CHAPTER 2

OIL AND DETERGENTS

On the Cornish beaches about 10000 tons of detergent fluids were used to treat about 14000 tons of crude oil. What were the properties of these two major pollutants?

It might have been supposed that a cut-and-dried answer could be given at least with regard to the physical and chemical properties of the oil, and that, although information might not be made public for trade reasons, it would be available also for the properties of the detergent components. This was, however, far from true. Moreover, little was known of the probable biological effects either of crude oil or of detergents.

The brief account in this chapter depends partly on the information kindly supplied by British Petroleum (Trading) Ltd (BP) and detergent manufacturers, and partly on the results of simple and often empirical tests in the Laboratory, prompted by field observations.

THE OIL

Kuwait crude oil is a dark-brown liquid smelling like diesel fuel and having the consistency of heavy engine oil. It is a complex mixture of hydrocarbons containing appreciable quantities of sulphur and traces of metals such as nickel and vanadium.

After it is discharged on the sea, crude oil undergoes a series of changes over a period of months. At least this can be said, but it is not yet possible to give a confident account of what exactly happens to an oil-spill that remains at sea. In the absence of artificial treatments its probable fate may be assessed by reference to its physical properties.

Table 1 shows the composition of Kuwait oil (specific gravity 0·869) in terms of boiling-point fractions. From this it may be inferred that the oil will lose about 25 per cent of its volume by evaporation within the first few days. Evaporation continues at a progressively diminishing rate for some weeks, during which the oil is further eroded by photo-oxidation and bacterial degradation. If the oil stays at sea for three months or more there should theoretically remain persistent asphaltic residue representing perhaps 15 per cent of the original amount. Similar residues collect on the sides and bottoms of the storage tanks of tankers, and in the fuel tanks of oil-burning ships. The black tarry lumps, now all too familiar on British shores, are normally derived from the latter source, but occasionally they may

Table 1. *Composition of crude oil in terms of boiling point of fractions*

Fraction	°C	Loss of wt (%)	Loss of vol. (%)	Specific gravity at 15·5 °C of residue
1	Up to 100	9·0	11·8	0·895
2	Up to 200	13·0	27·7	0·9255
3	Up to 300	38·1	43·6	0·955
4	Up to 400	53·1	58·5	0·983

represent the end-product of weathered crude oil. Indeed, N. K. Adam (1935), in a pioneer investigation of the oil-pollution problem on our coasts, and to whose account we still have to turn for a picture of the fate of oil at sea, believed that refined fuel oil, if remaining at sea, would ultimately end as a residue of small aggregated asphaltic lumps. Adam, having conclusively shown that the world's oceans had not acquired a continuous molecular film of oil, gave a coherent explanation in physical–chemical terms of how oil was steadily disappearing. It is curious that he gave no consideration to the possible role of bacteria in helping this degradation, though Orton (1924) had already appreciated that the weathering of floating oil involved bacterial decay. The importance of bacteria is now, of course, well recognized (see ZoBell, 1963); but many aspects of the changes crude oil may be expected to undergo after release on the sea surface are still obscure. Research on this problem is urgently needed.

In practice the actual time course of the degradation processes must be influenced by several environmental factors including temperature, wind, wave action, thickness of the oil and its degree of dispersion; but perhaps the most important factor is the tendency of the oil to form emulsions with sea water. Such emulsion may be oil-in-water (as is milk) or water-in-oil (as is butter), and the emulsification so modifies the physical properties of the oil as to render unreliable most predictions of the life of oil at sea. The oil from the 'Torrey Canyon' certainly formed water-in-oil emulsions of variable composition, and it is this which accounts for the thick consistency and variable colour, quite unlike the original, of the oil masses observed at sea and on the Cornish beaches (Plates 3A, 6C, 7A, B, C, 13A, 14A, B). Attempts in the laboratory to reproduce these water-in-oil emulsions by shaking with sea water, or by exposing oil and sea water in open containers out of doors for several days, all failed. Oil vigorously shaken with sea water immediately settled out, re-forming a layer of the same thickness as at the start. It remained the original very dark colour in all experiments. However, the chocolate-coloured type of stranded oil could be imitated by adding a little detergent (BP 1002) to the mixture.

