BREAKING OF FRESH AND WEATHERED EMULSIONS
BY CHEMICALS

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ABSTRACT: *Oil discharged at sea can form water-in-oil emulsions that make pollution control more difficult. This paper deals with laboratory tests to evaluate the relative efficiency of different emulsion breakers under different conditions. The influence of mixing energy on phase separation rate is shown for a synthetic 75-percent-water emulsion formed with partially evaporated Arabian Light.*

A weathering experiment was conducted inside a floating system at the oil terminal of Antifer. The emulsion stabilization that makes emulsion breakers inefficient under ordinary conditions is measured by laboratory tests. On the basis of a laboratory study, it is shown that this phenomenon could be attributed to a low rate of photo-oxidation.

Techniques of using emulsion breakers in the field are discussed.

Finally, it is shown that when oil is left in the environment, an emulsion-breaking action is favorable to the degradation of oil.

Introduction

The formation of a water-in-oil emulsion, called chocolate mousse, is frequently observed after an accidental oil spill at sea. It causes a considerable increase in viscosity, thereby increasing the difficulty of pollution control operations. Offshore or on-shore pumping tends to become impossible with conventional pumps, dispersants become ineffective, and mixing sorbents with oil becomes very difficult. At the same time, since the volume of the pollution is multiplied by a factor of four or five, storage and transportation capacities must be increased considerably.

In the *Amoco Cadiz* incident, these difficulties appeared quickly. Research had begun shortly before that time, using laboratory tests to try to evaluate the effectiveness of different emulsion-breaking products on different types of emulsions. Some of these products were used in the field, in the gathering, and in the onshore transfer system. It was found that some effectiveness could be obtained in breaking emulsions provided that sufficient mixing was afforded. However, it was also found that 2 or 3 weeks after the accident, emulsion breakers became ineffective on aged emulsions at ordinary temperatures.

Research therefore was continued to determine the important parameters concerning the effectiveness of emulsion-breaking products and to examine weathering processes leading to the stabilization of emulsions.

Likewise, to the extent that oil appears to be relatively persistent in the natural environment when it is in the form of an emulsion, it would be interesting to examine its behavior in the presence of products having an emulsion-breaking nature.

Properties of water-in-oil emulsions

The breaking up of water-in-oil emulsions is an important process in the production and refining of crude oil. Therefore, a great deal of attention has been paid to it from a practical standpoint for a long time, although no clear explanation of the phenomenon from the theoretical standpoint has been found.

It was after the *Torrey Canyon* incident that the consequences of oil emulsification were first appreciated from the standpoint of its impact and the evolution of offshore pollution.

Berridge et al. (1968) showed that such emulsions can contain up to about 80 percent water, and found some correlation between the stability of emulsions and the asphaltene content of crude oil.

Later, MacKay et al. (1973) attempted to determine the nature of the asphalt compounds responsible for the stability of water-in-oil emulsions, and like Canevari (1969) they reached the assumption that each water droplet is encapsulated in an envelope having a plastic nature.

Measurements of the physicochemical properties of water/oil interfaces revealed the importance of the interfacial viscosity and of the film compressibility on the stability of emulsions (Jones et al., 1978).

The dynamic viscosity of fresh emulsions depends on several parameters:
- nature of the oil (chemical composition and viscosity)
- water content of the emulsion
- mode of formation (stirring energy)
- temperature.

For the present study, synthetic emulsions were created in the laboratory by the following process: in a 1-liter thermostat-controlled reactor equipped with a stirrer having two curved vertical blades 15 mm in width (so as to sweep 75 percent of the horizontal cross section) and rotating first at 500 and then at 1,000 rpm, synthetic seawater was added over a period of 20
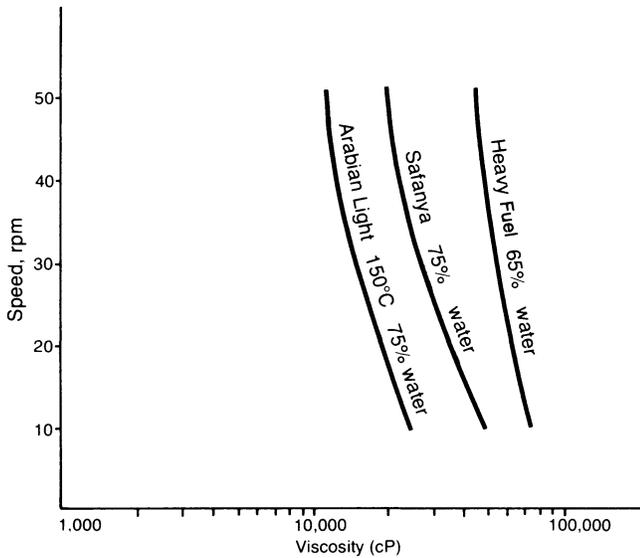
Figure 1. Brookfield viscosity of different emulsions at 20°C.

