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LABORATORY EXAMINATION OF MATERIALS SUBMITTED  
FOR TREATING THE TORREY CANYON OIL SPILL

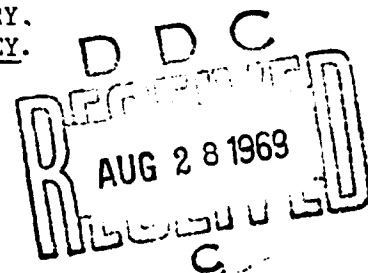
by

C. E. Carpenter, L. F. Butcher and A. S. Huxley.

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ADMIRALTY OIL LABORATORY.  
FAIRMILE, COBHAM, SURREY.

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ADMIRALTY OIL LABORATORY  
PAISLEY COAST  
SURREY

Laboratory Examination of Materials Submitted  
for Treating The Torrey Canyon Oil Spill

by

C. E. Carpenter, L. F. Butcher and A. S. Huxley.



Superintendent,  
A.O.L.

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## History

The Torrey Canyon struck the rocks off the coast of Cornwall on 18th March, 1967. Within a few hours the ship had been surveyed from a helicopter by Naval personnel and the ship was declared a total loss. Pollution Clearance Board, which was set up to deal with the oil spillage.

The only method for dispersing oil at sea that was used by the Royal Navy at that time was the use of dispersants. With a dispersant the oil is broken up into small droplets of oil which are then carried away by the wind and waves. The oil is then ignited with a jet of water from a fire hose, blowing the boat through the treated oil spill. The dispersant is then dispersed by the wind. The Navy given the task of trying to disperse the oil so it could reach land, as the oil was not being removed from the Devonport Dockyard was not sufficient. The oil was dispersed with spray equipment. A dispersant was set up at Maritime HQ Plymouth which among other things had to purchase the required quantity of suitable dispersant.

The operational requirements had been increased to 1,000 gallons of dispersants a day. There was some doubt as to the possibility of obtaining such a large quantity, but the contract was awarded to a firm, within a few days, to arrange for the dispersant supply. The dispersant manufacturer in this country at the time was not capable of producing 10 times the daily requirement, Maritime HQ was within a few days almost besieged with hopeful dispersant orders, but claiming to have no stock product for dispersant. At this point the Admiralty Oil Laboratory, which was then at the Naval Base, Devonport (Navy) was asked to provide the dispersant.

Admiralty had a limited stock of dispersant, but it was a priority item for the programme for dispersant. In 1966 the dispersant was associated with the pollution control programme carried out in Portland Harbour by Warley (previously known as DMR, now Ministry of Technology). Since then the work has been carried out in dispersing the use of chemical dispersants on HM ships, and a dispersant DG Ships 699. The dispersant was used to clean the pollution from materials. This dispersant was used for the dispersant cleaning of the 100 dispersant, and it was used for dispersant against the Torrey Canyon oil spill.

The dispersant requirements for Maritime HQ were for DG Ships 699.

## Dispersant Test

The dispersant was designed to ensure that the dispersant was used in the dispersant. The dispersant was used in HM ships, and it was used for dispersant in the dispersant.

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## 2. Cleaning Tests based on DGS/6992

A test surface is prepared by stoving a reference furnace fuel oil onto a metal plate. The soiled plate is then sprayed with detergent and after a soak time of 30 minutes washed with sea water. In this report the sea water used was synthetic sea water made up to the formulation in IP Standard for Petroleum and its Products Method No 135/64.

While the cleaning test was not particularly relevant during the time the oil was still floating on the sea, the results did give some indication of the rate of penetration of the detergent into the oil film, and once the oil was driven ashore coating beaches, rocks and jetties, the cleaning properties became of prime importance.

Cleaning tests to DGS/6992 are carried out on 12" x 12" panels, but because of the large number of TC detergent samples and limited oven capacity for stoving the test panels, their size had to be reduced. Initially 3" x 1" panels were used, but it was found difficult to obtain on them an even stoved oil film. Finally 6" x 3" panels were chosen, as shown in Fig. 1. Where differentiation between similar products was required, or where a detergent was borderline between being accepted or rejected on cleaning properties a check test was carried out using 12" x 12" panels.

Detergents were placed in one of five classes according to their cleaning test results. Classes were:-

- Class 1, Majority of fuel oil removed
- Class 2 Approximately 75% fuel oil removed
- Class 3 Approximately 50% fuel oil removed
- Class 4 Approximately 25% fuel oil removed
- Class 5 Negligible fuel oil removed

Consideration was given to the soaking time between spraying the detergent onto the test panel, and washing off with sea water. It was found that certain detergents would be assessed as Class 1 if the test panel was washed immediately after spraying on detergent, but if left for 30 minutes would be assessed as Class 5. In use on the beaches, it seemed unlikely that washing down would follow immediately after spraying on detergent, secondly oil films were likely to be much thicker on rocks etc., than on the test panels (approximately 0.15 mm), and finally in sunny weather the temperature of sand, rocks, etc., could be considerably more than the average 70°F laboratory temperature at which the panels were tested. For these reasons a "soak time" was considered essential, and was fixed for these tests at 15 minutes.

Results varied from complete removal to no removal of the stoved fuel oil. Figure 1 shows some panels after cleaning tests. Samples 8, 36 and 63 were assessed Class 1, while 30 and 39 were Class 5. Full results are given in Table 1.

Any detergent assessed Class 5 for cleaning properties was rejected.

3. Emulsification Tests based on DGS 6992

The test consists of emulsifying a Naval turbine lubricating oil OEP-69 to which is added 25% detergent (calculated on the volume of oil) with sea water and then noting the breakdown of the emulsion over a period of 5 hours. To give better differentiation, a further reading of emulsion breakdown was made after 24 hours for some of the better detergents.

Figure 2 shows a series of emulsion tests with OEP-69 (top) and crude oil (bottom) after approximately 5 hours standing. Sample 97 gave good emulsion stability, while 68 was assessed poor. The reduced separation into oil and water with crude oil emulsions can be seen. A full set of emulsion stability results are given in Table 1.

Although the Torrey Canyon was carrying crude oil, a very different product from the highly refined and additive treated turbine oil OEP-69, the latter was considered to be a more difficult oil to emulsify and therefore would give better differentiation between the good and bad detergents. The best materials showed little emulsion breakdown after 24 hours, the poorest gave almost complete separation within 1 hour. Later when a supply of crude oil (Kuwait Export Crude) from the same source as the oil carried by the Torrey Canyon was obtained, the tests were repeated using crude oil with the better detergent materials. The results which are given in Table 1, confirmed that in general, emulsions of crude oil and sea water were more stable than emulsions with OEP-69.

4. The need for additional tests

As reports came in on the dispersal of the oil slicks at sea, it became apparent that emulsification of the detergent treated oil mainly occurred through wave action and to a lesser extent from the wash from the spraying vessels. The emulsion test in DGS/6992 designed to simulate passing the treated oil-sea water mixture through a centrifugal bilge pump, was hardly appropriate for this work and might even be giving misleading results. In a number of instances it was found that due to the energetic stirring and the particular water/oil ratio used, water in oil emulsions were being formed in the emulsion test and these would be assessed as satisfactory, whereas they are even less satisfactory than no emulsification.

With the emphasis changed from bilge cleaning to oil dispersal it was obvious that a more realistic test was required. Little work has been published on the evaluation of detergents of this nature. J. C. Taylor<sup>12</sup>, in a lecture to the Institute of Petroleum gave a method used by Esso, but this did not simulate dispersal by wave action and was rather time consuming. The USA have a specification<sup>13</sup> for a Solvent Emulsifier Oil Slick, but this requires large quantities of sea water and also a considerable number of man-hours per sample tested.

Two approaches were tried at AOL:-

- (a) Emulsion formation with low input of energy and high water to crude oil ratios, using the swirling table emulsion test.
- (b) Measurement of the interfacial tension between sea water and detergent treated fuel oil.

5. Swirling Table Emulsion Test (STET)

The STET was developed in a matter of days from equipment that was easily obtained and was intended to, as closely as possible, simulate the conditions pertaining to oil dispersal at sea. During test development it was constantly in mind that a test of this type would need to be capable of:-

- (a) Rapidly comparing samples from different suppliers
- (b) Using little operation time
- (c) Being capable of surveying a range of treatment levels
- (d) Being reasonably repeatable
- (e) Using cheap easily obtainable equipment

Figure 3 shows the table (4) in use, with 4 tests being run simultaneously.

(a) Outline of Method

2 ml. of the crude oil is floated on the surface of 50 ml. of 3% sodium chloride solution in a 100 ml. squat form beaker and the appropriate amount of the detergent added. The beaker is swirled gently and observations of the degree of emulsification of the contents are made at regular intervals. These observations are combined to give a single rating number for each treatment rate.

(b) Test Procedure

50 ml. of 3% sodium chloride solution were placed in a prepared beaker and 2 ml. of the crude oil added. The requisite amount of the detergent was pipetted onto the oil, i.e. 0.1 ml. for the 5% treatment, 0.2 for the 10%, and 0.4 for the 20%. The table was set swirling at 130 cycles per minute. After one hour of swirling the table was stopped and the contents of the beaker examined. This was completed as rapidly as possible as some separation takes place on stopping, particularly in the early stages of the test. The contents were rated as follows:- (See Figure 4).

- |          |   |
|----------|---|
| Rating 1 | Complete emulsion formed  |
| Rating 2 | Emulsion with slick   |
| Rating 3 | Emulsion with oil film  |
| Rating 4 | Emulsion spread to the bottom of the beaker but still little reduction in the oil layer |
| Rating 5 | No significant emulsification   |

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The swirling was continued for a further hour and another assessment made. A further three periods of swirling for 1 hour, were carried out, assessing at the end of each hour.

(c) Test Results

An abridged list of the hour by hour assessments is shown in Table 2. There is considerable difficulty in comparing such a group of numbers and they were condensed to yield single rating numbers. Two methods of doing this were tried:-

(a) The sum of the ratings minus 5 to give an unweighted rating number in a scale from 0-20. Products with a rating number (unweighted) of 0 being completely emulsified in one hour and those with a rating number of 20 still being completely separate after 5 hours swirling.

(b) The sum of the products of the ratings and the number of hours on test minus 15, yielding a rating number (weighted) scale from 0-60. There is little to be gained from using the latter method regularly, the results not showing much greater resolution than the unweighted rating numbers. When, however, it is necessary to resolve fine differences between detergents at the poorer end of the scale, the weighted rating number will favour products that with time produce complete emulsions instead of those that yield partial emulsification at an early stage and never progress beyond this state. It should be emphasised that the differentiation is between the less meritorious products, which tend to be somewhat bunched together when using the unweighted rating number.