The water-in-oil emulsion may contain up to 80 per cent water. It follows that whereas the mass of oil may be appreciably reduced by evaporation after a period at sea the bulk of the emulsified material may yet exceed that of the original oil. It is also noteworthy that as evaporation proceeds the mass of oil not only diminishes but its density increases (Table 1). This has practical consequences when attempts are made to sink the oil by application of dense powdered material. A sample of emulsion taken from the Bay of Biscay on 18 May (some 50 days after release) by R.V. 'Sarsia' contained 50 per cent sea water and the specific gravity of the oil fraction was 0·97. This corresponds to a loss of about 50 per cent of the original oil, the specific gravity of which is 0·869 at 15·5 °C (cf. Table 1). The French navy were successful in sinking oil emulsions of this kind by applying powdered chalk (Chapter 9), but to have sunk the same oil soon after release would have required six times as much chalk.

In the seas around Cornwall and on the Cornish beaches the principle of the cleansing operation was, in essence, to convert the viscous water-in-oil emulsion to a milk-like oil-in-water emulsion (Plates 4 A, 5 A, 10 A, 22 A, B, 23 A, B, 28 C) and so allow it to disperse in the great bulk of the sea.* This was achievable by treating the water-in-oil emulsion with detergent (Plate 5 A) followed wherever possible by mechanical agitation. However, the emulsions were not readily formed under the conditions that obtained, and even when they were produced they were apt to be unstable (p. 21). Oil separated from unstable emulsions by floating upwards, just as the cream settles out on top of milk (Plate 1 A, B). This oil, as seen in shallow shore pools, or in laboratory vessels, was black and fluid, much as it originally had been in the tanker. When separation occurred in the sea just offshore under different conditions a paler colour was typical (Plate 6 A). Observations on the North Cornwall coast, in particular, showed that some of the oil very soon separated from detergent emulsions and that only a proportion could have been dispersed effectively. Aided by onshore winds the separated oil returned, either in a liquid condition or mixed with fine sand and fragments of seaweed, leading to secondary pollution (Plates 3 B, 6 A, B, 13 B). Even as early as April oil masses weighted with sand were observed on the sea bed (Plate 6 C).

Elsewhere in this report the water-in-oil emulsion which polluted the beaches is usually referred to as 'oil' and when reference is made to

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* Dispersal in the sea, if effective, implies (1) that the small particles into which the oil is split are so scattered that they will not re-aggregate, and (2) that the oil is thus converted to the best possible state for attack by oil-consuming bacteria, which will eventually destroy any that has not evaporated. Thus the most ideal detergent cannot of itself destroy the oil.

emulsification it applies to the formation of a dispersible oil-in-water emulsion, unless otherwise stated.

Floating oil is not a serious hazard to marine life in the open sea save in the case of birds, thousands of which have died as a result of contact with oil from the 'Torrey Canyon'. Oil deposited on the coast is, however, severely damaging to coastal amenities and may affect shore animals by smothering them. Nevertheless, we were surprised how well such conditions could be tolerated and survived by many shore animals. Limpets, for example, were found to recover completely even after they had been left under an apparently continuous oil layer (Plate 9B). Indeed, limpets have been observed to be grazing on rocks coated with weathered oil, ingesting it without noticeable harm (Chapter 4; Plate 9C). No actual toxic effects of the oil have been noted either in shore or pelagic animals. Several intertidal algae survived after oil had settled on their fronds. In the splash-zone the lichen *Xanthoria* proved able to survive under a hardened oil layer (Plate 18C).