Proportioning pump
for emulsion breaker

Figure 2. Schematic of laboratory test of emulsion breakers.

minutes by means of a proportioning pump to 200 ml of oil. The mixture was then stirred for 90 minutes.

Figure 1 shows the mean viscosity values measured at 20°C with a Brookfield viscosimeter for emulsions containing different amounts of water and formed with Arabian Light topped at 150°C (AL 150), Safanya, and heavy fuel oil.

For the 75-percent water emulsion with AL 150, Table 1 gives the viscosities measured with a Rotovisco RV 12 viscosimeter.

Table 1. Viscosity (Rotovisco) of 75-Percent Water, 25 Percent Arabian Light 150°C Emulsion

Temperature, °C	Viscosity (cP) at shear rates	
	3.74 s^{-1}	1.87 s^{-1}
20	26,620	39,500
15	40,360	61,830
10	60,970	91,030

All these measurements show a plastic-type behavior for the emulsions, with viscosity decreasing as the shear rate increases.

For crude oils, the increase in viscosity becomes appreciable only beginning with water contents of about 60 to 65 percent.

More energetic stirring conditions may lead to more viscous emulsions, but the synthetic emulsions formed in the experimental conditions described above appeared to be sufficiently representative of emulsions formed in the natural environment.

Microscopic examination of synthetic emulsions with 75 percent water and formed with Arabian Light showed that the size of most of the water droplets was between 1 and 10 μm.

Under the experimental conditions described above, crudes with a low asphalt content, such as Nigerian Light or Zarzaitine (Algeria), do not form stable emulsions.

It must be noted that independent of its asphalt content, the high viscosity of oil may be the major cause of emulsion stability: according to Stokes law, the rate of sedimentation of the disperse-phase droplets decreases with increasing viscosity of the continuous phase.
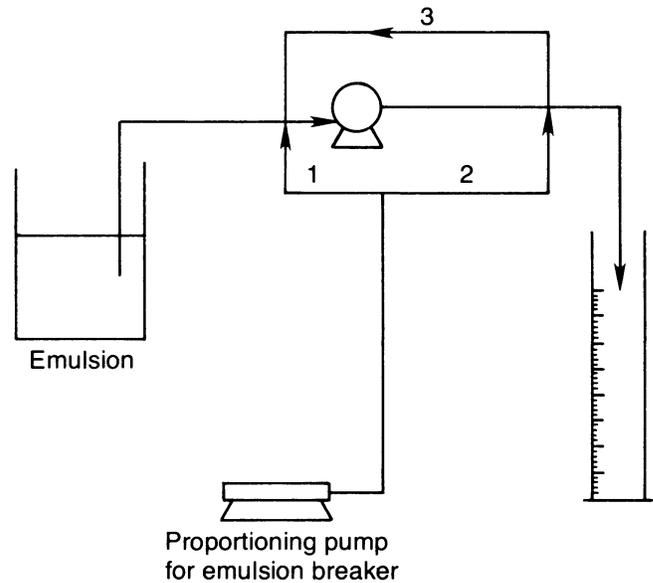
Breaking up emulsions in the laboratory

Description of laboratory test. Figure 2 shows the procedure used for measuring the effectiveness of emulsion-breaking products with regard to most of the emulsions.

An adjustable-throughput peristaltic pump was used to feed 100 ml of emulsion in the space of 1 to 2 minutes into a graduated test tube in which the volume of water separated was read as a function of time (Procedure I).

The demulsified product was injected by a proportioning pump whose throughput was adjusted as a function of the dose of product wanted.

Injection was either before or after the peristaltic pump (conditions 1 and 2), and the mixture could be subsequently recirculated through the pump (condition 3). These different conditions serve to test the emulsion-breaking product at various mixing-energy levels.

