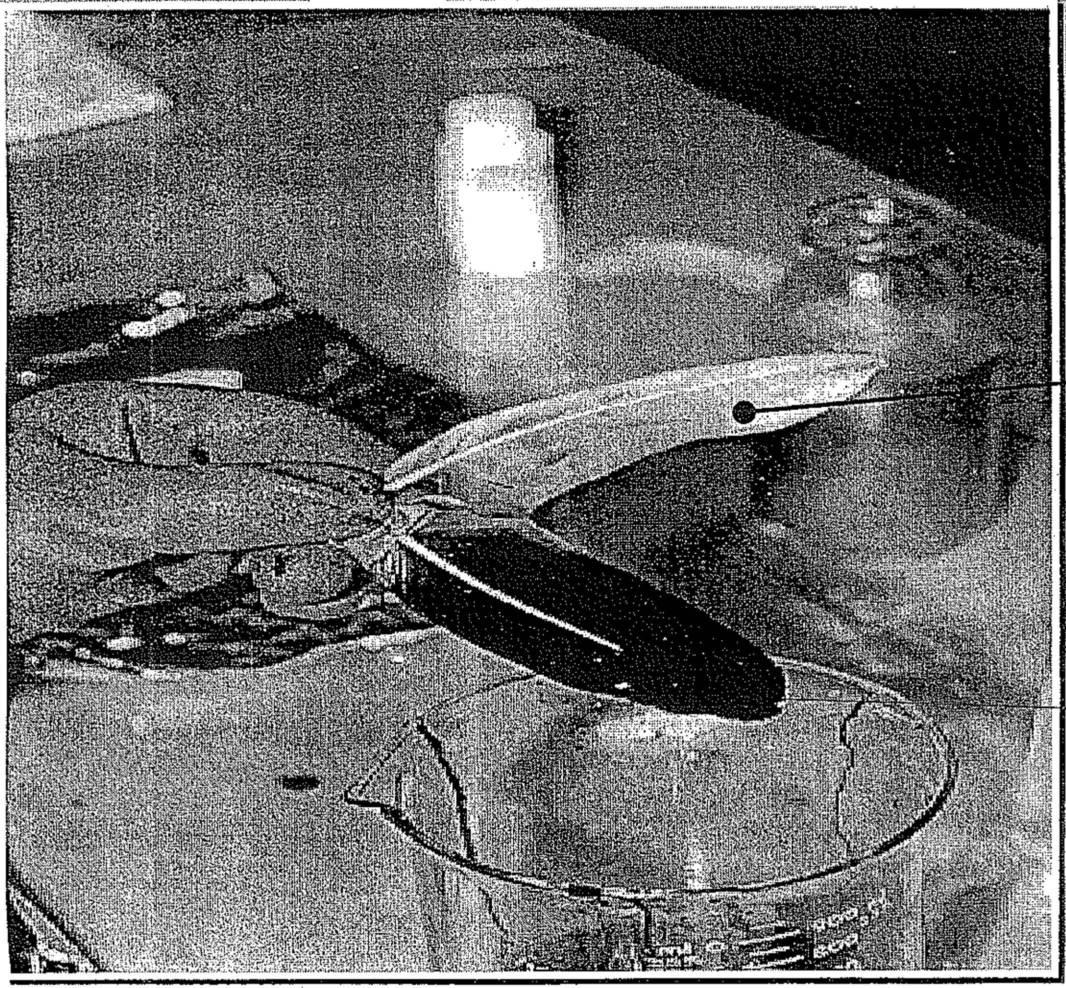
Bird Feather Tainting Orimulsion vs. Fuel Oil



Orimulsion

Fuel Oil

Orimulsion®

Detection / Monitoring

A particularly important part of the response strategy

- AEA Technology / Steptech Instruments test work - sub-surface dispersed Orimulsion detected and quantified using fluorometers (as per Sea Empress monitoring).
- Encouraging preliminary work using sonar to remotely detect sub-surface dispersed Orimulsion. Further work required.