Stranded oil sticks all too readily to surfaces, offering considerable resistance to the force of waves and hoses. After settling, the oil layer becomes appreciably thinner, as it loses contained water and its own more volatile fractions. At the same time the oil becomes darker, whatever its original shade of brown, and eventually quite black. Typical examples of the blackened strand lines could be seen on granite boulders of the Land's End area, and around Hayle Estuary, where the oil had been left untreated. Plate 27 shows oil-blackened shores in Guernsey and Brittany.

DETERGENTS

Detergents are classified as ionic and non-ionic. Ionic detergents readily dissociate in solution and the effective portion may be positively (cationic) or negatively (anionic) charged. Non-ionic detergents, on the other hand, do not dissociate in solution to any significant degree.

The bulk of detergents used to deal with the 'Torrey Canyon' oil were non-ionic. When they were used no froth was produced, as so frequently with the more familiar household detergents. Household detergents release oil or grease from soiled articles by altering the surface tension of the oil so that it is no longer firmly held. Slight mechanical agitation will then dislodge the oil or grease, drops of which become dispersed in the form of an emulsion. It is not necessary for the emulsion to be stable, since it is normally quickly removed by rinsing.

However, for treatment of oil at sea, or on beaches, a stable emulsion is needed so that the oil may be more effectively dispersed. Some experiments on the stability of detergent–oil emulsions are described later in this section. The detergents used for this purpose are mixtures of two or more compounds, a surfactant, an organic solvent and a stabilizer. The surfactant, often an ethylene oxide condensate, is the primary oil emulsifier; the solvent enables the surfactant to mix with the oil and form an emulsion. Substances such as coconut oil diethanolamide, when present, stabilize the emulsion formed.

All the solvents contain a proportion of aromatics. The higher the proportion of aromatics, the more effective is the solvent, but at the same time the more toxic.

The surfactants used, unlike those employed in household detergents, are 'hard'; that is, they are not readily destroyed by micro-organisms.

The following proprietary detergents were reported as having been used:

Gamlen Oil Spill Remover
Atlas
Snowdrift
Basol AD6
Gramosol
BP 1002
Dasic Slickgone
Petrofina Unisolva
TC4 (Drew Chemicals)
Esso F. 6155
Houghtosafe 112
Whittakers G.P. Degreasant

Some examples of the composition of these, indicated by code numbers not related to the above list, are:

Detergent no. 1: 66% solvent containing 24% aromatics, remainder cetyl phenyl ethylene oxide condensate
Detergent no. 2: 70% solvent containing 43% aromatics
15% tall oil
15% nonyl phenyl ethylene oxide condensate
Detergent no. 3: 75% solvent containing 76% aromatics
25% mixture of ethylene oxide condensate and calcium petroleum sulphonate
Detergent no. 4: 85% kerosene extract with a high proportion of aromatics
12% nonyl phenol ethylene oxide
3% coconut diethanolamide
Detergent no. 5: 75% solvent containing 83% aromatics
7·5% tall oil
2·5% triethanolamine
10% dodecyl benzyl sulphonate as the ammonium salt
5% non-ionic detergent

Some physical properties of BP 1002 and methods of estimation

The Laboratory experiments described in this section examine certain physical properties of the detergent BP 1002. This detergent was used on a much greater scale than any other, especially on the shore. Samples of the detergent and its separate fractions were made available to us by BP Trading Limited, who also kindly undertook some of the analyses reported later.

Properties of solvent

(*a*) Density: 0·874 at 17 °C.

(*b*) Miscibility with sea water at 17 °C: 100–150 ppm (w/v) remain in the water phase some hours after shaking solvent with sea water.

(*c*) Boiling point: fractional distillation at atmospheric pressure yielded four fractions, of which the first two had a sulphurous smell.

Boiling point (°C)	% by volume of solvent	Toxicity compared with whole solvent as 100*
Below 120	1–2	45
Below 165	7	45
Below 185	18	80
Residue boiling above 185	74	78

* See page 143.

(*d*) The solvent has a characteristic smell, which can be detected at low concentrations. Sea-water solutions containing $\frac{1}{2}$ ppm BP 1002 are easily distinguished from detergent-free sea water by smell.