For emulsions that were too viscous to be sucked up by the pump, the test tube was preloaded, and the emulsion-breaking
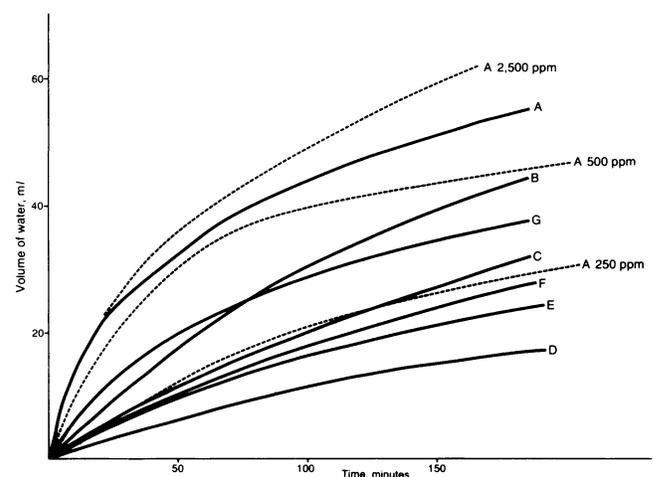
Figure 3. Emulsion-breaker test—Procedure I.1. AL 150°C 75% water. T=21°C. Emulsion breakers at 1,000 ppm except as indicated.
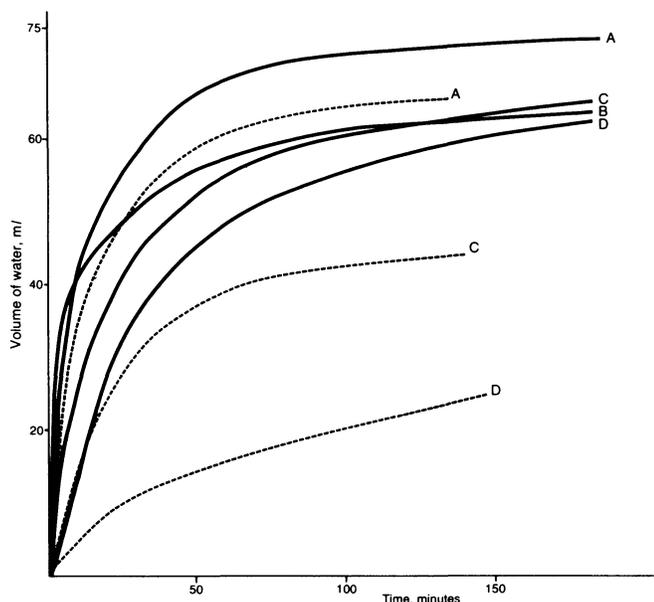
Figure 4. Emulsion-breaker test—Procedure I.2. AL 150°C 75% water. Solid line, T = 21°C; broken line, T = 12°C. Emulsion breakers at 1,000 ppm.

Figure 5. Emulsion-breaker test—Procedure I.3. AL 150°C 75% water. T = 20°C. Emulsion breakers at 1,000 ppm.

product was injected by a syringe along the entire height of the vertical axis; the mixture was then stirred by a propeller with four vertical blades rotating at 500 rpm for a given length of time, with the propeller being positioned at one-third and then at two-thirds of the height (Procedure II).

Effectiveness of emulsion breakers. Figure 3 shows the emulsion-breaking curves obtained at 21°C with Arabian Light 150°C containing 75 percent water, with different commercial formulations injected in doses of between 250 and 1,000 ppm according to Procedure I-1. Above 500 ppm, the gain in effectiveness is relatively slight.

When the products are mixed more effectively in the emulsion (Procedure I-2), a significantly higher phase separation rate can be observed (Figure 4). Procedure I-3 does not make for any appreciable improvement, considering the precision of the method, except for product A.

However, for the Safanya emulsion, which is more viscous than the Arabian Light emulsion, the more effective mixing achieved with Procedure I-3 leads to a much greater emulsion-breaking rate (Figure 5). When a gear pump is used behind the peristaltic pump so as to obtain even more energetic swirling (modified Procedure I-3), some products were also made more effective. For example, in the case of Arabian Light, the use of higher doses than 1,000 ppm does not make for much gain in effectiveness.

In all cases, the injection of an emulsion-breaking product immediately caused a considerable drop in the viscosity of the emulsion, before any phase separation. As an example of this, for the emulsion of AL 150 with 75 percent water treated with 1,000 ppm of product A according to Procedure I-2, the viscosity of the emulsion measured at 20°C at the pump outlet by a Brookfield viscosimeter was 5,400 cP at 10 rpm.