The full list of results for the STET is given in Tables 3 (unweighted) and 4 (weighted).

Considering the results as from Table 3, the materials can be divided into three groups:-

- Group I      Efficient emulsifiers at all 3 treatment rates  
                 e.g., TC 10, 16, and 51.
- Group II     Increasing emulsification efficiency with  
                 increasing treatment rates e.g. TC 17, 31,  
                 38, 98.
- Group III    Low emulsifying efficiency at all treatment  
                 rates, e.g. TC 3, 7, 11, 96.

Table 5 shows these groupings in approximate descending order of merit, and in addition gives an approximate percentage of surfactant, type of surfactant, and percentage aromatics in the solvent, where known. More detailed analytical results are given in Part 3 (Confidential) of this report.

It was hoped that some pattern as to the requirements of a good emulsifying detergent would appear from the results in Tables 3, 4, and 5 but it is considered that no definite conclusions can be made without a large quantity of more detailed analysis on a greater range of products.

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There is an indication that the surfactants should be a mixture of non-ionic and ionic materials, and only products with such combinations of surfactants received the top rating in this test.

There is also an indication that there must be some aromatics in the solvent, perhaps 20 to 25%. Except for TC 61 which is believed to have an aromatic content of less than 10% and TC 49 with an aromatic content of 17%, no product has a rating less than 15 with an aromatic content less than 24%.

The percentage of surfactant in the detergent does not necessarily give any indication of emulsification efficiency, although products with the top rating, with the exception of TC 98 have a minimum of 20% surfactant. However, just increasing the surfactant does not necessarily increase emulsification efficiency, e.g. TC 97 and 98 differ only in surfactant content having, 10% and 5% respectively. TC 38 and 39 also differ only in surfactant content, having 50% and 20% respectively. With both these pairs of products, there appears little difference in emulsification performance despite the differences in surfactant content.

It seemed from these results that there was no easy way to obtain an efficient detergent by composition specification, and that efficiency would have to be assessed by practical testing of each product.

(a) With "Chocolate Mousse"

Much, if not the majority, of the beach contamination was found to be water in oil emulsion with a high water content and not aged crude oil with relatively little water. The sea water content varied up to about 70%, (the theoretical maximum for close packed spheres) at which level the contamination had the appearance and consistency of chocolate mousse. Such emulsions are readily prepared in the laboratory by stirring or gently swirling the appropriate amounts of oil and water together for a sufficient period of time. The efficiency of the detergents was found to vary when tested on the oil emulsion and a further merit assessment was requested to find the best products to deal with this "chocolate mousse"

The STET was modified to obtain this information by placing two grams of an emulsion of the oil from the Torrey Canyon that had been removed from a beach, in the beaker and then added 0.2 ml. of the chosen detergent and allowing the sample to stand for 15 minutes. 50 ml. of the sodium chloride solution were then added and the beaker placed on the swirling table and the test carried out as for testing for emulsion forming ability. Assessment was made of the degree of dispersion of the emulsion and its type. These were rated on the same scale as was used for the emulsion forming test. The sample of emulsion used contained 70% of water and the treatment rate, calculated on the oil content was therefore approximately 30%. The results are given in Table 6.

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One non-detergent material that acted in a different manner was also tried, this was sawdust treated with TC 45 to render it lipophilic and hydrophobic. This was sprinkled on the emulsion before the water was added and at the end of the test was well worked into the emulsion to form an easily handled semi solid. No oil appeared to be liberated into the water in this case.

A different detergent order of merit was obtained in this modified Swirling Table Emulsion Test with samples of water in oil emulsion. However, as materials being used at that time (marked with an asterisk in Table 6) were among those given top ratings, it was considered unnecessary and practically operationally unworkable to recommend one manufacturer's product as suitable for dealing with the crude oil in the area of the Torrey Canyon, and another manufacturer's product for the emulsified oil when it reached the beach.

## 6. Interfacial Tension Measurements

### (a) Introduction

Detergents used in treating oil spills can be assessed by their effect in reducing the oil-water interfacial tension. Thus, a spreading coefficient S for one liquid on another is considered by Davies and Rideal (1963) (5) and is given by the expression

$$S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW})$$

where  $\gamma_{WA}$  is the water-air surface tension,  $\gamma_{OA}$  the oil-air surface tension and  $\gamma_{OW}$  the interfacial tension. As the interfacial tension is reduced the spreading coefficient increases, and minimal energy for emulsification is approached as interfacial tension approaches zero.

Of the two most commonly used methods for measuring interfacial tension, namely the du-Nouy tensiometer and the "drop-weight" method, the latter lends itself to the more accurate measurement of low values of interfacial tension and was the method employed in the experiments described. Essentially the "drop-weight" method consists of forcing the oil through a fine capillary to be released in individual drops into the surrounding water. The volume of the drop as it is released gives a measure of the interfacial tension provided the drops are formed sufficiently slowly. Thus the interfacial tension  $\gamma_{OW}$  is related to the volume of the drop according to the equation,

$$\gamma_{OW} = \frac{V_d (\rho_w - \rho_o) g}{2\pi a} \quad (1)$$

where  $2a$  is the external diameter of the capillary,  $\rho_w - \rho_o$  is the difference in densities of the water and oil,  $V_d$  the volume of the oil drop and  $g$  the acceleration due to gravity. For the same oil containing small amounts of the different detergents  $\rho_w - \rho_o$  may

be taken as a constant to a first approximation and the interfacial tension of the oil containing detergent and the sea water  $\gamma'_{ODW}$  can be compared directly with that of the untreated oil-sea water by expressing it as a percentage in the equation

$$\frac{\gamma'_{odw}}{\gamma'_{ow}} = \frac{V_{od}}{V_o} \cdot 100\% \quad (2)$$

Corrections to equations (1) and (2) must be made because all of the oil does not completely leave the tip of the needle as the drop is released and the interfacial tension may not act vertically. In this connection a correction factor  $\phi_{ow}$  which is a function of the needle diameter and the volume of the drop must be applied to equation (1) to give

$$\gamma_{ow} = \frac{\phi_{ow}(\rho_w - \rho_o)g}{2\pi a} = \phi_{ow} \gamma'_{ow} \quad (3)$$

and to equation (2) giving

$$\frac{\gamma_{odw}}{\gamma_{ow}} = \frac{\phi_{odw}}{\phi_{ow}} \frac{V_{od}}{V_o} \cdot 100\% \quad (4)$$

where  $\gamma_{odw}$  and  $\gamma_{ow}$  are the corrected interfacial tensions.

According to Davies and Rideal (5) in "Interfacial Phenomena" the factor  $\phi$  is the same for all liquids and use has been made of Figure 1-23 of this book in making correction to the measurements.

#### (b) Experimental

The interfacial tension apparatus shown in Figure 5 consists of a hypodermic needle and a pyrex syringe joined to a precision bore pyrex tube calibrated to 0.01 ml. (limb A). Air pressure to form the drops was supplied to limb A by running water into a suitable reservoir. The drops were released into the sea water which was contained in limb C. The third limb was added to facilitate the initial filling of the apparatus. The end of the hypodermic needle had been ground flat and, prior to each measurement, was dipped in a silicone fluid. The measurements were made in a thermostatic bath at a temperature of  $21.5 \pm 0.1^\circ\text{C}$ . Because of the rapid loss of the volatile fractions from crude oil this work was carried out with Navy 75-50 fuel oil as the base oil and this was released into sea water. Preliminary experiments showed that convenient measurements could be made with concentrations of 2% by volume of detergent blended into the oil.

The air pressure was regulated over the first few drops so that the time of formation of the drops was of the order of  $1\frac{1}{2}$  to 2 minutes. For the smallest drops (with the better detergents) somewhat smaller times were accepted. According to the size of the drops the number forming 0.1 ml. or the volume for 25 drops was determined

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such that an efflux of a minimum of 0.1 ml. was observed for the oil containing detergents. For the base oil alone the volume of 10 drops was determined. It was noticed that the time of formation of drops was approximately constant over the period of efflux and this indicates that if any absorption of the surfactant from the interface into the sea water occurs it is not appreciable in its influence on the interfacial tension at the concentrations involved (approximately 0.1 ml. oil containing 2% detergent into 40 cc. sea water).

Figure 6 shows a typical drop (just before release) formed with the base oil containing 2% of a moderately good detergent. A value of 28.1 dyn. cm.<sup>-1</sup> (25.6 uncorrected) was found for the interfacial tension between the base oil and sea water using equation (3). Values of the interfacial tension for the oil containing 2% of the different detergents before and after correction are expressed as a fraction of this in Table 7.

Measurements of the interfacial tensions of two of the detergents (Nos. 17 and 51) were made at different concentrations to determine the concentration dependence. The normalised interfacial tension relative to the base oil plotted against the concentration is shown on a log-linear scale in Figure 8 for the two detergents. Straight lines have been drawn according to the equation.

$$\frac{\gamma_{odw}}{\gamma_{ow}} = e^{-c/m} \quad (5)$$

where C is the per-cent concentration by volume and m is a constant different for the two detergents.

Since it is known that drop size increases with the rate of formation of the drops because of the formation of a tail to the drops, measurements were made in order to estimate the significance of this effect with one of the detergents - No. 17, at a concentration of 2%. For this measurement a hypodermic needle of larger external diameter (0.066 cm.) was used to give bigger drops. The larger drops were needed to interrupt a light beam to a photo-electric cell which was made to operate a Schmitt trigger and thence a camera which simultaneously photographed the calibrated limb of the interfacial tension apparatus and a 10 second stop watch, a count being recorded on a digital counter. The light source and lens, the photo-electric cell, and the stop watch were in watertight jackets in the thermostatic bath. Flat plate windows were inserted in the water-containing limb of the interfacial tension apparatus and a black cellulose paint was used to limit the beam to a narrow pencil of light. Figure 7 shows a photograph of the complete apparatus. As the pressure was increased the size of the drops increased and their volume was calculated from the volume required to form ten drops at each pressure. The effect of the time of formation on drop size and hence on the calculated interfacial tension for sample No. 17 is shown in Figure 9. The dashed line indicates the value of the interfacial tension expected from the previous measurement with the smaller hypodermic needle with a time of drop formation of 1 1/2 minutes, showing good agreement.

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### (c) Discussion of Results

Table 7 shows that all the detergents studied were effective in reducing the interfacial tension between the base oil and sea water. The time of formation of the drops is not important for times of formation greater than  $\frac{1}{2}$  minutes as is evident from Figure 9 and would not significantly alter the values given in Table 7. However, the estimated accuracy of the measurements in Table 7 is no better than  $\pm 3\%$  at a value of 20% relative to the base oil and about  $\pm 0.5\%$  at 1% relative to the base oil. This accuracy is considered reasonable in view of the small values of the interfacial tension.

