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FIELD TESTS OF ELASTOL AND DEMOUSSIFIER

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ABSTRACT

The effectiveness of two oil spill treating agents were tested at sea. The agent Elastol, which imparts a viscoelastic property to oil, and a demoussifier (Brand M) were applied to ten test slicks laid midway between Nova Scotia and Sable Island. Observations of the physical characteristics of the treated slicks and chemical analysis of oil samples taken from the slicks at time intervals ranging from one to six hours indicate that both agents are at least as effective as they have been shown to be in laboratory and large-tank tests. Application of the demoussifier in concentrations ranging from 250-4000 ppm effectively prevented the formation of water-in-oil emulsions and broke up pre-existing emulsions. When applied at levels between 1000 and 9000 ppm, Elastol was found to increase the viscoelasticity of crude oil to a greater extent than was expected on the basis of results from laboratory tests. Application effects were not noted with either product. Due to weather conditions at the time of the field trials, it was not possible to determine the effect of the treating agents on the ability to recover the oil.

INTRODUCTION

To aid in the recovery of petroleum hydrocarbons spilled at sea, two chemical agents to modify the physical properties of spilled oil recently have been introduced. Elastol™[1] is a proprietary formulation that comprises a high molecular weight isobutylene polymer coated with a metallic soap. These compounds are insoluble in water, but form solutions in non-polar solvents which exhibit viscoelastic behaviour. Oil slicks floating on water that have been so treated have enhanced cohesive forces and thus should be more easily contained, collected and separated from the water. Small scale laboratory tests of the effect of this material on the physical properties of oil have been undertaken by the manufacturer (Waters and Haderman 1987) as well as by Environment Canada (Bobra et al. 1987a) who have also studies these materials in a meso-scale outdoor tank test. The results of these studies show that the elasticity of various oils is indeed enhanced and that tank-confined slicks have significantly modified in their physical characteristics. Consequently, further large-scale ocean tests were recommended.

Certain types of petroleum oils are prone to form water-in-oil emulsions (mousse) which adversely affect such cleanup procedures as mopping, skimming, and pumping (National Research Council 1985). The high

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[1] General Technology Applications, Inc., Manasssas, VA.

water content (30-50% and higher) also inhibits combustion. A surface active agent to break water-in-oil emulsions was also tested as a part of this project. The agent tested was Brand M, a liquid demulsifier-demoussifier, as formulated by Environment Canada. It contains a variety of polymeric agents in a hydrocarbon carrier.

MATERIALS & METHODS

Logistics

Field operations were mobilized at the Canadian Coast Guard Station at Mulgrave, Nova Scotia. The test were conducted at sea from the CCGS Mary Hichens. Ten slicks were laid near 44°15'N 61°50'W which lies about halfway between Halifax and Sable Island. This area is at least 60 km from the nearest coastline. The tests took place on Sept 9 (demoussifier) and September 10 (Elastol) 1987. The locations where the slicks were laid are shown on figure 1.

Slick laying procedure

Two petroleum mixtures were used in the field trials: 1) Alberta Sweet Crude Oil (waxes and asphaltenes removed) and 2) a mixture (50:50) of the crude oil and Bunker A (Bunker C cut with ca. 20% diesel fuel). The mixture was prepared by pumping the oils (crude oil first followed by Bunker A) into a large (23,000-liter) cylindrical tank. Volumes were determined geometrically from dipstick level measurements. The crude oil was stored in a second storage tank. Both tanks were subsequently secured to the aft deck of the Mary Hichens.