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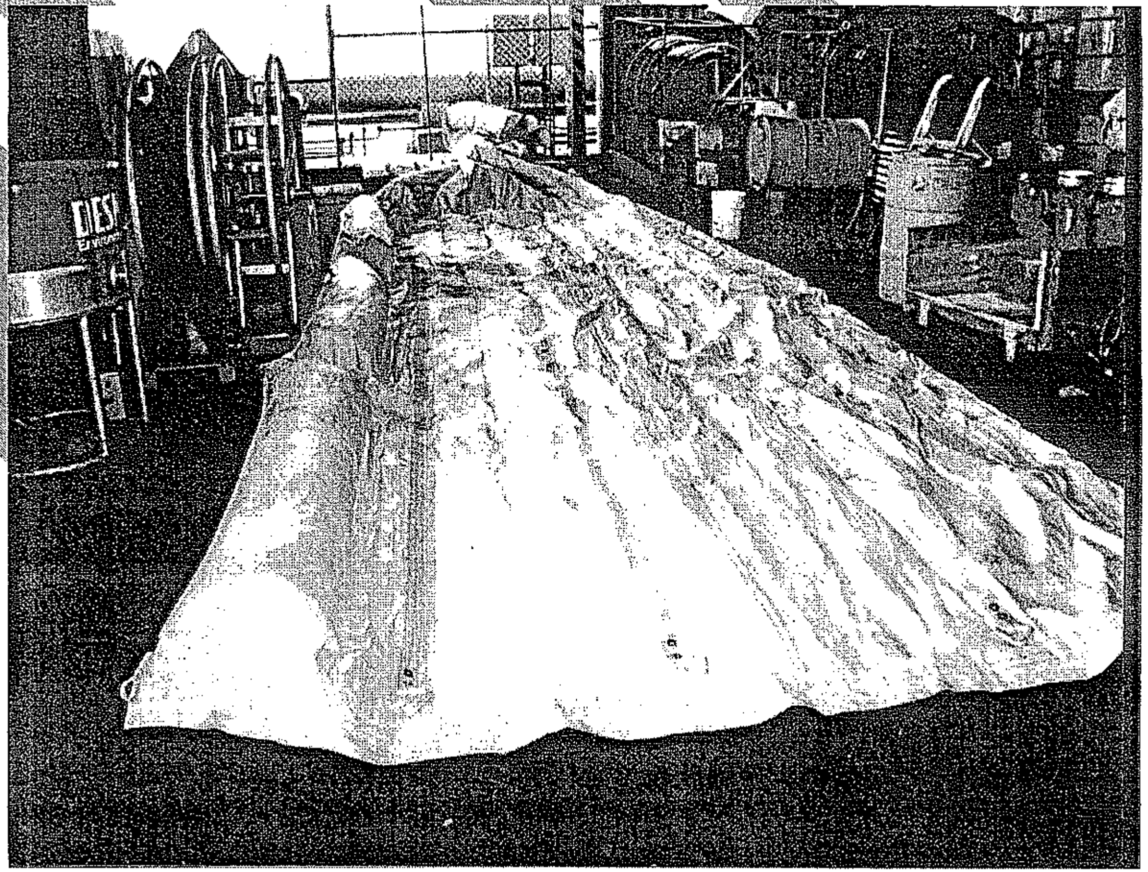
ORIMULSION Containment - deep skirted booms

JACKSON NET (U.K.)

CAPE CANAVERAL ORIBOOM (USA)



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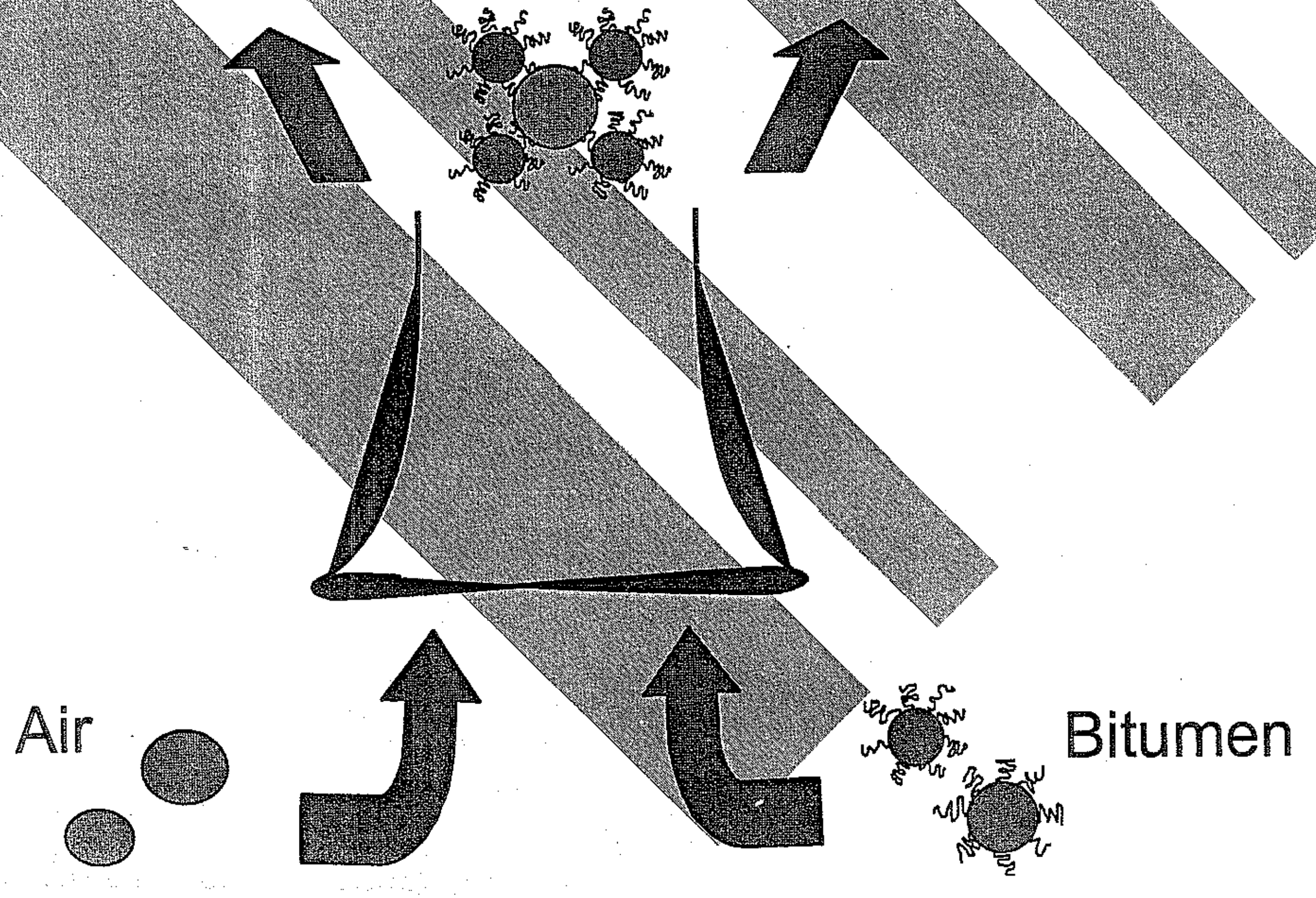
Orimulsion Spill Recovery Equipment ERE Skimmer and PNP Refloater