The concentration dependence of the interfacial tension with the two detergents No. 17 and 51 approaches the logarithmic law of equation 5 as is evident from Figure 8. It is unlikely, however, that this law holds for all the detergents in view of the different solvents and the differing hydrophilic-lipophilic nature of the surfactant molecules, but it may serve as a first approximation and is included for that reason. According to the logarithmic law the values of  $m$  would range from 0.50 for sample No. 51 to 1.44 for sample No. 4 and the concentrations required to reduce the interfacial tensions to any particular value would be in the same proportions. Sample 4 appears to be the least effective in reducing the interfacial tension from Table 7, and was also less effective in the emulsifying tests.

The increasing drop size with increasing rate of formation of the drops shown in Figure 9 for sample No. 17 is due in part to the formation of a tail to the drops, but is also dependent upon the rate of diffusion of the surfactant molecules to the surface of the drops; that is the size of the drops is dependent in part on the age of the surface. This is only important when the time of formation of the drops is less than one minute.

Returning to Table 7, the most effective detergents in reducing the interfacial tension between the base oil and sea water would appear to be sample Nos. 51, 8, 22, 5 and 1 in that order. One problem raised by this method was the indication that much smaller quantities of detergent would be sufficient to emulsify the oil, than were found to be required in practice. This is in part almost certainly due to the much more efficient mixing in the laboratory tests.

Because of the man-hours required for these determinations, one operator being fully occupied in doing a maximum of four tests in a day, this method was used mainly as an aid in determining cost/effectiveness of materials purchased by Director of Contracts.

### 7. A Note on Detergent Analysis

The majority of the materials supplied were solutions of surfactants in hydrocarbon solvents. In some cases there were also present nitrogenous materials, and water, which interfered with the removal of solvents by distillation, and which needed to be checked for in the distillate.

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The solvent was removed from the sample by vacuum distillation to the first indication of breakdown of the residue and the weight/weight content calculated. In the initial stages the solvent fractions were characterised as hydrocarbons and the gross nature of the material inferred from boiling range/specific gravity/refractive index, later it was possible to add more detail to these observations by quantitative infra red, extraction of the aromatic and olefin fraction with sulphuric acid/phosphorous pentoxide, (IP Method 145/55) gas chromatography and finally by fluorescent indicator adsorption analysis on silica gel (IP Method 156/67 T). In general these methods showed fair agreement. The F.I.A. results were more readily obtained and showed greater consistency. The solvents were from a comparatively narrow boiling range, the majority being between 150-240°C.

In some cases the distillation of solvent caused the sample to lose nitrogen bases, these were determined separately by steam distillation of the sample made alkaline with sodium hydroxide. The nitrogenous bases being trapped in standard acid and the excess acid titrated.

The residues were characterised by infra-red spectrometry and in some cases examined further by liquid chromatography by the methods described by Longman and Hilton (8). This aspect was however, severely restricted by staff shortage.

The majority of surfactants were found to be ethylene oxide condensates, or mixtures containing such compounds. The leaching of ethylene oxide condensates from the treated oil into sea water was examined in a limited number of cases. The emulsion at the end of 5 hour swirling in the STET test was stirred into 3 litres of 3% sodium chloride solution. The resulting emulsion was allowed to separate and the lower clear water layer examined for surface active material. Initially this was by surface tension measurements using the du Nolly Tensiometer (IP 90/55 T). The results were compared with standard solutions made from the detergent under examination. It was found in some cases that the results indicated that far more surface active material had leached into the sea water than had been originally added to emulsify the oil. Limited work to try and leach surface active material from untreated crude oil into sea water was unsuccessful, so this method was abandoned.

There are several methods for determining ethylene oxide condensates. It had been hoped to use a thin layer chromatographic method (10), but due to the delay in the supply of reagents for this the method proposed by Kho and Stolten (9) and (7) was used. The results are given in Table 8.

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## 8. Non-Detergent Materials

In addition to detergents a variety of other materials the majority being oil sinkers were received at AOL. These were:-

- (a) Crystalline materials for scattering on beaches at low tide.
- (b) A liquid for treating absorbents to make them lipophilic.
- (c) Absorbing materials.
- (d) A coagulant.

### (a) Crystalline Materials

It was suggested that these materials could be scattered over an oil contaminated beach at low tide, or onto a clean beach at low tide on which it appeared likely that oil would come ashore on the next tide. The use of equipment for gritting icy roads was suggested for scattering the crystals. Then as the tide came in, the crystals would dissolve forming a "powerful" cleaning solution which would lift the oil off the beach, or prevent it settling on the beach, so that it could be carried out to sea with the receding tide.

TC 40 is sold as a degreaser for concrete floors in garages, etc., and is a highly alkaline powerful degreasant. Tests with TC 40 on crude oil soaked sand in the laboratory were not very promising. Emulsification tests were carried out by dissolving the crystals in sea water and then emulsifying the solution with oil. This produced a very unstable emulsion which rapidly separated out into oil and salt water (See Table 1).

TC 57 is similar to TC 40, but the solution is nearly neutral. Emulsion stability while still assessed poor, was better than TC 40.

Neither of these products were considered promising enough to recommend for a large scale trial. Unless very large quantities of crystals were used, dilution by the incoming tide as the crystals slowly dissolved would give only a very dilute solution. Also if there was sufficient oil on the beach for the crystals to become completely coated with oil, solution formation as the tide came in would be very slow. Finally as emulsion stability was poor, any oil that was "lifted off" the beach as the tide came in, would be likely to be deposited again as the tide went out or if carried out deposited again on another beach.

### (b) Lipophilic Promoting Liquid

The manufacturers claimed TC 45 could be used to treat any dry absorbent, e.g. sawdust, straw, at about 5% addition, to make such material lipophilic. It was also claimed that the lipophilic material could be stored without deterioration; this was considered to be a hope, rather than a fact proved from long term storage trials of bulk material.

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Sawdust treated with 5% of TC 45 was sprinkled onto crude oil floating on sea water. A sufficient quantity of sawdust was used to just absorb the oil. Initially the oil soaked sawdust floated, but over a period of months the majority sank to the bottom of the container. At the end of eight months the quantity of oil released from the sawdust amounted to little more than a mono-molecular film on the surface of the sea water.

Various absorbent materials in group C, that appeared hydrophilic in character were treated with 5% of TC 45. In all cases lipophilic characteristics were improved.

Limited trials were carried out in Devonport Dockyard by staff of the Captain of Dockyard, and TC 45 assessed as promising.

For dealing with smaller spills the use of this material on a suitable substrate, e.g. straw, wood shavings, would enable the oil to be removed from the sea and burnt. Suitable equipment for removing the oil soaked substrate from the sea would have to be developed.

(c) Absorbing Materials

With the exception of two non-granular samples TC 147 and 148, all materials were tested for oil absorption and retention of the absorbed oil. The method used was as follows:-

Into a 500 ml measuring cylinder was placed 400 ml of sea water and 10 ml of crude oil was floated on the surface. Sufficient absorbent was sprinkled onto the surface to just absorb the oil, and the weight of absorbent used determined. Dry sand, as a cheap readily available material was included in these tests. The results are given in Table 9.

TC 74, TC 93 and TC 118 on these limited tests appeared satisfactory absorbent/sinking agents for crude oil. The oil had not reappeared on the surface some months later when the cylinders were removed and washed up. TC 93 (a treated chalk) was in finely powdered form. TC 74 and TC 118 were in larger particles and tended to sink through the oil layer more rapidly without absorbing as much oil as their potential capacity. All these three were already lipophilic and there was little probable advantage in treating these with TC 45.

A sample of natural sponges TC 100 appeared highly lipophilic, but unless some means could be devised to incorporate these lumps of sponge into a continuous process for absorbing oil, squeezing it out and then absorbing oil again, their use would be very restricted.

Two types of glass fibre "mat", TC 147 a thin (approximately 2 mm) rather brittle sheet, and TC 148 a thicker (approximately 20 mm) softer and more flexible sheet were examined. Both materials show lipophilic properties and readily absorb crude oil, probably due to the resin treatment of the fibres. Both materials after

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soaking in sea water will absorb crude oil, with the displacement of the sea water, although complete displacement does not occur.

This type of material can be unpleasant to handle, and its disposal when soaked with oil, other than by burying, would be a problem. For this reason the use of other materials that could be burnt, e.g. sawdust treated with TC 45 or plastic foam would appear preferable.

(d) A Coagulant

It was claimed that TC 62 when mixed with its weight of crude oil would solidify it, so that it could be removed as a "cake".

TC 62 was sprayed into the oil floating on sea water, mixed with sea water and the oil added, and sprayed with a powerful jet into oil floating on sea water so that all components were vigorously mixed together. In all cases an increase in viscosity of the oil layer occurred, but no "cake" was formed, and the oil TC 62 mixture had to be treated as a liquid for removal purposes.

This material appeared to offer no practical advantage in dealing with spilt oil.

9. Discussion

It has been shown that the performance of the detergents varied according to whether the emulsion was prepared under high energy or low energy conditions. All detergents were tested in fact under high energy conditions (the emulsification stirring test in DG Ships/6992). When reports from those dealing with the floating oil indicated that a low energy test would be more appropriate, the swirling table emulsion test was developed, and was used for the final assessment on emulsion properties. The high energy test was still used for initial sorting as it was considered that if there was a rapid breakdown of the emulsion formed in this test, a poor result would be obtained with the low energy swirling table test (STET). Considering the results obtained using the Kuwait crude oil, all the detergents assessed good with the STET were assessed good on the 5 hour assessment in the DGS/6992 emulsification test. The limits laid down in this test - a maximum of 1 ml of oil and/or 15 ml of water released from the emulsion after 5 hours, were taken as a failure limit. After the first week when samples awaiting test started to accumulate, a detergent with a definite failure in the emulsion test or assessed 4 or 5 in the cleaning test, whichever test was done first, was put to one side and no more work undertaken.

Measurement of interfacial tension was tried as another way of determining the efficiency of the detergents. Possibly this method gives as good an answer as any in terms of absolute merit assuming ideal conditions of application and mixing. In practice this will not occur, the detergent losing volatile when it is sprayed, some oil receiving too little and some too much detergent, and mixing likely to be poor except

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where the oil film is very thin. Although there was a similarity in the order of merit of detergents determined by this and the SPET method, the latter was considered the more realistic test for picking the better products.

All the detergents used and all the more highly rated products were hydrocarbon solutions of surfactants. Some aqueous solutions were submitted TC 71, 77, 99, 101, 110, 117, 119, 120, 121, but these all gave a 5 rating in the cleaning test and in most cases emulsion stability was only fair.