These results reveal the need to maintain effective swirling so as to obtain a high separation rate in 20 to 30 minutes. The effectiveness scale observed with the different products can be seen to narrow when more effective mixing is obtained. For a low mixing-energy level, greater selectivity appears, reflecting the
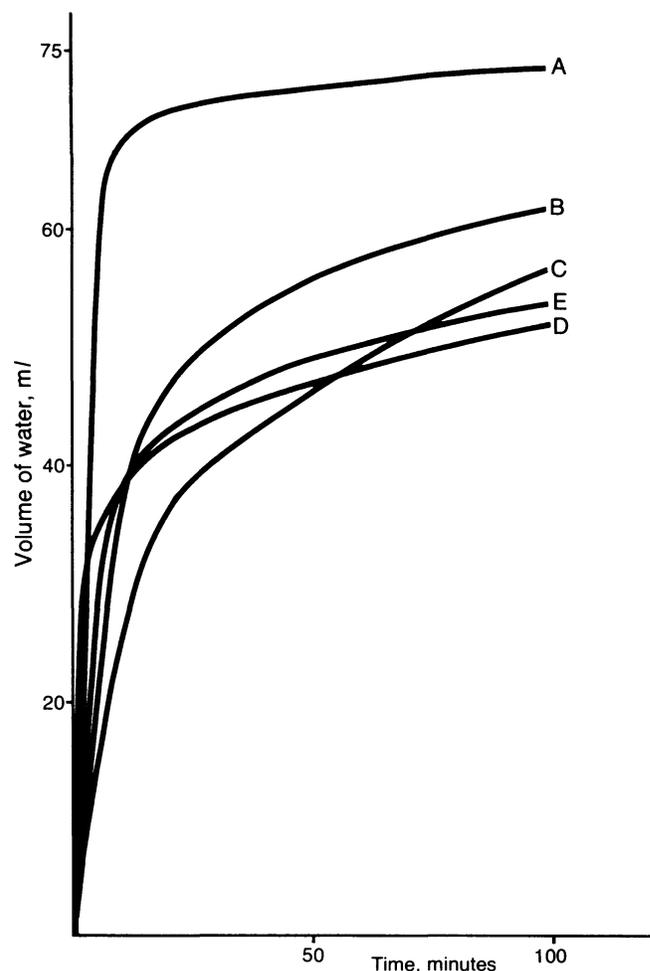
intrinsic effectiveness of the different products on the deformation of the envelope around each water droplet.

On the other hand, when mixing is very effective (Procedure II), most of the products succeed in almost completely separating the phases in less than 5 minutes. However, it should be pointed out that these extreme conditions are not representative of actual conditions of use.

The fact that various inversions were observed in the effectivity scale of the products, depending on the nature of the oil, suggests that in practice the prior selection of emulsion breakers must be made on the basis of mean effectiveness.

In the case of the Arabian Light emulsion, a marked selectivity of the products was found, even using Procedure I-2, when the entire operation was performed at 12°C (Figure 4).

Aqueous-phase analysis. For an Arabian Light 150°C emulsion with 75 percent water, treated with 1,000 ppm of different products according to Procedure I-1, the aqueous phase was analyzed after different settling times, using the Total Organic Carbon (TOC) measurement (Dohrmann apparatus), and the hydrocarbon content was determined by infrared spectrography of the carbon tetrachloride extract chromatographed on Florisil.

Table 2 shows that, except in the case of Product F, the contents after complete settling are comparable. As a first approximation, it can be estimated that 20 to 25 percent of the demulsified products pass into the aqueous phase.

Table 2. Aqueous Phase Analysis After Settling

	TOC (ppm)		HC (ppm)
Product	After 1 hr	After complete settling, 24 hr	After complete settling, 24 hr
A	240	140	16
B	290	225	14
C	305	170	12
D	150	115	15
E	295	165	27
F	520	750	95

With regard to the discharge of the aqueous phase into the natural environment, products will have to be selected that result in only moderate toxicity of the discharged water. An approved procedure must thus include a toxicity test. No such test has been defined.

Formation and aging of emulsions in the natural environment

To evaluate the validity of laboratory tests with synthetic emulsions and to determine the influence of various factors on the stabilization of emulsions aged in the natural environment, an experiment was performed from March 1979 to February 1980 in the oil terminal port of Antifer (Le Havre).

Inside a 26-m² floating metal enclosure (Figure 6), 400 liters of Arabian Light were poured in March 22, 1979. The oil layer was about 15 mm thick.

Samples were taken after 1, 2, 3, 6, and 10 weeks, and 5, 6, 7, and 11 months. The temperature of the water varied between 6°C in winter and 19°C in summer.

For each sample, Table 3 gives the water content of the emulsion and the evaporation rate deduced from the weight percent of the IBP-340°C fraction.

It can be seen that the evolution observed inside the enclosure subjected to moderate stirring should be much faster than in an open environment with a thin oil layer.

A demulsion test was performed on each sample at 20°C with 1,000 ppm of product A taken as a reference, using Procedure I-1.