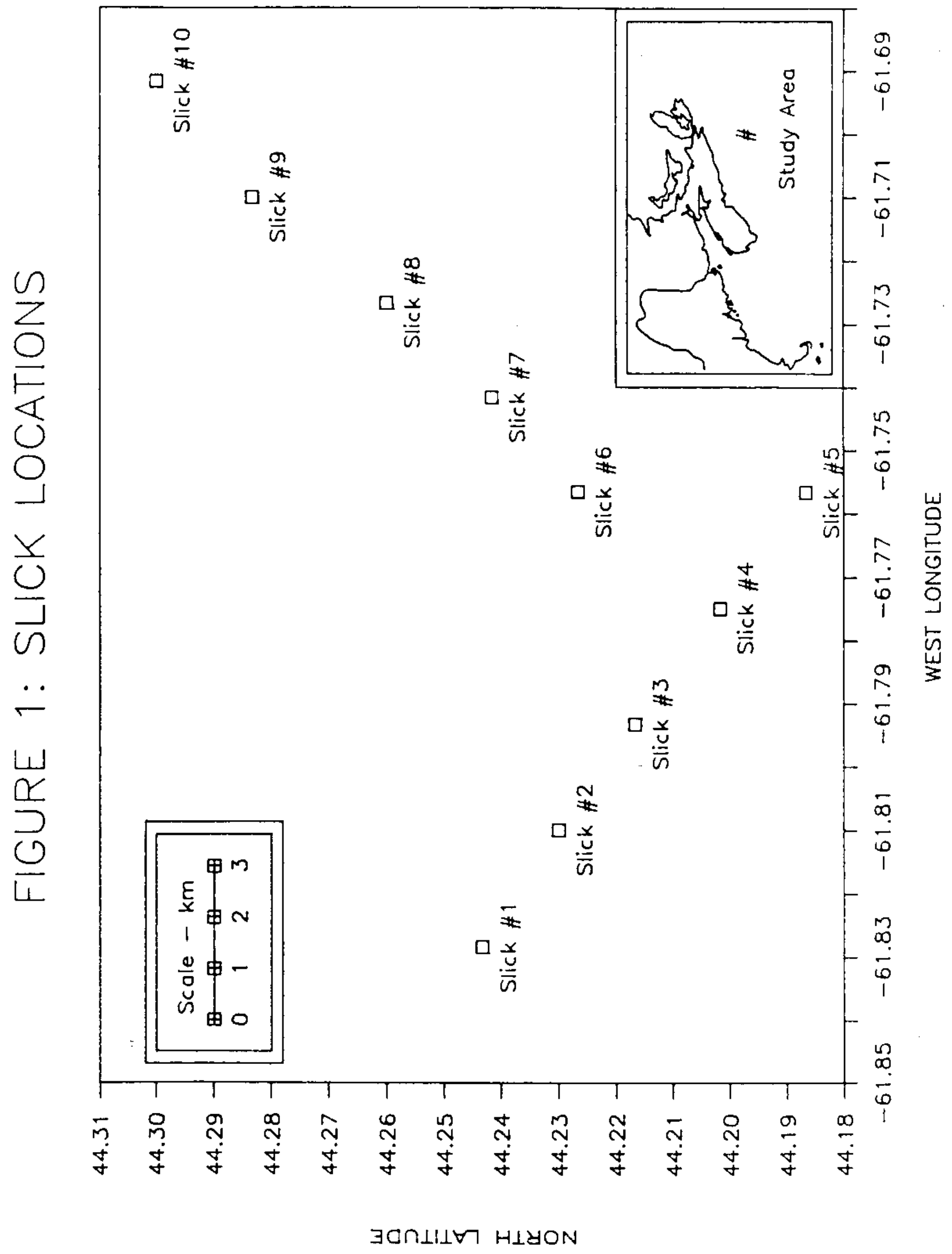
Prior to each spill, 800 liters (5 bbl) portions of oil were pumped from the large storage tanks into the spill tanks. In the case of the demoussifier trial, the spill tanks were discharged via a 2.5-inch hose equipped with flotation along its length and fitted with a paravane at the end to prevent flapping or snaking. The end of the discharge hose trailed approximately 10 meters behind the vessel while oil was being pumped. When the contents of the spill tank were completely discharged, a 2-way valve was actuated which allowed seawater to be pumped through the hose, thus flushing out the residual oil and minimizing the amount of oil trailed behind the ship as it proceeded to the next spill site. During the Elastol trials, the same plumbing arrangement was used to discharge the oil, but the end of the discharge hose was fixed near the starboard side of the ship, about 14 m ahead of the stern. This arrangement was used so that the oil could be treated as it passed by personnel on the aft deck.

Slick treatment procedure

One slick in both the demoussifier and Elastol trials was laid using oil that was treated with the appropriate agent immediately prior to discharge from the spill tank ('pre-treated' slicks). The agent was added to the spill tank concurrently with the oil being pumped from the bulk tank to ensure that the agent would be well-mixed with the oil.