Rate of loss of solvent from sea water

Large volumes of a 10 ppm (parts per million) solution of BP 1002 in sea water were placed in open containers and exposed in the open air. Solvent concentrations at different depths in the solution were determined at intervals by the third method given below. Similar results were obtained in two experiments, using 70 and 30 l. of solution (Fig. 2). After 35 hours the concentration of solvent had fallen to 5 ppm; after 95 hours it had fallen to $\frac{1}{2}$ ppm. In the open sea evaporation would be more rapid. At concentrations around 10 ppm, the solvent tends to rise to the surface, as is seen by placing solutions in stoppered columns and determining solvent concentrations in upper and lower parts of the column after some hours. In one such experiment, where the initial concentration was 5 ppm, after

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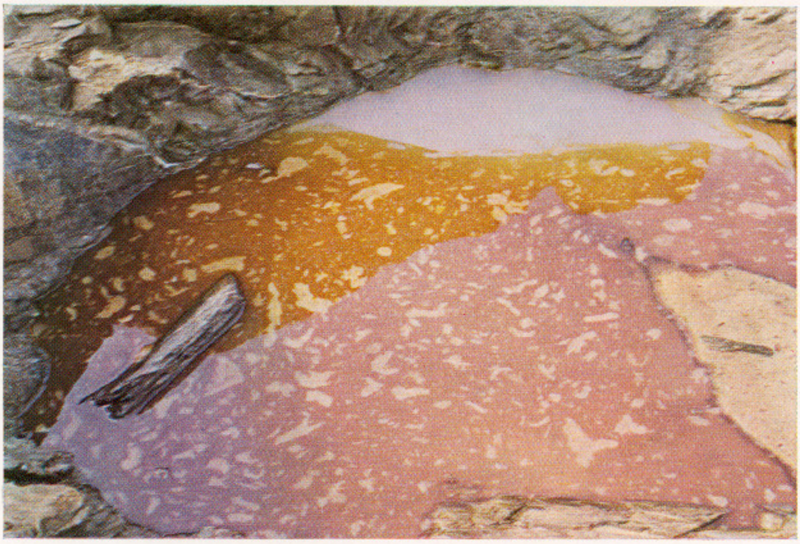
PLATE I

Treatment of oil with detergent may give varying results and mixtures of varying colours. **A**, Watergate Bay, 15 April: heavily oiled sand adjacent to rocks that had recently been hosed with detergent/freshwater mixture. The pool of white emulsion had patches of re-separated oil (resembling the original Kuwait crude oil) which had not formed an emulsion with the detergent as shown in Plate 2. **B**, Booby's Bay, 8 April: orange-brown partially emulsified oil floating on detergent solution in a high-water rock pool. **C**, Kynance Cove, 20 April: orange-brown oil emulsion after detergent treatment oozing down from boulders near high-water mark.

PLATE I

A



B

C

(*Facing p.* 16)

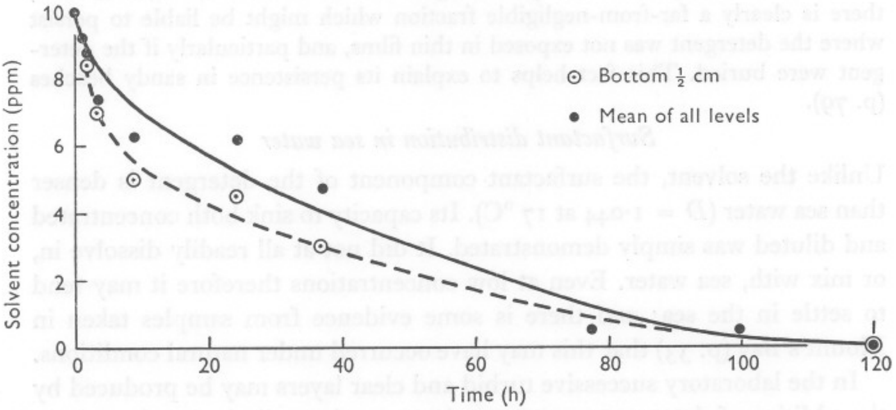


Fig. 2. Rate of loss of solvent fraction of BP 1002 from large volume of 10 ppm solution in sea water in open container.