Progressive stabilization was observed (Figure 7), and on and after September 12, 1979, none of the products tested were able to cause the slightest phase separation.
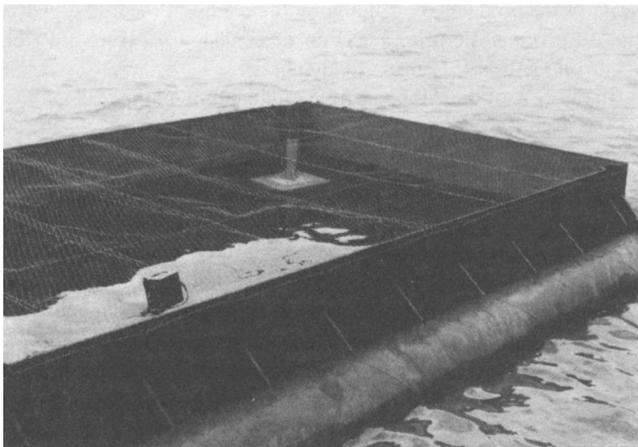
Table 3. Analysis of Samples From Antifer Experiment During 1980

Parame- ter, wt%	Mar. 29	Apr. 5	Apr. 15	May 3	June 3	Aug. 9	Sept. 12	Oct. 25	Feb. 22
Water	76	78	73	79	75	67	65	67	68
PI-340°C	28	23	25	25	11.5	12.5	11	10	9
Evap.	29.5	33.8	32	32	42.4	41.7	42.7	43.4	44

On February 20, 1980, a series of tests was performed on the emulsion. The demulsion tests performed at 20°C using Procedure I-3 gave no separation with any of the products at doses of between 1,000 and 4,000 ppm. Only Procedure II, in particular with 4,000 ppm of product B, showed a 50-percent water salting-out rate in 5 hours, provided stirring was performed at 500 rpm for 1 minute every hour. A similar result was obtained at 50°C with products A, B, D, E, and G with only two periods of stirring.

The stabilization of the emulsion apparently cannot be attributed to the increase in its viscosity. Indeed, the measurement of the viscosity of the emulsion with a Brookfield viscosimeter on February 20, 1980, gave the following results at 20°C: 24,000 cP at 10 rpm, 11,000 cP at 20 rpm, and 2,800 cP at 50 rpm. These are considerably lower values than for the synthetic emulsion of Arabian Light 150°C and 75 percent water.

This conclusion is reinforced by the following observation: since for the emulsion dated February 20, 1980, the oil phase approximately corresponded to an Arabian Light 310°C residue, a sample of this emulsion was refluxed with an Arabian Light 150–310°C distillate so as to reform an emulsion containing Arabian Light 150°C whose viscosity measured at 20°C by a Brookfield viscosimeter was 1,600 cP at 10 rpm. It proved impossible to break up this emulsion at 20°C with any of the products tested, using Procedures I-2 or II.

It can be seen, however, that the refluxing of a synthetic emulsion does not bring about any marked destabilization. An emulsion of Arabian Light 310°C with 70 percent water (Brookfield viscosity of 160,000 cP at 10 rpm) refluxed with 35 percent, compared with distillate 150–310°C residue (viscosity of refluxed emulsion at 20°C = 23,500 cP at 10 rpm), is broken up only very slightly by the products tested, using Procedure I-2.

On the contrary, a synthetic emulsion with 75 percent water, made from Arabian Light 150°C reformed by refluxing a 310°C

Figure 6. Antifer experiment—floating enclosure.
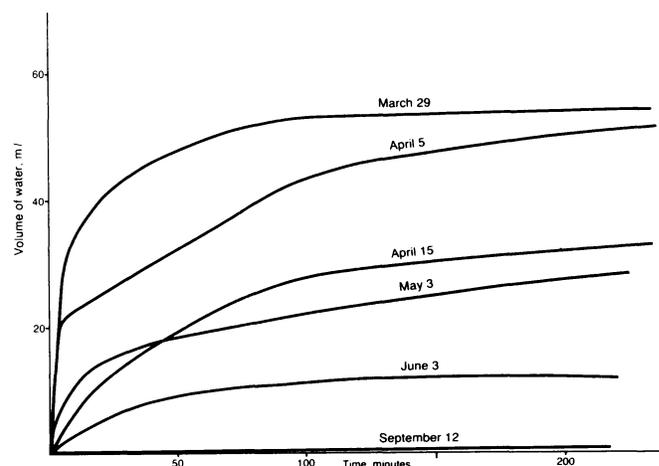
Figure 7. Antifer experiment—stabilization of emulsion.

residue, although more viscous (99,000 cP at 10 rpm), is broken up by the products tested, using Procedure I-2, but with a slower rate than the one measured in the reference test.