It was expected that non-ionic surfactants would be found in detergents offered for emulsion formation with sea water. In fact the majority of detergents contained mixtures of non-ionic and ionic surfactants - the latter being present in the order of 10% or less in the mixture. It was suggested that the presence of a small amount of ionic surfactant enhanced the activity of the non-ionic part. All the detergents rated good for emulsion properties contained a mixed non-ionic and ionic surfactant.

The nature of the hydrocarbon solvent without doubt affects the efficiency of the detergent. It appears that at least 20% needs to be aromatic in nature. It seems likely that it is necessary for there to be a proportion of aromatics to carry the surfactants into the oil. All except one of the highly rated detergents had a solvent containing 20% or more of aromatics. It has been argued that the toxicity of the solvents increased with increasing aromatic content, but this factor was not considered at the time. Halogenated solvents were however banned as they were considered a health hazard to the users - one detergent in particular contained 72% of carbon tetrachloride.

The non detergent materials were not used around the Cornish peninsula. The only ones which AOL tests showed to be effective were a few of the absorbent/sinking materials including the one the French claimed they used successfully. (It is probable that what reached the French coast was the chocolate mousse, the 70 to 80% water in oil emulsion). This treated chalk is a very fine powder which is known to scatter in clouds in even a light breeze. The two other sinkers which dealt adequately with crude oil in the laboratory were of larger particle size and tended to sink through the oil rather fast without seemingly taking with them as much oil as they could absorb. There must be some balance between the most efficient particle size for sinking of the oil with the least difficulty in application.

It was also noted that there were possibilities in the use of a liquid claimed with some justification to be lipophilic promoting. This might in conjunction with straw, wood shavings, etc., be of value in dealing with smaller oil spills, or treating booms to be placed across estuaries.

AOL was required to advise Director of Contracts (Navy) on the best products to buy and using the STET and cleaning test the "top-ten" detergents were picked. This in fact grew to thirteen due to changes in formulation and a late received sample. Table 10 in this report in fact lists fourteen and Table 11 lists some of the other

detergents which were used in the first rush mainly because they were available very quickly.

Many manufacturers were disappointed in that their products were not on the recommended list, but in the majority of cases, products formulated for another use, were taken off the shelf and hopefully submitted to AOL. One firm in fact unthinkingly offered a product which they were using with success to clean ship tanks. They overlooked the fact that in normal use it was an advantage if the emulsion formed during cleaning broke rapidly on standing so that the oil could be recovered.

AOL were also required to assist Director of Contracts in assessing if the prices charged for detergents were fair and reasonable. The analytical data obtained by AOL which showed surfactant content to vary from less than 5% to 50%, and "solvents" to vary from water to nearly 100% aromatics, did enable an estimated cost to be calculated. This was available to Director of Contracts (Navy) in his negotiations on prices.

#### 10. Conclusions

(1) From figures supplied by the manufacturers the production capacity of detergents in this country is more than adequate to meet any future emergency similar to the wrecking of the Torrey Canyon, even if the oil released was greater by a factor of 2 or 3. Additional supplies could also be obtained from many European countries.

(2) An efficient detergent is likely to contain a mixed non-ionic/ionic surfactant dissolved in a hydrocarbon solvent of which a minimum of above 20% will be aromatic in nature.

(3) Because of the wide range of formulations offered and the difference in test results, it would seem prudent to produce a specification, essentially based on performance tests, and to have an approved list of detergents before the next Torrey Canyon type of incident. AOL is producing a specification to govern purchases for Navy use.

(4) Of the various other materials and suggestions submitted to AOL, only the use of sinking materials appeared a practical proposition for dealing with a large oil spill. From the limited work on these materials, the two main problems would be (a) the design of efficient apparatus for shipboard use to scatter the sinker and (b) the determination of optimum particle size/weight of sinkers to prevent either blowing away in windy conditions or sinking too rapidly through the oil before absorption can occur.

#### 11. Acknowledgements

Considerable disruption of AOL's normal programme of work was caused by the emergency and this lasted for seven to eight weeks

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The Superintendent wishes to express his appreciation of the staff who worked more than their required hours including shift work to keep some apparatus running twenty four hours a day. Particular mention must be made of Mr. C. J. Spilman who dealt with the DGS.6992 specification cleaning of emulsion tests and progressed the samples through the laboratory.

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## APPENDIX A

### Extract from Material Specification No. DG Ships/6992

#### Bilge Cleaning Material

##### 1. Scope

This specification covers the supply of a liquid cleaning material suitable for use in bilges of machinery spaces of HM Ships.

The material shall be suitable for application by means of a portable sprayer, working under a pressure of 25 psi.

The material shall combine with accumulations of fuel, lub. oil and grease and when washed with a jet of sea water a stable emulsion shall be formed.

##### 4. Materials

The bilge cleaning material shall be a homogenous blend of chemicals, free from suspended matter or sediment, and stable in storage for at least 12 months within the temperature range of 14 to 140°F. It shall be non-toxic, non-corrosive and shall not require the use of any special protective clothing. It shall not have an abnoxious smell or be unpleasant in use in confined spaces.

##### 6. Testing

Samples taken from any portion of the supply shall comply with the following requirements:-

Test	Test Limit	Method
Flash point °F	NIL	IP.34
Explosivity % Max.	10	Fed. Standard 791 No. 1151
Cleaning properties	More than 95% of the FFO film removed	Appendix A
Emulsification properties after 5 hours		Appendix B
Oil separation ml Max.	1	
Water separation ml Max.	15	

A. Cleaning Test

5 grams of Admiralty reference furnace fuel oil "I" is brushed over a 12" x 12" metal panel (Aluminium alloy N.S4 is a suitable material). The panel is stoved at 120°C for 18 hours, in a horizontal position. After cooling, the panel, in a vertical position, is sprayed with 50 ml of the cleaning material, allowed to stand for 30 minutes, and then washed with a jet of synthetic sea water (made up to the formulation in method IP.135) until no further oil is removed.

B. Emulsification Test

40 ml lubricating oil OEP-69	)	Are placed in a Herschel tube
30 ml synthetic sea water	)	and stirred at 1500 rpm for
(made up as in method IP.135)	)	5 minutes at room temperature.
10 ml cleaning material	)	

The emulsion is allowed to stand at 60°F ± 5°F and the volumes of emulsion, water and oil noted at ½, 1, 2, 3, 4 and 5 hours.

(This is a modification of method 11 of DEF.2000)



TABLE I  
RESULTS OF EMULSIFICATION AND CLEANING TESTS

Sample Ref.	Emulsification Test								Cleaning Assessment
	With OEP 69				With Crude Oil				
	After 5 hours		After 24 hours		After 5 hours		After 24 hours		
	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	
TC 1	Tr	7	-	-	Tr	4	1	17	1
TC 2	2	23	-	-	-	-	-	-	3
TC 3	Tr	4	-	-	1	3	2	11	1
TC 4	0	9	-	-	Tr	0	Tr	4	4
TC 5	0	13.5	-	-	0	4.5	Tr	16	1
TC 6	0	21	-	-	0	4	Tr	13	1
TC 7	0	22	-	-	0	7	0	17	3
* TC 8	Tr	0	-	-	-	-	-	-	1
* TC 9	0	6	-	-	-	-	-	-	1
* TC 10	0	0	-	-	-	-	-	-	1
TC 11	Tr	18	-	-	Tr	7	Tr	17	3
TC 12	Tr	18	-	-	-	-	-	-	1
TC 13	40	21	-	-	-	-	-	-	3
TC 15	0	19	-	-	0	8.5	1	19	1
* TC 16	0.5	0	-	-	0	12	0	20	5
* TC 17	Tr	0	-	-	0	0	0	1	2
TC 18	Tr	18	-	-	0	7	1	12	2
TC 19	0	7.5	-	-	0	3	-	-	5
TC 20	0	6.5	-	-	0	6.5	1	18	2
TC 21	Tr	8	-	-	-	-	-	-	1
TC 22	0	6	-	-	0	3.5	2	14	3
TC 23	0	17	-	-	0	8	Tr	19.5	1
TC 24	0.5	5	-	-	0	0	1	4	2
TC 25	Tr	6.5	-	-	0	6.5	0.5	18	3
* TC 27)									
* TC 28)	2	29	-	-	-	-	-	-	1
TC 29	2	31	-	-	-	-	-	-	5
TC 30	Tr	17.5	-	-	0	5	0	16	5
TC 31	Tr	7	-	-	0	1.5	Tr	7	4
TC 32	0	17	-	-	0	5.5	0	16	3
* TC 33	0	9	-	-	-	-	-	-	5
* TC 34	0	4	-	-	-	-	-	-	5
* TC 35	0	5	-	-	-	-	-	-	5
TC 36	Tr	15	-	-	0	6.5	0	17.5	1
* TC 37	Tr	13	-	-	-	-	-	-	5
TC 38	0	7	-	-	0	4	-	-	4
TC 39	0	6	-	-	0	2	-	-	5
TC 40	28	34	-	-	-	-	-	-	-

Tr = Trace

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Table 1 - Sheet 2

Sample Ref.	Emulsification Test								Cleaning Assessment
	With OEP-69				With Crude Oil				
	After 5 hours		After 24 hours		After 5 hours		After 24 hours		
	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	
TC 43	47	29	-	-	3	3	10	3	1
TC 44	2	28	-	-	-	-	-	-	1
TC 47	0	14.5	-	-	-	-	-	-	5
TC 48	0	12	-	-	0	5	0	15	3
TC 49	1	28	-	-	0.5	2.5	2	9	2
TC 50	4	0	-	-	5	0	11	0	3
* TC 51	Tr	4	-	-	0	0	Tr	15	3
TC 52	Tr	16	-	-	1	4	-	-	1
* TC 53	13	8.5	-	-	-	-	-	-	2
* TC 54	42	5.5	-	-	-	-	-	-	1
TC 55	Tr	19	-	-	-	-	-	-	2
TC 56	0	6	-	-	0	5	1	15	3
TC 57	2	35.5	-	-	-	-	-	-	-
TC 58	2.5	29.5	-	-	-	-	-	-	5
TC 59	1.5	30.5	-	-	0	0	0	Tr	5
TC 60	1	24	-	-	-	-	-	-	2
TC 61	2.5	31	-	-	0	0	40	40	3
TC 63	1	3	-	-	1	5	2	15	1
TC 64	7	0	-	-	-	-	-	-	1
TC 65	5	22	-	-	-	-	-	-	2
TC 66	2	33	-	-	-	-	-	-	1
TC 67	0	16.5	-	-	0	5	0	14	1
TC 68	1.5	11	-	-	0	2	0	29	5
TC 69	1.0	0	-	-	0	0	0	10	1
TC 70	Tr	21	-	-	-	-	-	-	2
TC 71	-	-	-	-	-	-	-	-	5
TC 72	0	6	0	17	1	11	1	26	2
TC 73	2	21	-	-	-	-	-	-	4
TC 75	Tr	21	-	-	0	5	0	15	2
TC 76	18	16	-	-	-	-	-	-	1
TC 77	8	29.5	-	-	-	-	-	-	5
TC 78	0	18	-	-	-	-	-	-	4
TC 79	0	16	-	-	0	5	0	15	4
TC 80	2	30.5	-	-	Tr	28	39	29	5
TC 81	1	15	-	-	-	-	-	-	3
TC 83	1.5	30.5	-	-	1	0	2	0	3
* TC 84	0	0	Tr	5	2	Tr	3	6	4
TC 85	4	18.5	-	-	0	3	1	9	4
TC 86	Tr	18	-	-	0	8	1	9	3
TC 87	1.5	18.5	-	-	0	5	0	17	5
TC 88	0	15	-	-	-	-	-	-	3
TC 89	0	8	-	-	0	6	Tr	16	5
TC 90	0	12.5	-	-	0	2	Tr	7	4