All other slicks (except the control slicks) were treated after laying using specially constructed applicators. Modified Campbell-Hausefield sandblasters (Power Blast Model AT1210) were used to dispense both the demoussifier and Elastol (figure 2). The modified apparatus was designed by Environment Canada after evaluating several application systems on the basis

FIGURE 1: SLICK LOCATIONS



of their uniform distribution characteristics, portability and ruggedness, safety and simplicity. Extensive testing of the distribution pattern obtained by use of this applicator was undertaken by Bobra et al. (1987b). The applicators used for Elastol were fitted with vented hoppers to ensure continuous flow of the powdered agent. Similar modifications to the sandblasters were not required for application of the liquid demoussifier.

During the demoussifier trial, the slicks were treated immediately after they were laid (except for slick #4 whose treatment was delayed for 6 hours) from small sample boats. The procedure that was generally followed was to approach the slick from up wind and spray the slick with the agent while the sample boat traversed the slick in a zig-zag pattern until the downwind side of the slick was reached. This process was repeated until the entire dose of the treating agent had been applied.

During the Elastol trial, heavy seas prevented the use of the sample boats. As explained earlier, the oil was sprayed with the agent as it passed by personnel operating the treatment applicators on the aft deck of the vessel.

Sample collection

Samples at various time intervals were taken from the slicks with the aid of plastic mesh baskets on the end of aluminum poles. The baskets are of a type commercially available for removing debris from swimming pools; the poles were fabricated by Environment Canada. The baskets were swept half-submerged through the slicks and when a sufficient amount of oil had been collected, the plastic mesh was snipped from the frame and allowed to fall into a 5-liter pail which was then labelled and sealed. Care was taken to obtain representative samples of the slicks, i.e. samples were not taken from sheen areas or exclusively in thickly covered areas.

During the demoussifier trial, samples were collected from small sample boats. For each slick, samples were taken approximately one hour and four hours after the application of the demoussifier. In the case of slick #1, a third sample was obtained 24 hours after application. During the collection period, the samples were periodically returned to the laboratory aboard the Mary Hichens to enable prompt analyses for water content and viscosity.

Heavy weather was encountered during the day of the Elastol trial; consequently all sampling was done from the deck of the Mary Hichens. Baskets on extension poles were used to collect the samples, usually from the port side of the ship. All other sampling procedures were the same as in the demoussifier trial.

Analytical procedures

Oil samples taken from the slicks were processed as soon as possible on board the Mary Hichens where the following determinations were made: water content (spectrophotometry), viscosity (Brookfield), and elasticity (die swell).

The die swell apparatus used was similar to that described by Bobra (1987a) but used a mechanical syringe pump rather than air pressure as the driving force. The assembly comprised a plastic syringe fitted with a 12 gauge needle with the end cut at 90°. The syringe was filled with oil and a steady flow of oil established by means of the mechanical pump. The swelling of the stream of oil as it emerged from the tip of the needle was photographed with a Polaroid camera connected to a Leitz microscope.

RESULTS

Meteorological/oceanographic conditions

Meterological observations (wind speed and direction, temperature, sea state) were taken at regular intervals by the watch keeper on the bridge of the Mary Hichens. Wave height and frequency data were collected by a waverider buoy. These data were collected to enable us to assess the effect of the wave climate on behaviour of the slicks. In particular, a high-energy climate favors the formation of water-in-oil emulsions. Waves also are a source of energy for mixing the treating agents with the oil slick.

The energy of the surface waves increased dramatically between the time the trials began on the morning of 9 Sept. and the evening of 10 Sept. The amount of wave associated energy that the slicks experienced can be estimated by the relationship,

$$E = \frac{pgH^2}{8} \qquad (1)$$

where **p** is the density, **g** the acceleration of gravity, and **H** the wave height. It is sufficient for the purpose of comparing wave energies at different times during our experiment to allow that the energy is proportional to the square of the wave height.

As table 1 shows, the relative wave energy increased by a factor of seven during the trials. The significant wave height increased from 0.5 m to 2.5 m and breaking waves were evident throughout this period.

Table 1: Relative wave energy

Day/Time		Relative wave energy
09/09/87	1400	1.0
	1800	2.2
	2200	7.7
10/09/87	0400	4.7
	0800	7.0
	1600	6.7

Physico/chemical measurements demoussifier-treated slicks

The first five slicks laid using the crude/bunker mixture and were treated with the following concentrations of Brand M demoussifier:

Table 2: Demoussifier treatment concentrations

ID	Concentration of demoussifier	Comments
Slick #1	1000 ppm	Medium dose
Slick #2	250 ppm	Low dose
Slick #3	0 ppm	Control slick
Slick #4	4000 ppm	High dose (delayed treatment)
Slick #5	1000 ppm	Medium dose (pre-treated)

Oil samples were collected from the slicks approximately one hour and five hours after being treated. Table 3 and figures 3 and 4 show the results of the viscosity and water content measurements that were made on these samples on board the ship.