An emulsion with 68 percent water was formed in the laboratory with "Antifer" residue obtained by distillation from the sample taken on February 20, 1980, and refluxed with 35 percent distillate to reform Arabian Light 150°C. This emulsion (viscosity 8,600 cP at 10 rpm) proved to be stable under the same conditions as above.

Therefore, under the standard conditions retained for the emulsion aged in the natural environment, characterized by an average water droplet size of about 1 μm (Figure 8), the stability can be caused only by the intervention of other phenomena.
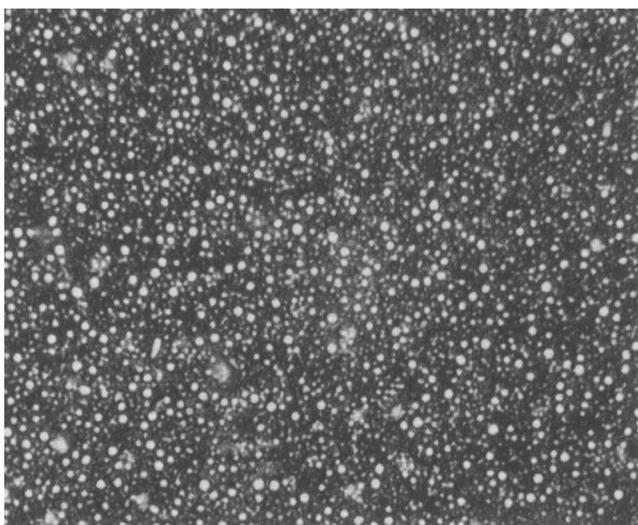
Figure 8. Photograph of "Antifer" emulsion (February 20, 1980).

The stabilization of sediments by microparticles is a plausible hypothesis in the present case because of the presence of calcareous rocks on the coast at the experimental site. A method was developed (washing, centrifuging, filtering) to determine the amount of calcareous and siliceous sediments in the emulsion. The emulsion dated February 20, 1980, contained 0.6 percent (1.4 percent compared with the oil) of sediments having particle size between 20 and 100 μm. An analysis is being made to evaluate the evolution of the sediment content and its possible influence on the stabilization of emulsions.

The formation of oxygen compounds with a surfactant nature by the biological or photo-oxidized degradation of hydrocarbons may have a stabilizing effect on emulsions. The accumulation of compounds of natural origin in the emulsion may also result in the same effect.

In the experiment performed at Antifer, a C=O band at 1,710 cm^{-1} was observed by infrared spectrography; it was particularly intense in the sample taken on May 3, 1980. However, this phenomenon might be caused by a phytoplankton bloom occurring at the same time because the intensity of the IR band decreased afterwards before again rising on February 20, 1980, to a level corresponding to an appreciable concentration of oxygenated product characterized by the ratio of optical densities relating to C=O (1,710 cm^{-1}) and CH$_2$ (1,460 cm^{-1}) OD (CO)/OD (CH$_2$) = 0.42.

Effect of photo-oxidation. In an attempt to determine the effect of oxygenated products eventually formed in a weak concentration by photo-oxidation, a series of laboratory tests was performed involving an irradiation of a layer of crude oil (mean thickness, 0.3 mm) by using a fluorescent lamp emitting in the solar ultraviolet and the violet (between 300 and 450 μm with a maximum at 365 μm).

The Arabian Light 150°C thus irradiated for 132 hours showed a concentration of oxygenated products corresponding to OD(CO)/OD(CH$_2$) = 0.08.

After refluxing the residue resulting from a partial evaporation (28 percent) to essentially re-create a 150°C topped Arabian Light, an emulsion with 75 percent water was formed and then subjected to the breakup test with 1,000 ppm of product A, using modified Procedure II with small volumes of emulsion. For Zarzaitine 150°C (a crude with very little asphalt) irradiated up to an oxidation rate defined by OD (CO)/OD (CH$_2$) = 0.07, the emulsion made with unoxidized oil is very unstable whereas the emulsion made with the photo-oxidized oil is particularly stable.

Conclusion. The stabilization of emulsions by aging at sea or on the coast may partly be caused by the increase in viscosity as the result of evaporation but is mainly caused by changes in their composition.

Whereas the influence of microparticles incorporated in the emulsion remains to be cleared up, it appears that the products of photo-oxidation, even at very low concentrations, are liable to cause a considerable stabilization of emulsions. Research is being pursued to investigate the impact of products resulting from the biodegradation of hydrocarbons.