Tr = Trace

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Table 1 - Sheet 3

Sample Ref.	Emulsification Test								Cleaning Assessment
	With OEP-69				With Crude Oil				
	After 5 hours		After 24 hours		After 5 hours		After 24 hours		
	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	
TC 91	0	27.5	-	-	0	3	Tr	11	4
TC 92	0	10	-	-	0	6	Tr	14	5
TC 94	2	30	-	-	0	29	0	30	4
TC 95	0	15	-	-	0	3	1	10	2
TC 96	0.5	15.5	-	-	0	6	Tr	14	3
TC 97	0.5	0	1	2	0	0	1	0	4
TC 98	0	0	Tr	4	0	1	1	4	3
TC 99	0	11.5	-	-	0	13	1	19	5
TC101	0	31.5	-	-	0	22	50	30	5
TC102	0	15	-	-	0	4	Tr	14	2
TC103	Tr	13.5	-	-	1	3	2	12	5
TC104	0	2	Tr	5	1	0	1	0	5
TC105	1.5	0	2	2	0	0	0	7	5
TC106	3	0	4	0	0	0	1	0	2
TC107	Tr	3	Tr	15	0	2	0	7	2
TC109	1	17	-	-	0	3	Tr	10	1
TC110	2	33	-	-	0	13	1	18	5
TC114	Tr	16	-	-	-	-	-	-	2
TC115	1	12	-	-	0	5	Tr	14	3
TC116	1	0	4	Tr	-	-	-	-	5
TC117	16	1	-	-	1	0	4	0	5
TC119	3	20	-	-	0	23	1	30	5
TC120	-	-	-	-	-	-	-	-	5
TC121	40	34	-	-	-	-	-	-	5
TC122	1	7	-	-	Tr	4	6	15	4
TC123	50	30	-	-	0	24	44	26	4
TC124	20	21	-	-	1	4	2	12	5
TC126	0	12	-	-	0	6	Tr	15	1
TC127	0	15	-	-	0	4	0	13	4
TC128	41	37	-	-	-	-	-	-	3
TC129	55	25	-	-	-	-	-	-	1
TC130	2	15	3	26	0	9	0	19	3
TC131	0	15	0	23	0	6	0	17	3
* TC132	-	-	-	-	-	-	-	-	4
TC133	11	14	32	22	0	15	50	18	3
TC134	0	14	Tr	23	0	5	0	15	1
TC135	30	30?	30	32	1	6	2	17	1
TC136	0	10	Tr	21	0	9	0	20	2

Tr = Trace

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Table 1 - Summary

Sample Ref.	Emulsifier Test								Cleaning Assessment
	With OEP-69				With Crude Oil				
	After 5 hours		After 24 hours		After 5 hours		After 24 hours		
	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	ml. of oil	ml. of water	
TC137	-	-	-	-	-	-	-	-	4
TC138	3	35	37	38	-	-	-	-	5
TC139	0	19	0	23	-	-	-	-	-
TC140	2	16	3	23	-	-	-	-	-
TC141	0	37	-	-	-	-	-	-	5
TC142	42	28	42	29	0	3	0	14	1
TC143	0	23	1	29	0	0	Tr	0	4
TC144	0	11	1	20	0	4	0	11	2
TC145	1	0	1	0	2	12	3	21	4
TC146	2	4	2	13	0.5	2	0.5	5.5	-

Tr = Trace

\*Notes

- TC8, 9 and 10      Were samples from different batches of the same material.
- TC16 and 17      Differed only in that TC16 had a higher emulsifier  
content and therefore a lower solvent content.
- TC27 and 28      Had to be mixed in a 1:1 ratio and then with 20 parts of  
kerosene. These were carried out with this mixture.
- TC33, 34, 35,  
37, 53, 54,  
84 and 132      Contained unblended solvents, and would not be  
acceptable for this reason.
- TC51              Similar to TC8, 9, and 10, but with the emulsifier  
content halved.

TABLE 2

An abridged list of the hourly ratings obtained  
in the Swirling Table Emulsification Test

Sample Reference	TC 3			TC 5			TC 10			TC 17			TC 24		
Treatment Rate %	5	10	20	5	10	20	5	10	20	5	10	20	5	10	20
Rating after 1 hr swirling	5	5	5	2	2	2	1	1	1	4	2	1	5	5	5
Rating after 2 hrs swirling	5	5	5	2	2	2	1	1	1	4	1	1	5	5	5
Rating after 3 hrs swirling	5	5	5	2	2	2	1	1	1	3	1	1	4	4	4
Rating after 4 hrs swirling	5	5	5	2	2	1	1	1	1	3	2	1	4	4	4
Rating after 5 hrs swirling	5	5	4	2	2	1	1	1	1	3	2	1	4	4	4
Rating Number (Unweighted)	20	20	19	5	5	3	0	0	0	12	3	0	17	17	17
Rating Number (Weighted)	60	60	55	15	15	6	0	0	0	33	10	0	48	48	48
Sample Reference	TC 30			TC 36			TC 39			TC 49			TC 63		
Treatment Rate %	5	10	20	5	10	20	5	10	20	5	10	20	5	10	20
Rating after 1 hr swirling	5	4	4	5	5	4	4	4	3	5	5	4	5	5	4
Rating after 2 hrs swirling	5	4	3	5	5	4	3	3	1	5	4	3	5	5	3
Rating after 3 hrs swirling	5	4	2	5	5	4	3	2	1	4	3	1	4	5	3
Rating after 4 hrs swirling	5	4	2	5	5	4	3	2	1	4	3	1	3	4	2
Rating after 5 hrs swirling	5	3	1	5	5	4	2	2	1	4	3	1	2	3	2
Rating Number (Unweighted)	20	14	7	20	20	15	10	8	2	17	13	5	14	17	9
Rating Number (Weighted)	60	40	14	60	60	45	26	19	2	38	34	7	34	31	22

TABLE 3

Unweighted Rating Numbers, Obtained in the  
Swirling Table Emulsification Test

Treatment Rate	5%	10%	20%
Rating Units	Sample Reference (Prefixed TC)		
0	10, 51, 107	10, 16, 51, 61, 107	10, 16, 17, 31, 51, 61 98, 107 (4) (69) (22)
1	16	97,	38, 97,
2	-	38, (69)	39,
3	61	17	4, 5, 69, 83, 22
4	-	-	-
5	5	5	49, 127
6	(69)	31 (4)	1, 32
7	-	69, 83	30, 92, 106 (56)
8	38	39	-
9	-	-	56, 63, 134
10	39, 98	1, 4, 92, 106, 134 (22) 67	104, 67
11	-	98	-
12	17	-	103, 09, 122, 126
13	-	20, 49	20, 21, 126, 134
14	63, 69, 83, 92, 106, 67	30, 56, 103, 134 (56)	115, 136
15	4, 22, 97	22, 32, 122, 127	25, 36
16	(4)	109, 126	2
17	24, 31, 49, 115, 126	21, 24, 63, 104, 115	6, 24
18	20, 134, 127, (134)	126	48
19	-	136	3, 102
20	1, 2, 3, 6, 7, 11, 18, 21, 23, 25, 30, 32, 36, 48, 56, 96, 102, 103, 104, 109, 122, 126, 136 (22) (56)	2, 3, 6, 7, 11, 18, 23, 25, 36, 48, 96, 102	7, 11, 18, 23, 96

NR Where a number is in brackets it denotes repeat values obtained at some later date.

TABLE 4

Weighted Rating Numbers, obtained in the  
Swirling Table Emulsification Test

Treatment Rate	5%	10%	20%
Rating Units	Sample Reference (Prefixed TC)		
0	10, 51, 107	10, 16, 51, 61, 107	10, 16, 17, 31, 51, 98, 61, 107
1	16	97	38, 97,
2	-	38	39
3	-	98	69
4	-	-	-
6	-	-	4, 5, 22
7	-	-	49
9	-	31	1
10	61	17	-
11	-	-	83
13	-	-	32
14	-	-	30
15	5	5	-
17	-	69	-
18	-	-	92, 106
19	38	39	-
20	-	-	-
21	-	83	-
22	-	-	56
23	-	1	104
24	-	106, 92	-
25	-	-	63, 109
26	39	-	-
30	98	4	-
31	-	-	103
33	17	-	122, 126
34	63	49	21
35	-	-	-
36	-	-	134
37	69, 92, 106	56, 134	-
38	-	20	20
40	-	30, 103	-
41	-	122	-
42	83	109	-
45	4, 22, 97	22, 32	25, 36
46	31	63, 104, 126	2
48	24, 49, 126	21, 24	24
51	134	-	6, 48
55	20	-	3, 102
60	1, 2, 3, 6, 7, 11, 18 21, 23, 25, 30, 32, 36, 48, 56, 96, 102, 103, 104, 109, 122	2, 3, 6, 7, 11, 18 23, 25, 36, 48, 96, 102	7, 11, 18, 23, 96

TABLE 5

Grouping of results from Swirling Table Emulsion Tests

Group I Good emulsifier				Group II Moderate emulsifier				Group III Poor emulsifier			
TC REF.	% Emulsifier	Nature of Emulsifier	% Aromatics in Solvent	TC REF.	% Emulsifier	Nature of Emulsifier	% Aromatics in Solvent	TC REF.	% Emulsifier	Nature of Emulsifier	% Aromatics in Solvent
*10	50	NI + I	60	*17	30	NI + I	25	63	19.5	NI	High
*51	25	NI + I	77	31	20	NI + I	95	20	10	NI	92
*16	40	NI + I	25	61	28.5	NI + I	low	*25	10	NI	58
				*98	5	NI + I	99	36	12	NI + I	low
				38	50	NI	High	*2	30	NI + I	7.5
				97	10	NI + I	99	*24	40	NI	7.0
				39	20	NI	High	6	24	NI + I	43
				*69	33	NI + I	62.5	48	10	NI	High
				4	17	NI	81.5	*3	30	NI + I	16
				*5	21	NI + I	66	102	14	NI	73
				*22	30	NI	94	7	8	NI + I	15
				49	10	NI + I	17	11	30	NI	28.5
				*1	33.5	NI	24	18	25	NI + I	76
				83	17	NI	84	23	28	I	90
				32	19	NI + I	94	96	12	NI + I	
				30	10	NI	16				
				92	10	NI	20				
				106							
				*56	12	NI	57				
				104							
				109							
				103							
				122		NI					
				21	10	NI					

NI Non-ionic

I Ionic

\* Indicates most efficient products according to DGS/6992 emulsion test.



