

THE EFFICIENCY OF INDIGENOUSLY MANUFACTURED POLYURETHANE FOAMS AND DISPERSANTS IN THE REMOVAL OF SPILLED OIL

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ABSTRACT

The absorbing capacities of a brand of Indian polyurethane foam and four different indigenous dispersants were tested in the laboratory using spills of heavy furnace oil. Polyurethane foam was found to absorb about 100% its own weight of oil. It could be reused after the oil was squeezed from it. The dispersants were effective in removing the oil completely if these were used with oil in the ratio of 1:1. Of the 4 dispersants tested, one was found to be non-toxic and this particular brand was found to be most effective.

Oil pollution is becoming widespread as a result of our dependence on the oil-based technology for producing energy. Oil pollution creates complexity in the marine food chain and the stability of some of the hydrocarbons in the food chains may lead to potentially dangerous situations. Oil passes through different trophic levels in the sea and eventually reaches organisms which are harvested for human consumption. A more serious situation arises as a result of its accumulation in human food. The long term effects of poisons coming from crude oil may be of the nature of carcinogenic compounds.

Another concern is the possible damage to marine ecology by oil pollution. Several biological processes which are important for the survival of marine organisms and which occupy key positions in the life processes of marine organisms are triggered through extremely low concentrations of chemical messengers in sea water. The interference with chemical messengers may lead to adverse effect on the survival of some marine

species either directly or through other organisms which provide link in the marine food chain.

World transport of crude oil across the seas has been estimated as 1400 million tonnes (MT) per year which is 58% of total annual production of 2400 MT (Brummage, 1973). About 54% of this marine transport, approximately equivalent to 756 MT, is taken from the Gulf countries and is carried across the Arabian Sea. Of this 317 MT goes to Far East and Japan (Wong, Green and Cretney, 1976). This transportation of crude in the Arabian Sea is of direct concern to India as substantial quantities of tar balls appear on our beaches in certain months (Anonymous, 1975, 1976). The estimates of annual oil spill in the sea vary between 2.2 and 4.9 MT (Revelle, Wenk, Ketchum and Corino, 1971; Brummage, 1973) which is roughly equivalent to 90-200 litres/sec. Any approximation of the total oil spill in the Arabian Sea is yet to be made.

Different physical and chemical means have been suggested to clean up accidental

and/or intentional oil spills on the sea. Application of the most suitable method depends on weather, sea, state, distance from land etc. In any case physical methods are to be preferred as they remove the oil without affecting the marine ecosystem significantly. Chemical methods should be applied only as a last resort because of their toxic nature.

So far only one study has been carried out in India on the efficiency of one brand of indigenous polyurethane foam for the oil removal (Bhandare and Sen Gupta, 1976). In this paper, we report two other methods for removing the oil from sea water. The first one is "to absorb the oil with absorbing material and then to remove the absorbent together with the oil" and the second one is "to disperse the oil by the dispersant". We used heavy furnace oil in all our tests.

Removal of oil by the absorbing material

In this method the absorbing material used was a brand of Indian polyurethane foam having pore number 1500/cm². This foam is of light spongy material. When spread over floating oil, it rapidly absorbs the oil and still floats. The oil-saturated foam chips can be collected and oil from them can be removed by squeezing them

by pressure roller. The squeezed foam can be used again for absorbing more oil.

Retention capacity of foam with smaller amount of oil

Weighed quantity of oil was added to sea water contained in a cylindrical jar and the mixture was stirred well for about 10-15 minutes. After allowing it to settle for about 30 seconds, the emulsion was filtered through a pad of foam (74 cm in diameter and 1.5 cm thick) weighing about 4 g fitted to a Buchner-funnel. The filtrate was then extracted with aliquots of hexane. The final hexane extract was evaporated to dryness and the oil residue was weighed. The same experiment was repeated by doubling the quantity of oil. The results are presented in Table I.

Retention capacity of the foam at higher concentration of oil

Weighed quantity of oil was uniformly spread in a rectangular tank containing sea water so that it had 1 mm thick layer of oil. The mixture was then stirred well and allowed to settle. After settling, weighed quantities of foam chips (0.5 cm thick) were added till the entire oil was absorbed. The oil was then squeezed out from the foam chips and weighed. The results are given in Table II.