Techniques of implementation in the field

During the coastal cleanup operations after the *Amoco Cadiz* incident, several emulsion breakers were used, first in the open intermediate storage tanks located near the shore, and then injected directly into the mobile vacuum tanks used to pump the emulsion from the beaches. Although these two operational methods served to speed up the transfer of pollution by reducing the viscosity of the emulsion and partially breaking it up, however, they did not provide sufficiently effective swirling to quickly separate a large portion of the water.

To make more effective use of emulsion breakers, they must be injected on-line upstream from the pump at a flow rate that is adjusted as a function of the pumping throughput.

In France, the Total Company has developed a simple system that acts as a static mixer and can be attached to the suction system of vacuum tanks.

A similar system has been designed to be adapted to various flexible offshore storage tanks.

Likewise, consideration can be given to the direct spreading of emulsion breakers on offshore emulsion slicks to increase the efficiency of skimmers. However, preliminary tests performed in the laboratory, with slight stirring, have shown that the emulsion breaking action is very slow under such conditions. Research is being done along these lines to evaluate this technique.

From what has been said above, it should be clear that a better understanding must be gained of the aging phenomena of emulsions so as to try to adapt emulsion breakers to the breaking up of stabilized emulsions.

Biodegradation of mousse

After the *Tanio* oil spill, mousse floating on sea water was collected and studied in the laboratory by measurement of the oxygen consumption (Voith Sapromat) after adding mixed microbial culture adapted to fuel oil and after providing mineral salts as nitrogen and phosphorus sources. No activity was detected during the first 200 hours. On the contrary, another sample of the same mousse, treated with 1 percent w/w of a surfactant H in the flask for oxygen consumption, gave a positive reaction that could not be attributed to the surfactant itself (Figure 9). Microscopic observation of the untreated sample did not show any bacteria or fungi in the water droplets included in oil. This observation should be compared with a previous one related to the free water phase collected under mousse weathered in agitated buckets (Barridge et al., 1968). During the initial microbial activity on a whole crude oil before any appreciable degradation, the metabolic products enhance the formation of oil-in-water emulsions and therefore enhance microbial growth.
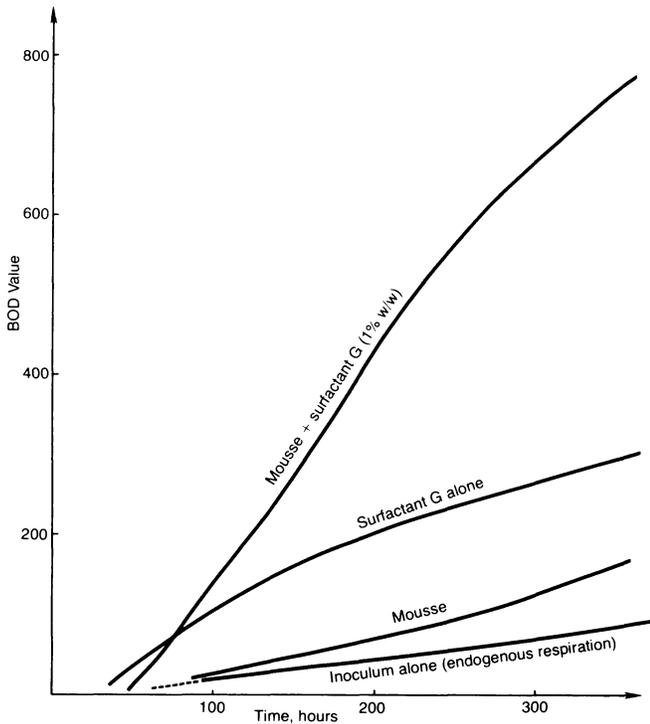
Figure 9. Oxygen consumption measured under agitation in artificial sea water supplemented by nutrients and inoculated.