TABLE 6

Modified Swirling Table Emulsification Test to  
compare the efficiencies of various detergents for  
beach cleaning.

Rating Units Unweighted	Sample Reference Nos.
3	TC 5 *
4	TC 17
6	TC 1*/3*/24*/25/6*/19/15
8	TC 51*
15	TC 61
16	TC 20/103
20	TC 96

\* Products used to clear Torrey Canyon Oil Spill

TABLE 7

Interfacial Tension

<u>Sample No.</u>	<u>% to Standard</u>	<u>Corrected</u>
1	7.0	7.9
3	12.9	14.1
4	26.3	27.5
5	6.2	7.0
7	19.8	21.0
8	2.1	2.5
17	8.0	9.0
20	10.2	11.3
21	9.2	10.2
22	4.9	5.6
23	15.1	16.4
24	12.2	13.3
25	22.8	24.3
51	1.4	1.8
56	19.2	20.4
69	14.5	15.7
97	10.0	11.1
102	14.5	15.7

**TABLE 8**

**Leaching of ethylene oxide condensates from treated crude oil**

<b><u>Sample No.</u></b>	<b><u>Weight of EOC found in water (mg)</u></b>	<b><u>Weight added (mg)</u></b>	<b><u>Percentage in water</u></b>
TC 5	42.0	55.5	76
10	48.0	50.5	95
16	37.5	131.5	28
17	43.5	114.0	38
31	42.0	51.0	82
38	61.5	204.0	30
39	51.0	62.0	82
49	37.5	47.6	79
51	27.5	29.5	93
61	15.0	42.8	35
69	3.0	23.5	13
83	28.5	53.0	54

**NB.** These results were obtained from treated crude oil containing 20% detergent.

TABLE 9  
Effect of adding absorbing materials to oil on sea water

T.C. Ref. No.	Material Type	Quantity Required to absorb 10 ml of crude oil gms.	Treatment of oil with absorbant.	Approx. quantity of oil released after 7 days. ml.	Approx. quantity of oil released after 6 weeks. ml.	Remarks
41	Oil absorbing granules	8.8	Absorbed oil & sank as individual granules. Once wet would not absorb oil.	5	6	Appears to be hydrophilic. At the end of 6 weeks the bottom layer of the sunk material appeared free of oil and small droplets of oil were appearing on top of the sunk material.
42	Vermiculite	4.0	Floated on surface as oily mass	All oil as oily mass with TC 42 on surface	All oil as oily mass on surface	Appears hydrophilic. A part, which appeared oil free had sunk after 6 weeks.
74	Oil absorbing granules	9.6	Granules tended to absorb oil, coagulate and sink as lumps	Trace only	Trace only	
82	Expanded Perlite	8.8	Absorbed oil and floated. Once wet would not absorb oil and tended to sink	All oil as oily mass with TC 82 on surface	All oil as oily mass on surface	Appears hydrophilic. approx. 50% which appeared oil free had sunk to the bottom in 6 weeks. Any wind during application would be likely to carry this material a considerable distance before it would settle.
93	Treated Chalk	27.9	As oil absorbed coagulation into lumps occurred which then sank. The powder itself floated.	None	None	Is lipophilic. A little excess added was still floating on the surface after six weeks.

/cont'd.....

TABLE 9 (cont'd).

Effect of adding absorbing materials to oil on sea water

T.C. Ref. No.	Material	Quantity required to absorb 10 ml of crude oil gms.	Treatment of oil with absorbant	Approx. quantity of oil released after 7 days ml.	Approx. quantity of oil released after 6 weeks ml.	Remarks
100	Natural Sponges	0.7	Rapidly absorbed oil and remained floating	Trace only	Trace only	These natural sponges appear lipophilic and rapidly absorbed the oil
118	Treated oil absorbing granules	26.0	The majority sank some finer particles remained floating on the surface	Trace only	Trace only	Material appears hard, and tended to sink fairly quickly, before it had absorbed very much oil. Appeared to have been treated to make it lipophilic
41 + 45	Oil absorbing granules plus amine	13.8	Sinks the oil readily	Trace only	A few small drops of oil	
82 + 45	Expanded Perlite plus amine	8.8	Better absorption than the untreated TC 82. Very little sank	All oil as oily mass with TC 82	Majority of oil as oily mass on surface	Approx. 10 to 20% of TC 82 had sunk to the bottom after six weeks.
-	Sand	33.7	Providing sand fell into the oil, it became coated with oil & carried it to the bottom. Globules of oil formed on the surface of the sunk sand	2	3	Globules of oil slowly oozed out of the sand all the time

TABLE 10

## THE BEST DETERGENTS

ACL Code Number	Emulsification Tests										Interfacial Tension with 2% of detergent in FFO as % of figures for untreated oil	Cleaning Test Merit Rating
	Stirring in cylinder (DGS-6992 Method)											
	With OEP-69											
	With Crude Oil											
	Separation in 5 hrs.		Separation in 5 hrs.		Separation in 24 hrs.		Swirling Table Merit Ratings (unweighted) with					
Oil ml	Water ml	Oil ml	Water ml	Oil ml	Water ml	5% Detergent	10% Detergent	20% Detergent				
*TC1	Trace	7	Trace	4	Trace	1	17	20	10	0	8	1
*TC3	0	4	1	3	2	11	20	20	20	19	14	1
*TC5	0	13.5	0	4.5	Trace	16	5	5	3	3	7	1
TC17	Trace	0	0	0	0	1	12	3	3	0	9	2
TC22	0	6	0	3.5	2	14	15	13	2	2	6	3
*TC24	0.5	5	0	0	1	4	17	17	17	17	13	2
TC25	Trace	6.5	0	6.5	0.5	18	20	20	20	15	24	3
*TC31	Trace	4	0	0	Trace	15	0	0	0	0	2	3
TC36	0	6	0	5	1	15	20	14	14	9	21	3
*TC69	1	0	0	0	0	10	10	5	5	2	16	1
*TC98	0	0	0	1	1	4	10	10	11	0	-	3
*TC107	Trace	3	0	2	0	7	0	0	0	0	-	2
*TC126	0	12	0	6	Trace	15	20	16	16	12	-	1
TC134	0	14	0	5	0	15	18	10	10	9	-	1

\* Detergents purchased - TC5 was modified and the new formulation called TC134

+ These products were of foreign manufacture

TABLE 11  
OTHER DETERGENTS PURCHASED IN THE FIRST RUSH

AOL Code Number	Emulsification Tests										Interfacial Tension with 2% of detergent in FFO as % of figures for untreated oil	Cleaning Test Merit Rating	
	Stirring in cylinder (DGS.6992 Method)						Swirling Table Merit Ratings (unweighted) with						
	With OEP-69		With Crude Oil		Separation in 5 hrs.		Separation in 24hrs.		5%	10%			20%
	Oil ml	Water ml	Oil ml	Water ml	Oil ml	Water ml	Oil ml	Water ml	Detergent	Detergent			Detergent
TC 2	2	23	Trace	4	Trace	1	17	20	16	-	1		
TC 4	0	9	Trace	0	Trace	Trace	4	15	2	28	4		
TC 6	0	21	0	4	Trace	Trace	13	20	17	-	1		
TC 7	0	22	0	7	0	0	17	20	20	21	3		
TC 9	0	6	-	-	-	-	-	-	-	-	1		
TC 10	0	0	-	-	-	-	-	0	0	-	1		
TC 11	Trace	18	Trace	7	Trace	Trace	17	20	20	-	3		
TC 12	Trace	18	-	-	-	-	-	20	20	-	1		
TC 49	1	28	0.5	2.5	2	9	17	13	5	-	2		
TC102	0	15	0	4	Trace	14	20	19	16	-	2		

Notes TC 2 was superseded by TC 24.

TC 6, 11 and 12 were from the same supplier, but had different formulations.

TC 9 and 10 were too viscous for spraying and were superseded by TC 51.

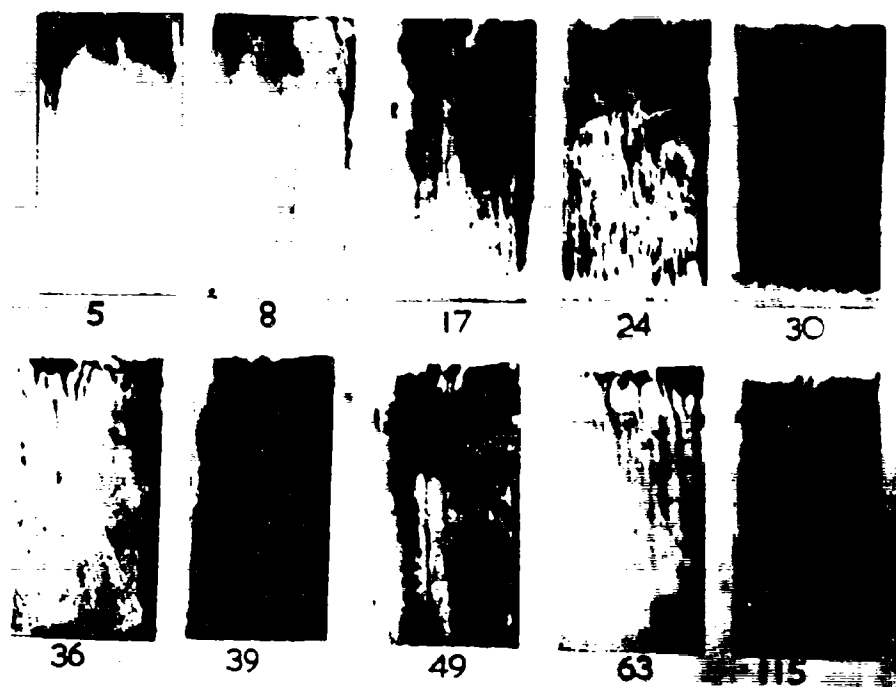


FIGURE ONE Cleaning Test. 6"x3" panels after cleaning.