3 hours a sample from the upper part of the column contained 6 ppm, lower down the concentration was 2½ ppm. Similar experiments with more concentrated solutions (e.g. 100 ppm) did not show layering.

Evaporation of detergent (BP 1002)

Some laboratory experiments were conducted on the undiluted detergent and its components to test their capacity to evaporate. The tests were carried out in a fume cupboard with air draught.

The whole mixture. Eighty ml (67·64 g by weight) was placed in an open Petri dish of 10 cm diameter. Half the weight was lost by evaporation in about 4 days, and 70 per cent in 11 days. The rate was continually becoming slower and in the next 11 days only an additional 5 per cent was lost. The graph was approaching exponentially a base-line representing 14 g (or 20·7 per cent by weight of the original sample).

The surfactant. This appeared not to evaporate at all.

The solvent ('*Kex*'). Eighty ml were placed in a Petri dish (experiment of 9 May). Sea water was used for comparison in a similar dish. It took 3¼ days for the sea water to evaporate to the point of leaving a deposit of moist salt crystals. In the same time the 'Kex' had lost barely half its volume; but it was steadily evaporating, and in 7 days had lost about three-quarters. From this point evaporation was hardly noticeable and at the end of the second week (23 May) the volume was measured at 17·5 ml (22 per cent of the original). This residue was found to be relatively persistent after transference to a small cylinder, which could be weighed easily. In this more confined vessel only 0·0176 g of the 'Kex' residue was lost between 31 May and 26 June, or 0·00068 g a day. It may be thought that 22 per cent was unduly high for the relatively persistent residue of a volatile solvent, and some allowance should perhaps be made for loss of the more volatile components from the can from which the sample was taken, since it was not newly opened. Perhaps the figure should be halved, but, even if so, there is clearly a far-from-negligible fraction which might be liable to persist where the detergent was not exposed in thin films, and particularly if the detergent were buried. This fact helps to explain its persistence in sandy beaches (p. 79).

Surfactant distribution in sea water

Unlike the solvent, the surfactant component of the detergent is denser than sea water ($D = 1{\cdot}044$ at 17 °C). Its capacity to sink both concentrated and diluted was simply demonstrated. It did not at all readily dissolve in, or mix with, sea water. Even at low concentrations therefore it may tend to settle in the sea; and there is some evidence from samples taken in Mount's Bay (p. 33) that this may have occurred under natural conditions.

In the laboratory successive turbid and clear layers may be produced by the addition of detergent to sea water in measuring cylinders under certain conditions, the differences between the layers presumably resulting from micelle formation.

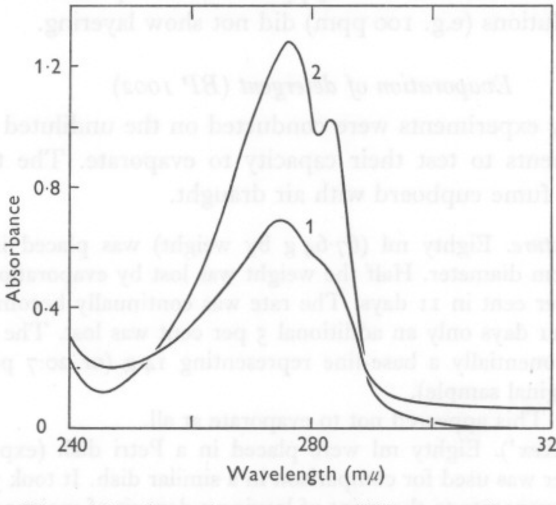


Fig. 3. Ultra-violet absorption spectrum of BP 1002 surfactant in sea water. 1, 50 ppm, 5 cm light path; 2, 500 ppm, 1 cm light path.