However, the degradation of weathered crudes and No. 6 fuel oil may follow different pathways yielding less extensive conversion of the petroleum. Because of the oil distribution, even in the presence of available nutrients and oxygen, mousse trapped in sediments or beach sand can be isolated and preserved indefinitely. Treatment in place by surfactant H releases oil which is degraded by aerobic microbes, although less rapidly than in the water column. By following the rate of oxygen consumption (Gilson differential respirometer) and hydrocarbon balance to corroborate the degradation, we can observe that bacterial activity is in direct

ratio to the amount of oil available (Figure 10). Further experiments will establish relationships between HLB values and surfactant effects on conditioning the oil in place for promoting the degradation of a spill reaching sandy coasts.
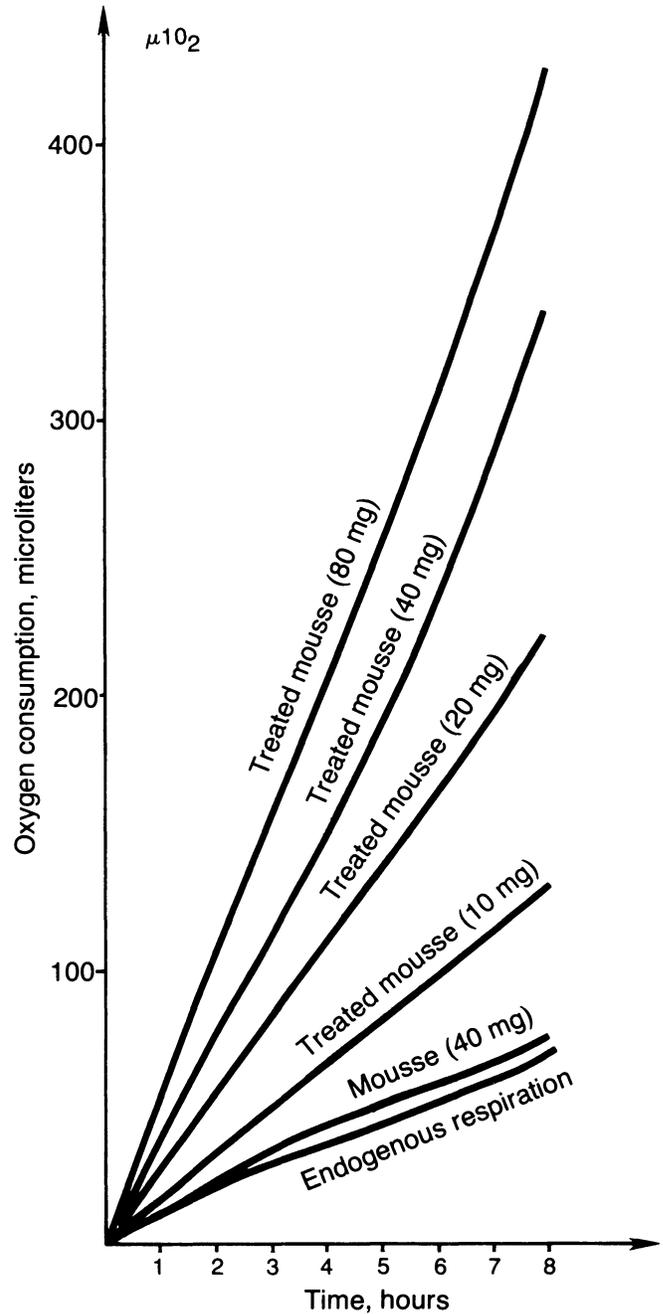
Figure 10. Respiratory activity of marine beach sediment with different quantities of treated mousse.

Conclusions

The laboratory tests that were studied can be used to evaluate emulsion-breaking efficiency under different mixing conditions.

The efficiency scale obtained with fresh emulsions is roughly conserved but can partially depend on operating conditions.

These results may be useful in the application of emulsion breakers in the field.

Weathered emulsions can be so stable that current emulsion breakers are ineffective at ordinary temperature. Emulsion stabilization can be caused by photo-oxidation but other phenomena can also be involved.

When mousse has formed, oil is more persistent in the environment. The use of emulsion breakers can promote the biodegradation of oil.

Acknowledgments

References

Berridge, S. A., M. T. Thew, and A. G. Loriston-Clarke. 1968. "The formation and stability of emulsions of water in crude petroleum and similar stocks." *Journal of the Institute of Petroleum*, **54**(539), pp. 333–353.

Canevari, G. P. 1969. "General Dispersant Theory." In *Proceedings of the 1969 Joint Conference on Prevention and Control of Oil Spills*, American Petroleum Institute and Federal Water Pollution Control Authority, New York, pp. 171–177.

Jones, T. J., E. L. Neustadter, and K. P. Whittingham. 1978. "Water-in-crude oil emulsion stability and emulsion destabilization by chemical demulsifiers." *The Journal of Canadian Petroleum*, April–June, pp. 100–108.

Mackay, G. D. M., A. Y. McLean, O. J. Betancourt, and B. D. Johnson. 1973. "The formation of water-in-oil emulsions subsequent to an oil spill." *Journal of the Institute of Petroleum*, **59**(568), pp. 164–172.