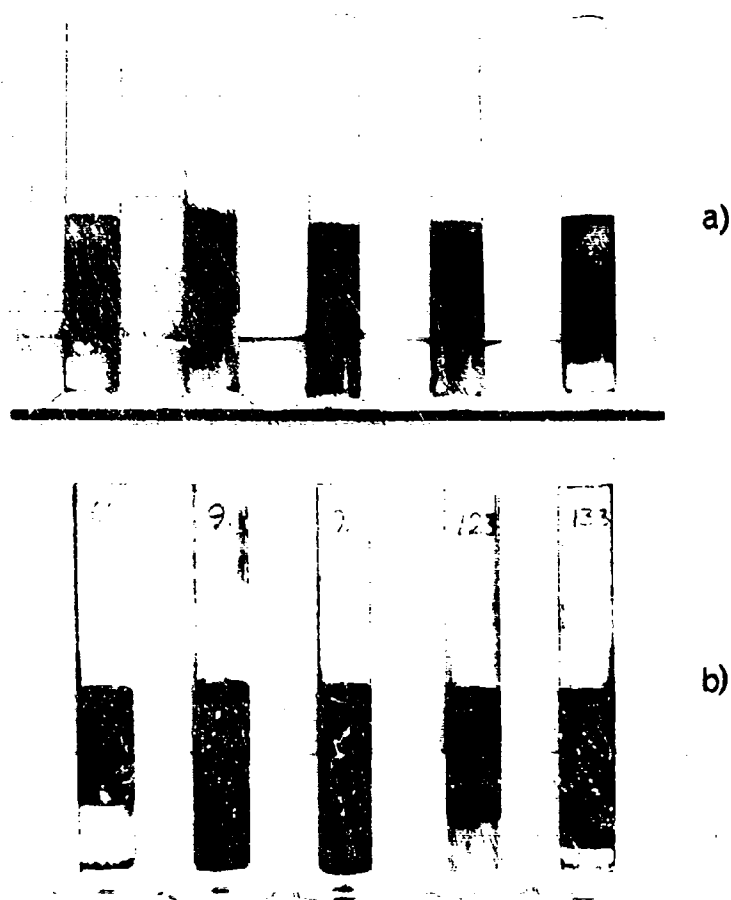


FIGURE TWO. Emulsion stability test.

a) with oil OEP 69.

b) with crude oil.

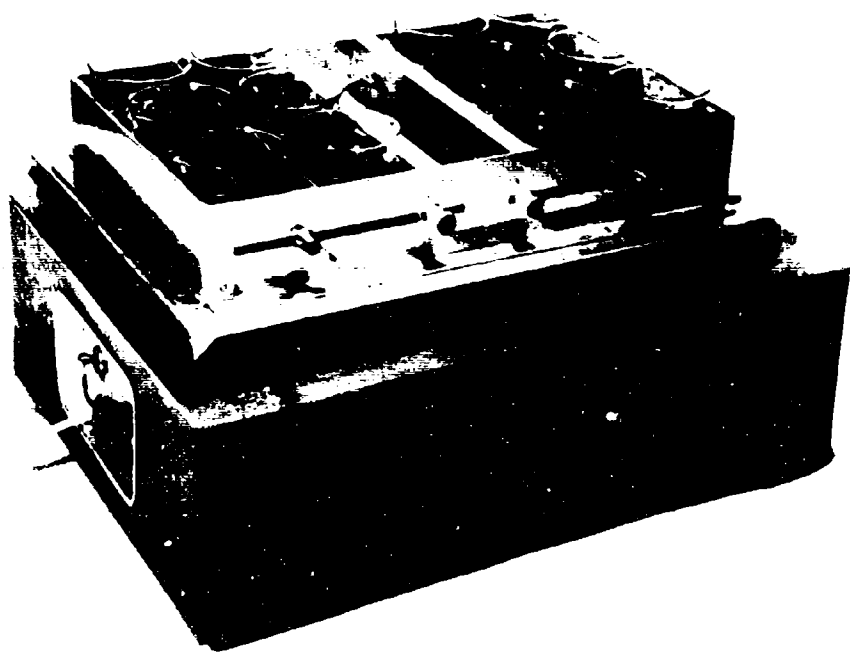


FIGURE THREE. The swirling table.

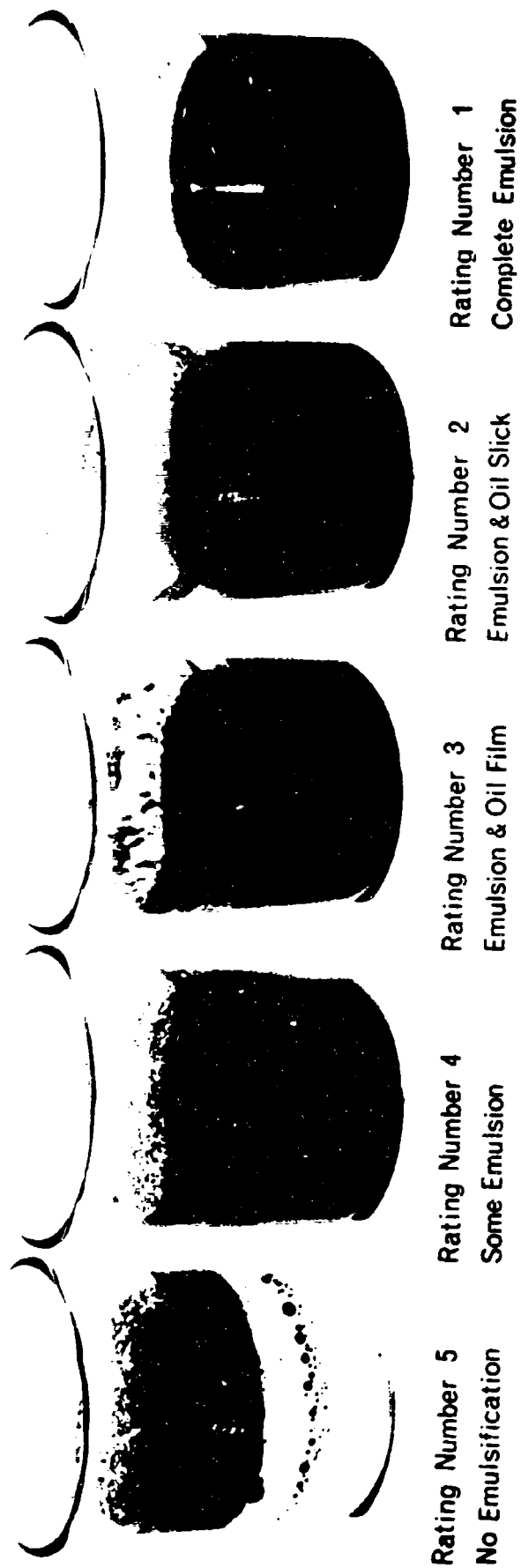


FIGURE FOUR: Swirling Table Emulsion Test, Typical Ratings

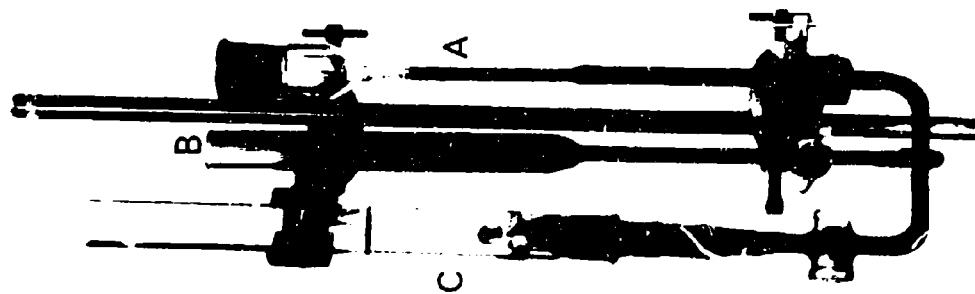


FIGURE FIVE. Apparatus.

# INTERFACIAL TENSION TEST

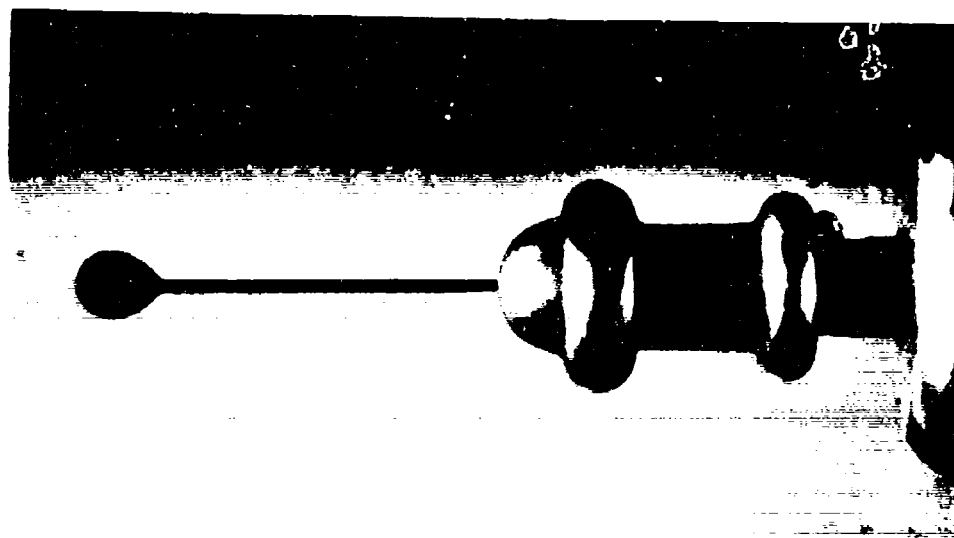


FIGURE SIX. Formation of  
oil drop.