Micelle formation of surfactant

Determinations (by cryoscopic methods) of the molecular weight of the surfactant at concentrations above 1 per cent in sea water indicated an approximate molecular weight of above 10000. Since the molecular weight of the surfactant is around 650 it is evident that molecular aggregates, or micelles, are formed. At lower concentrations the method used was un-

Table 2. *The relationship between the surfactant concentration and the ultra-violet absorbance at 275 mμ*

Concentration (*C*) (ppm)	Light path (*L*) (cm)	Absorbance at 275 mμ (*A*) corrected for turbidity	A/CL ($\times 10^{-3}$)
5	10	0·108	2·2
10	10	0·226	2·3
50	10	1·23	2·5
50	2	0·127	2·5
100	1	0·2	2·0
500	1	1·25	2·5

suitable, but further evidence of micelle formation was obtained by the use of ultra-violet spectroscopy. Fig. 3 shows the ultra-violet absorption spectrum of the major surfactant component of BP 1002 in sea water. Measurements in the range 5–500 ppm have been made. At 50 ppm a slight turbidity of the solution was apparent and at 100 ppm the turbidity was very marked. At 500 ppm the solution was clear and its spectrum indicated the formation of a new species of micelle in solution. At all concentrations examined except 100 ppm the absorbance at 275 mμ has been found to obey Beer's law (that is, was proportional to concentration) reasonably well after allowance has been made for the turbidity as estimated from the absorbance at 320 mμ (Table 2). The discontinuity found at 100 ppm is indicative of the formation of insoluble micelles at 100 ppm with subsequent regrouping to give a new dissolved species at higher concentrations. On the shore, concentrations of 100 ppm or greater were frequently observed.

By reducing the effective concentration of surfactant, micelle formation would be expected to reduce the toxicity of surfactant solutions in sea water, as well as affecting such physical properties of the detergent as its adsorption on to sand (p. 77).

Methods used in the determination of detergent concentrations in sea water

Three chemical methods were used, in addition to the bioassay methods described later (p. 141). The first two actually determine the amount of surfactant present and the third the amount of solvent.

Method 1

All the analyses by this method have been kindly made for us by BP Trading Limited at their Pumpherston laboratory. The method, devised by Conoco (Continental Oil Company), estimates surfactant in sea water and gives an accuracy and repeatability of ±3 per cent relative at the 20 ppm level. The procedure is as follows.

Place 100 ml of sample solution into a separating funnel. Add 15 ml of ammonium cobaltothiocyanate reagent (prepared from 620 g reagent-grade NH_4SCN plus 280 g reagent grade $Co(NO_3)_2 . 6H_2O$ diluted to 1 l. and extracted twice with benzene) and 35–40 g of sodium chloride. Shake to dissolve the salt and allow to stand about 15 min. Accurately add 25·0 ml of benzene to the funnel. Shake for 1 min, then let stand to allow the layers to separate. Draw off and discard the lower aqueous layer. Transfer the benzene layer to a centrifuge tube, stopper, and spin at 500–700 rcf for 10 min. Read the peak absorbance at about 320 mμ against a reagent blank using a Beckman DB Ultraviolet Spectrophotometer with a deuterium lamp and 1 cm cells; 4 cm cells can be used to improve sensitivity. (The spectrophotometer connects to a 100 mV recorder through a Beckman Scale Expander accessory, to scan the region between 340 and 315 mμ.) Compare the absorbance with the reading obtained on a sample of known concentration.

Alternatively peak absorbance can be read at 625 mμ against a reagent blank using an infra-red tungsten light source and cell.

The instrument used at Pumpherston is a Cambridge SP 500. Present experience at Pumpherston indicates that in the range 0–10 ppm this procedure gives an accuracy within ± 20 per cent on samples obtained under practical working conditions.

This method determines only nonylphenol ethoxylate and is not effective at concentrations of 1 ppm or less.

Method 2

This simple method was developed in this laboratory at an early stage in the operation.