Orimulsion®

FORCED ADHESION AND FLOTATION - FAF



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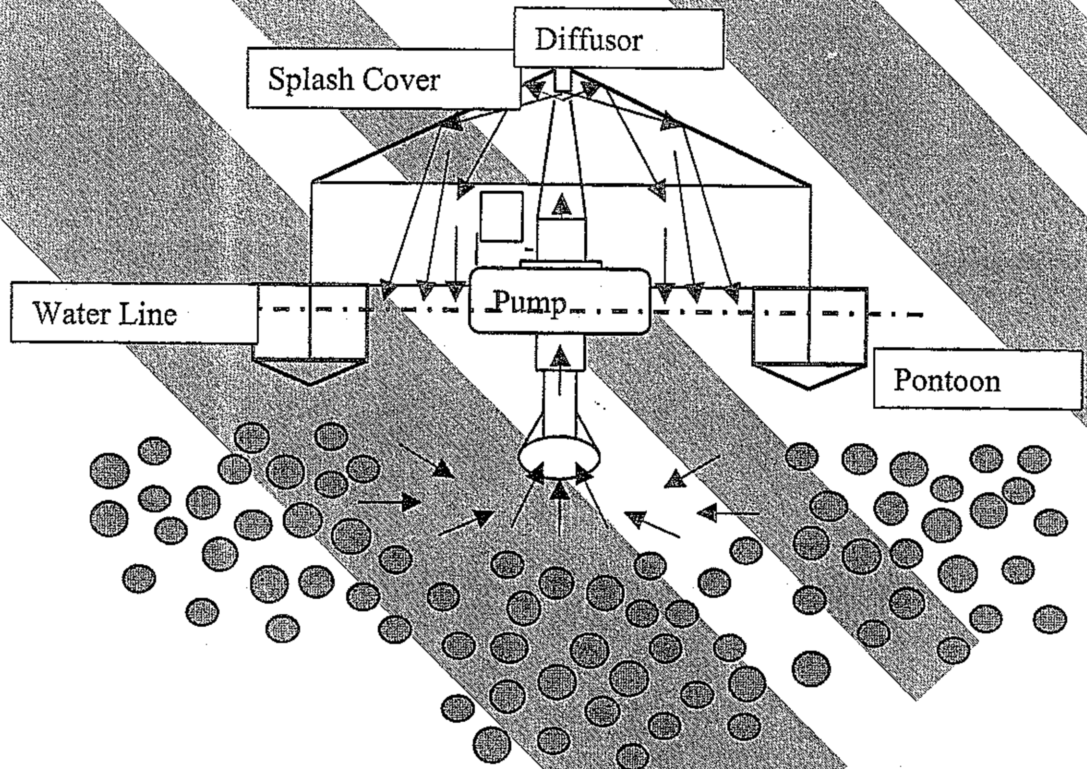
On Water Splash Reflotation - PNP Orimulsion Refloater



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Conclusions:

- A considerable amount of work has been undertaken over the past 11 years in terms of Orimulsion fate / behaviour, ecotoxicological properties and spill response (detection / monitoring, containment, recovery and clean up).
- All spills are different and within the generic term "oil" there are both similarities and differences between oils, and in comparison to Orimulsion.
- Bitor has tried to develop options and a "toolbox" for spill response. Always room to improve and do things in a better way - not Orimulsion specific.