Table I. Test showing the retention capacity of polyurethane foam with smaller amounts of oil. All weights are in grams.

Oil added	Concentration in filtrate	Oil retained by foam	Retention %	Average retention %
4.0098	0.0022	4.0076	99.94	99.94
8.0135	0.0040	8.0095	99.95	

Table II. Test showing the retention capacity of polyurethane foam at higher concentration of oil. All weights are in grams.

Oil added	Foam added	Oil retained by foam	Retention %
15.1331	30.0	13.7529	91

From Table I, it can be seen that with 4 gm oil, the percentage retention capacity was 99.94 whereas it was 99.95 when the amount of oil was doubled. In other words, the percentage retention capacity is independent of the

quantity of oil added. This retention capacity was further confirmed from the results of the experiment given in Table II in which the percentage retention capacity was found to be 91. It is known (Nelson-Smith, 1972) that polyurethane foam can absorb about 100% its own weight of oil, which was confirmed by our experiments. Further experiments with another brand of Indian polyurethane foam, having pore number 200/cm², have shown that its absorbing capacity is reduced when the quantity of oil is measured (Bhandare and Sen Gupta, 1976). Evidently, the size of the foam-pores plays an important role in this process.

Table II also shows that the foam used for absorbing the spilled oil was twice the quantity of oil. The foam chips spread over the oil soon got saturated by absorbing both oil and water. However, the percentage removal remained almost the same as it was in the earlier experiment (Table I). This shows that in the oil spills, occurring at sea, the quantity of foam will have to be more than the oil. However, the foam can be reused in west state after squeezing the oil out. Dried foam is not very suitable for this purpose, as after the retention of residues from the oil, it becomes brittle on drying. Instead of carrying a huge bulk of polyurethane foam the chemicals can be taken on board and by mixing them under agitation on the required quantity of the foam can be generated.

Removal of oil by dispersants

Dispersants usually consist of a powerful emulsifying agent (surfactant) dissolved in a solvent and an added stabilizer. When a sample of oil is treated with a combination of suitable emulsifier-solvent and the mixture is diluted with water

the stirred vigorously, the oil is dispersed into exceedingly small droplets. If the dispersion is allowed to stand without further agitation, an oily layer separates which can be redispersed by further stirring.

Usually, the task consists of two operations; firstly the uniform application of a dispersant to the floating oil and secondly the mixing of the treated oil with the upper layer with sufficient agitation to break up the oil slick into droplets. The same agitation will mix the small oil particles into large volume of water so that they are less likely to meet and recombine. Although, the natural action of wind and waves on the sea provides sufficient agitation, it is always necessary to mix up the oil with the water by mechanical stirring after having spread the emulsifying chemical on to the floating oil. The propeller of the ship, spraying the dispersant, is quite sufficient for this purpose.

In the present investigation four different dispersants were used to determine their oil removal capacities. These dispersants were produced indigenously and the samples were sent to us for testing. We numbered them in serial order and their active functional groups and probable compositions were determined (Solimabi and Topgi, 1977).

Oil removing capacity of dispersants

Suitable quantity of oil was spilled and dispersant added to sea spilled contained in a cylindrical jar and the mixture was stirred well. During the stirring the oil broke up into small particles. A substance like chocolate-mousse was formed which floated at the surface. It was skimmed up and the clear emulsified solution was treated