Table 3: Viscosity & water content of slicks 1-5

Slick #	Concentration of demoussifier	Viscosity (cp)		Water content (%)		Occurrence of mousse	
		1hr	5hr	1hr	5hr	1hr	5hr
3	0 ppm	6350	320000	88	95	++	++
2	250 ppm	2700	62250	54	93	–	–
1	1000 ppm	10000	84250	84	90	–	–
4	4000 ppm	2200	105000	72	90	+	+§
			22600		78		–†
5	1000 ppm*	970	38500	32	80	–	–

* pretreated; § at 6 hours - before treatment; † after treatment

The demoussifier was very effective in preventing large viscosity increases in the treated slicks. The samples taken from the slicks one hour after being treated showed relatively uniform viscosities in the range of 2000 to 10000 cp, with the pretreated slick having the lowest viscosity. The samples taken approximately five hours after treatment all had higher viscosities. The control slick exhibited the highest viscosity and a heavy mousse was prevalent. However, the slicks treated with the low and medium doses of demoussifier had dramatically lower viscosities than the untreated slick and no evidence of mousse was noted in either case.

The untreated slick #4 had a high viscosity and developed patches of mousse at the 5 hour time interval. When this slick was treated with demoussifier, the mousse began to break up and the viscosity measured one hour after treatment had fallen to 20% of the pretreatment level. The mousse broke up almost immediately in areas that were directly sprayed. The emulsion broke up over a period of minutes in other areas of the slick, where presumably the demoussifier flowed in from sprayed areas.

As figure 4 indicates, water content is not a good indicator of mousse formation; all slicks accumulated a large amount of water. While, some formed mousse as evidence by the reddish colouration, high viscosity and

FIGURE 3: VISCOSITY OF SLICKS 1-5

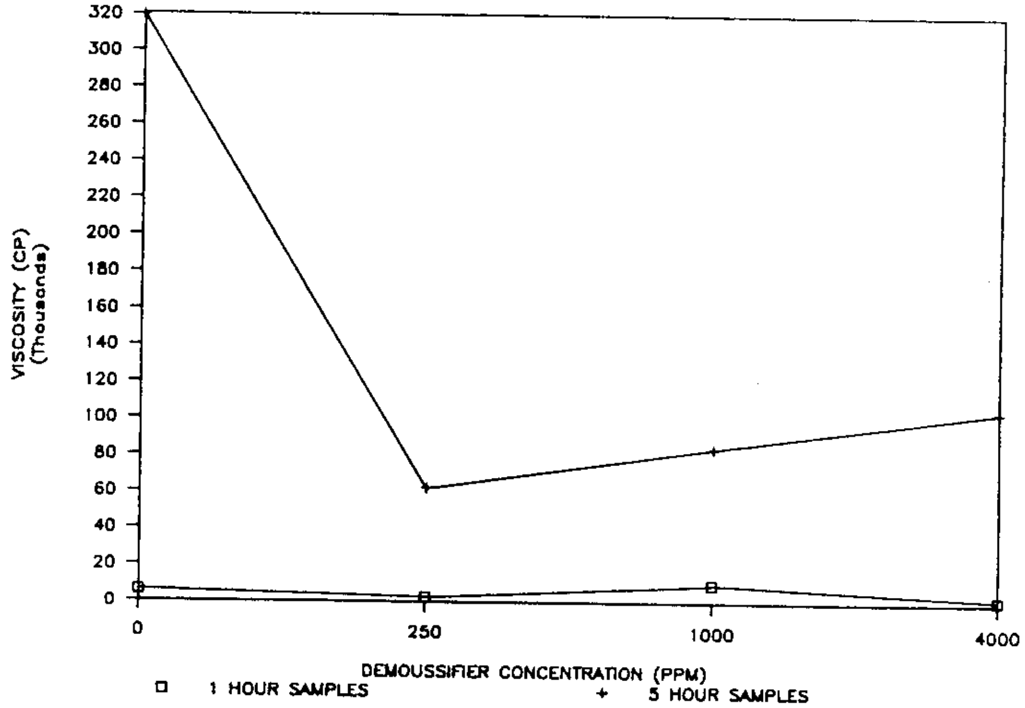
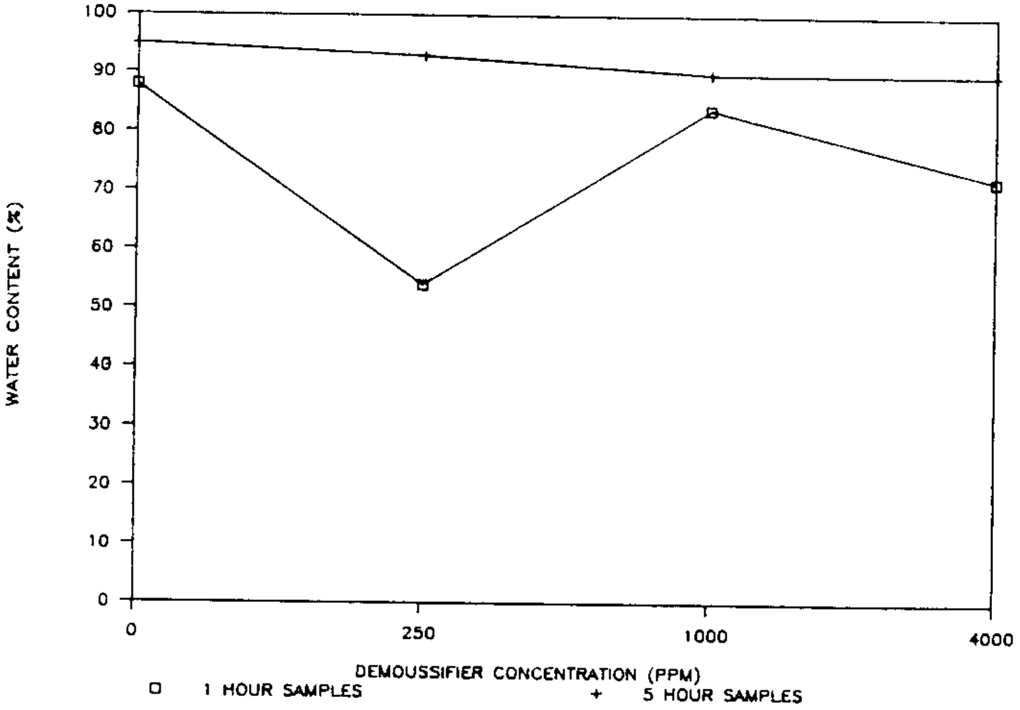