Add to 25 ml samples of the test solution in separating funnels 5 drops of an oil reagent ('3 in 1' oil saturated with Oil Red O and filtered through tissue). Shake vigorously for 15 sec. and stand for 3 min ± 10 sec. Separate and extract the aqueous layer with 4 ml chloroform. Read at 525 mμ in 1 cm cuvettes.

The calibration curves were linear over the range 0–5 ppm.

Method 3

This method was adapted from Gerade & Skiba (1960) and determines the amount of solvent present.

Using 50 ml test samples, extract into 3 ml of carbon tetrachloride. Shake the extract with 5 ml acid reagent (25 ml of 40 per cent formaldehyde in 500 ml concentrated sulphuric acid). Visual comparison with standards in the range 0–10 ppm gives values ± 5 per cent or better. The initial colour developed is pink, which after 30 min changes to orange brown.

The stability of detergent–oil emulsions

As already stated, the detergents act on the floating oil by producing a detergent–oil emulsion which is then supposed to be dispersed in the sea. The stability of such detergent–oil emulsions is important, for the more stable they are the better the dispersion. Some simple laboratory tests were made on this property.

Comparison between different detergents

A test was carried out on the stability of detergent/oil emulsions in sea water when there is no stirring; the results obtained give some indication of the relative efficiency of the different detergents tried.

Several detergents were used. In each case, 2 ml of detergent and 2 ml of Kuwait crude oil were mixed in a 100 ml measuring cylinder. Then 96 ml of sea water were added and the cylinder was sealed and shaken for 10 seconds. Oil started to settle out on the surface of the emulsion within a few minutes. As more oil settled out the emulsion column became lighter in colour and after about 2 hours there was considerable difference between the cylinders (Plate 2). In order of decreasing opacity of the emulsion the detergents were: Houghton, BP 1002, Gamlen, Gramosol, Whittaker, Slipclean, and Dasic.

These results suggest that Houghton detergent is best able to maintain an oil emulsion in sea water. It is also one of the most toxic detergents, as are BP 1002 and Gamlen. Dasic seems to be particularly poor in maintaining an oil emulsion in sea water and the water column cleared almost completely in a few hours. When the detergents only were added to sea water all except Dasic gave a milky emulsion. Dasic settled out on the surface of the water. It gave a perfectly good emulsion in fresh water and was extremely effective for washing off oil from all kinds of surfaces with warm tap water. The surfactant portion is largely anionic, and the preparation is presumably designed for use with fresh water.

Conductivity measurements made with 0·1 per cent solutions of detergent in distilled water verified that the surfactants of most of the detergents used are non-ionic; with the exception of Dasic and Teepol. These two detergents are least effective in sea water.

Deposited oil and BP 1002

The test reported above involved only 10 sec. shaking. Some other attempts were made to form a permanent emulsion with Kuwait crude oil and BP 1002, giving longer vigorous agitation and different amounts of sea water. With one mixture the emulsion, when left standing, showed no sign of separating until the next day, but the oil eventually layered out, and no better result was achieved than this.

With the oil collected on the shore, which, as has been explained, was already an emulsion of sea water in oil, the situation was appreciably worse. Though '*café-au-lait*' emulsions could be formed with different mixtures of oil, detergent, and sea water, these proved always to be very unstable and layering started at most within an hour or so. This was true even when the oil was first soaked with the optimum amount of detergent for about half-an-hour before sea water was applied.

Further comments

The formation of persistent emulsions in sea water does not take place readily, and detergents were often applied by methods that were largely ineffective, uneconomic, and wasteful of effort. This was particularly true of the methods used in dealing with the oil stranded on the shore. Thorough agitation by hosing, or by the natural agencies of wind, waves, and tide is essential for effective dispersal of oil, and these conditions were not always ensured.

As to spraying at sea, we have no information about its eventual effectiveness. It was genarally agreed by those taking part in the sea operations that dispersal was often achieved in the immediate neighbourhood of spraying. However, despite the large quantities of detergents used, large areas of undispersed oil persisted for weeks as extensive and discrete patches.