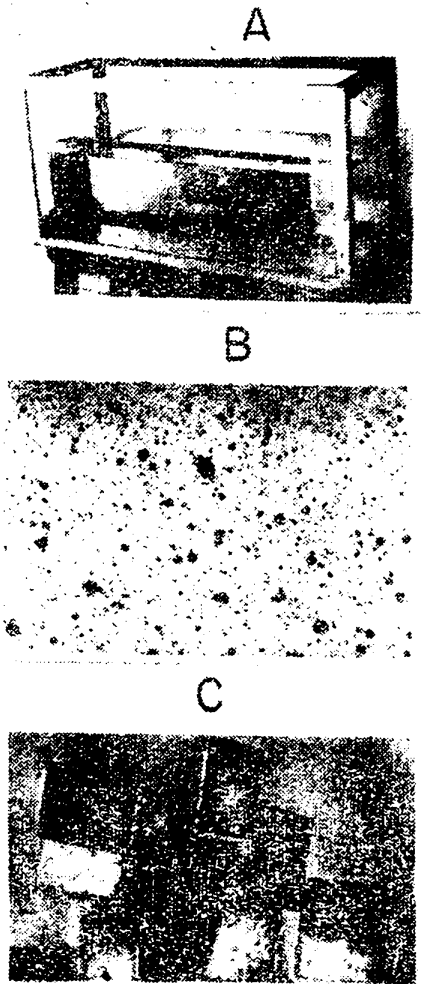


FIG. 1

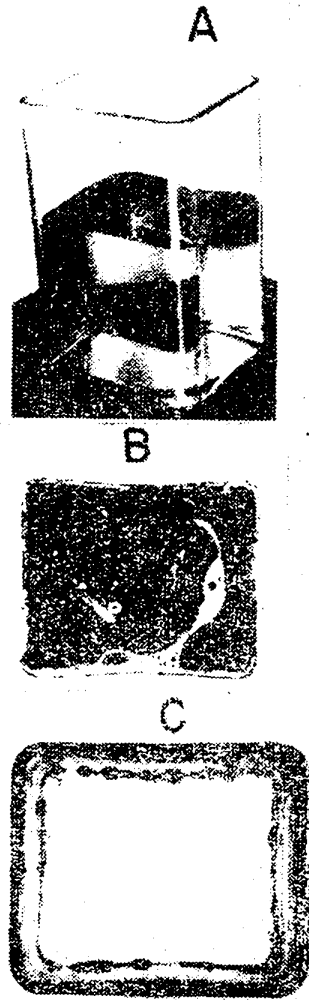


FIG. 2

Fig. 1: A: Rectangular tank containing sea water. B: Oil spreading uniformly over the surface of sea water. C: Oil absorbed by foam chips thereby making the sea water clear.

Fig. 2: A: Cylindrical jar containing sea water. B: Oil spread uniformly over the surface of sea water. C: After the addition of the dispersant.

Table III. Test with four different dispersants showing their oil removing capacity. All weights are in grams.

Dispersants	Oil added	Dispersant added	Oil left in water	Removed oil	Removed oil %
1	1.5921	1.5462	0.0138	1.5783	99
2	1.6420	1.5884	0.2502	1.3918	85
3	1.6203	0.9958	0.0314	1.5889	98
4	1.6047	1.0958	0.0730	1.5317	95

with hexane. The hexane extract was evaporated to dryness and the oil residue was measured. We obtained the optimum quantity of dispersant by treating a known amount of oil with varying quantities of dispersant.

The same experiment was repeated with the other dispersants. The results are given in Table III.

To make a satisfactory emulsion of floating oil, 2 parts of dispersant to 10 parts of oil are required, *i. e.*, the ratio of dispersant to oil should be 1:5 (Robinson, 1972). But our experiments indicate that with the Indian dispersants available with us, the ratio has to be about 1:1 to effect an efficient removal. The toxicity of all the dispersants has also been tested by studying their LC_{50} values using molluscs, crabs and prawns (Verlencar, Bhosle and Parulekar, 1977). It was observed that dispersants 2, 3 and 4 are highly toxic, while the dispersant No. 1 did not indicate much toxic property even at concentrations higher than 10 ppm.

Dispersants, however, are likely to be toxic to marine life. Hence, extreme care should be exercised to ensure that the dispersant in use is not over-treated and is less toxic than the oil itself, for, there is every possibility of the dispersant escaping into the marine environment without associating itself

with the oil-spill. It has been suggested (Revelle, Wenk, Ketchum and Corino, 1971) that even a mixture of oil and a non-toxic dispersant can become toxic to marine organisms. Tests with our dispersant No. 1, however, did not indicate this. Thus our conclusions are :

- (1) The brand of Indian polyurethane foam used in this study can absorb about 100% its own weight of oil irrespective of the quantity of oil present.
- (2) In actual oil-spill in the sea, the quantity of foam to be used should be more than the oil for the effective removal of oil.
- (3) For producing a satisfactory emulsion of floating oil, the ratio of indigenous dispersant to oil should be 1:1.
- (4) Dispersant No. 1 in our study was found to be non-toxic and also most effective in forming a dispersant oil complex.

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