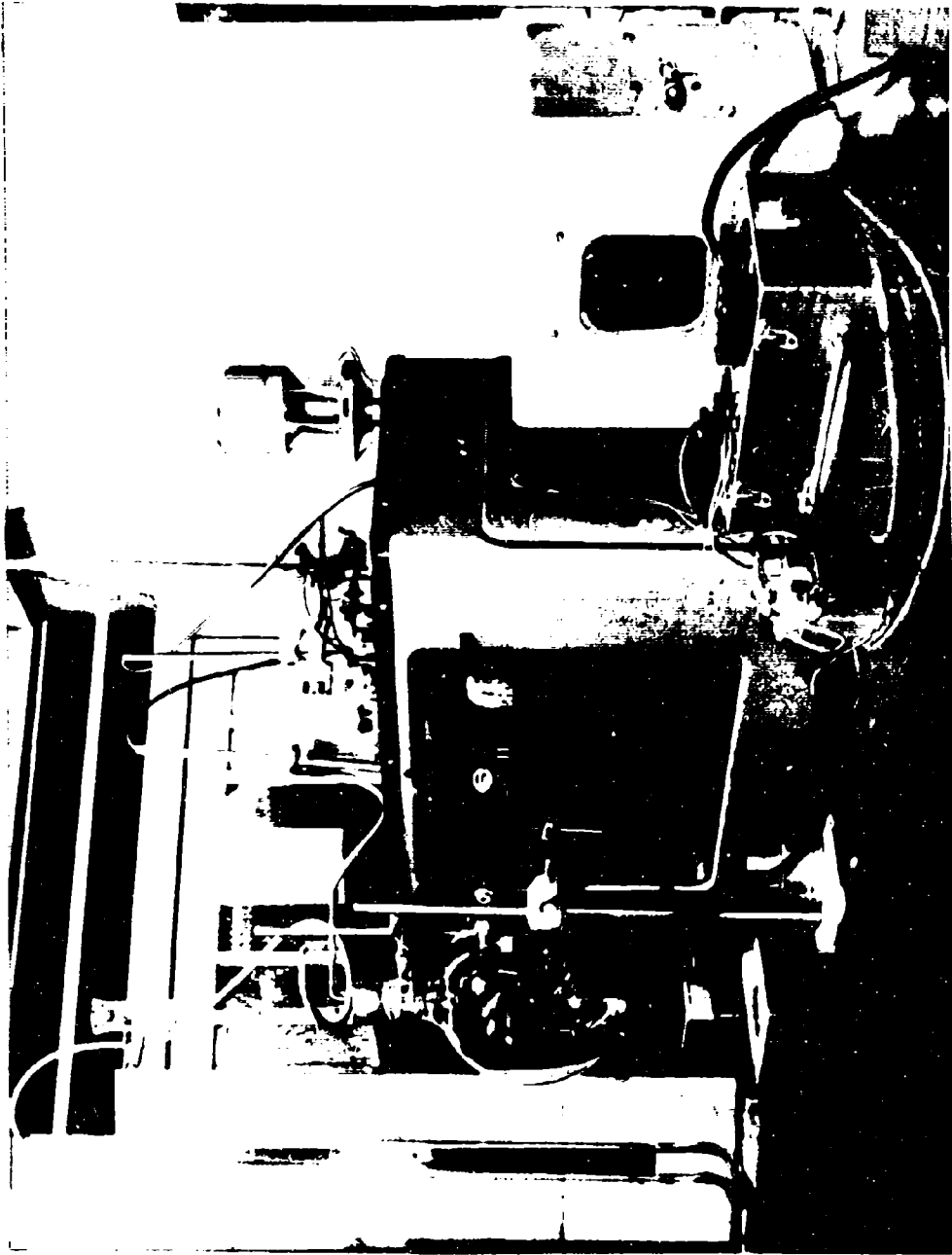
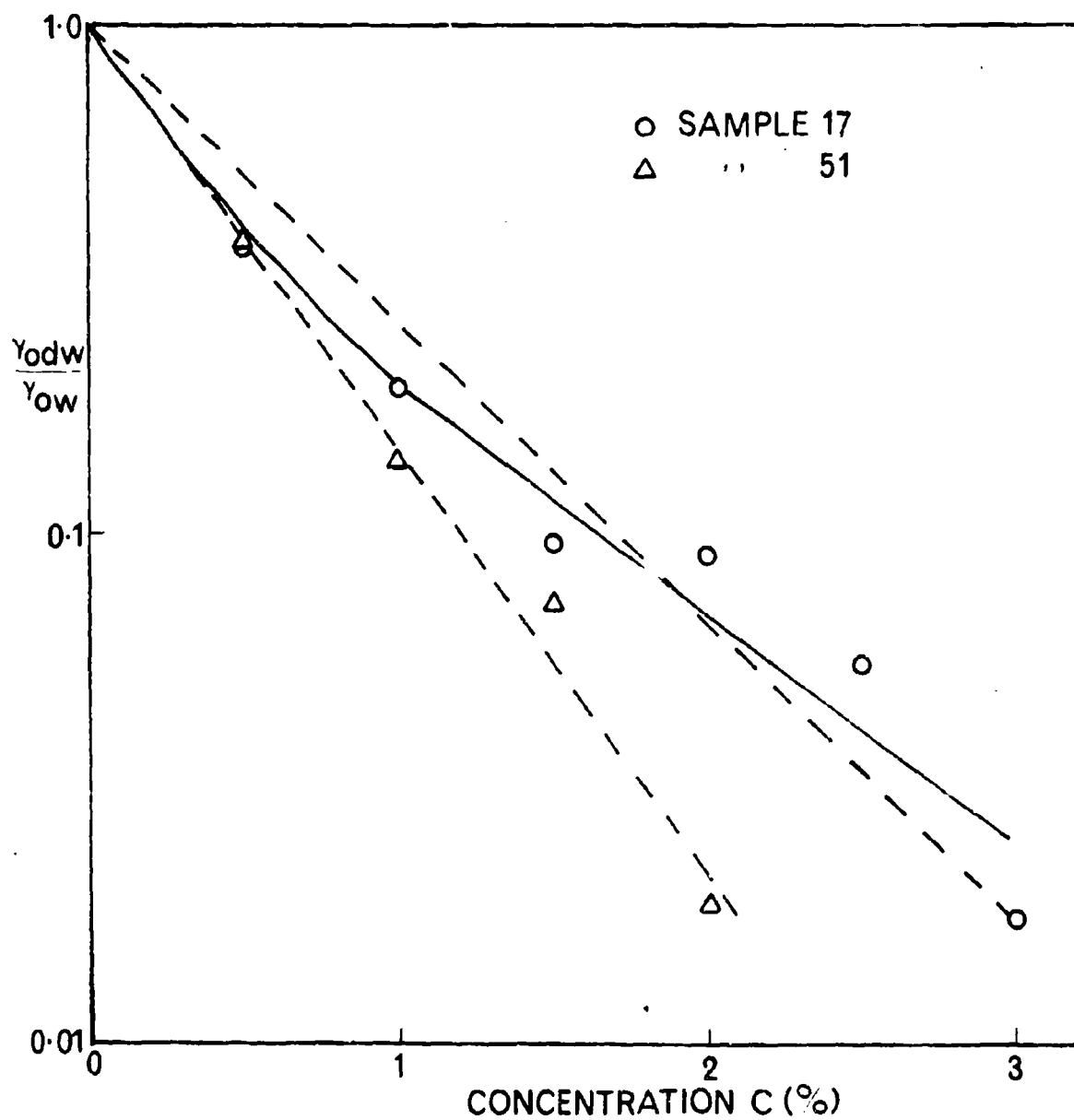
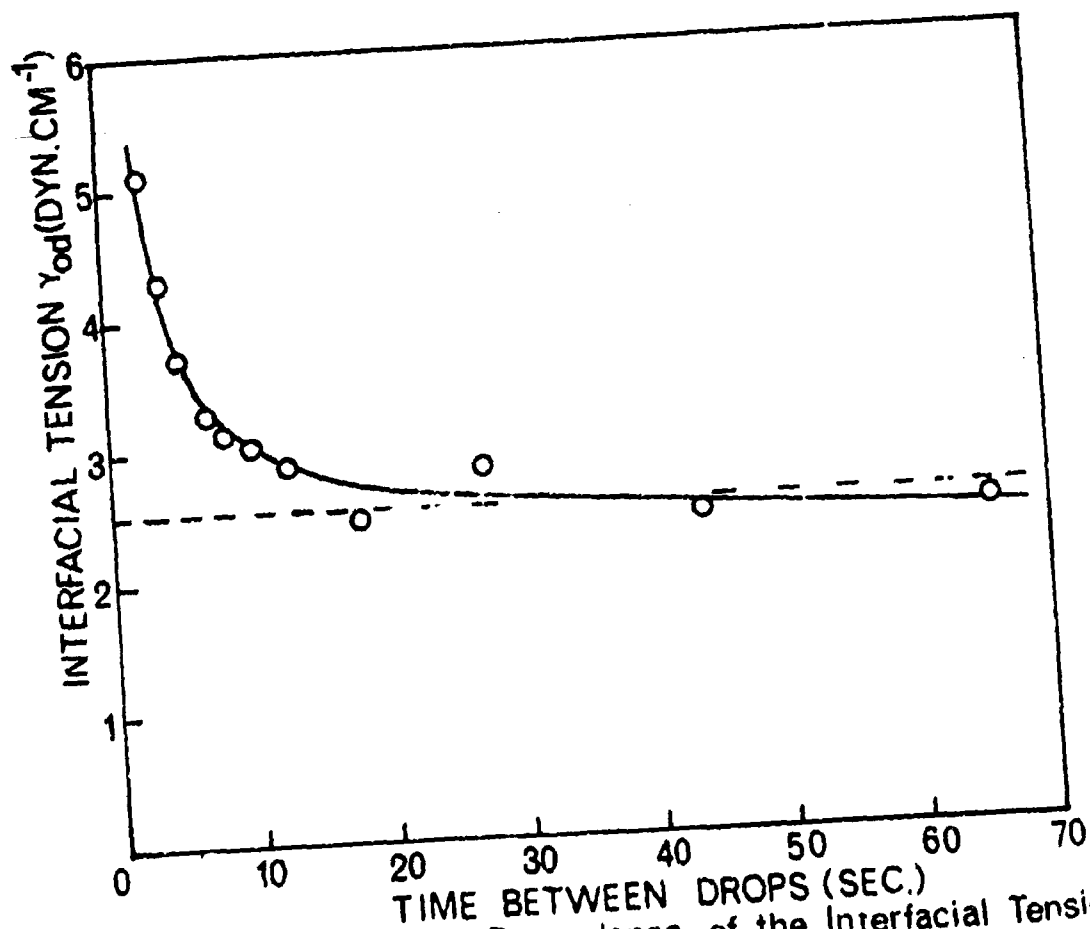


FIGURE SEVEN Semi-automated interfacial tension apparatus.



**FIGURE EIGHT** The Concentration Dependence of  $Y_{odw}/Y_{ow}$  for Samples 17 and 51



**FIGURE NINE** The Dependence of the Interfacial Tension on Time of Drop Formation for Sample 17.