FIGURE 4: WATER CONTENT OF SLICKS 1-5



stability, others did not but still had high water contents. Current models do not predict the high water contents observed during this field trial.

To summarize, the demoussifier appeared to work very well. The slicks treated with demoussifier at the time of laying and the pretreated slick had markedly lower viscosities and showed no tendency to form mousse while the untreated slicks became heavily moussified. Demoussifier applied to a slick that had already developed mousse had the effect of rapidly breaking up the emulsion.

Physico/chemical measurements Elastol-treated slicks

The five crude oil slicks laid during the Elastol trials were treated with the following concentrations of the agent:

Table 4: Elastol treatment concentrations

ID	Concentration of Elastol	Comments
Slick # 6	3000 ppm	Medium dose
Slick # 7	1000 ppm	Low dose
Slick # 8	0 ppm	Control slick
Slick # 9	9000 ppm	High dose (delayed treatment)
Slick #10	3000 ppm	Medium dose (pre-treated)

Oil samples were collected from the slicks approximately one hour and five hours after being treated. Table 5 and figures 5 and 6 show the results of the viscosity and elasticity (die swell) measurements that were made on these samples on board the ship.

Table 5: Viscosity & elasticity of slicks 6-10

Slick #	Concentration of Elastol	Viscosity (cp)		Elasticity (die swell)		"Observed" elasticity	
		1hr	5hr	1hr	5hr	1hr	5hr
8	0 ppm	187000	242000	0.99	0.99	none	none
7	1000 ppm	32250	228000	1.28	1.33	low	med
6	3000 ppm	29300	300000	1.33	1.35	med	high
9	9000 ppm	93000	696000	1.99	2.63	high	super
10	3000 ppm*	170500	156000	1.35	1.57	med	high

* pre-treated

The viscosity and die-swell measurements made on the oil samples taken from the slicks as well as observations of the physical properties of the slicks taken at sampling time all indicate that Elastol was effective in

FIGURE 5: VISCOSITY OF SLICKS 6-10

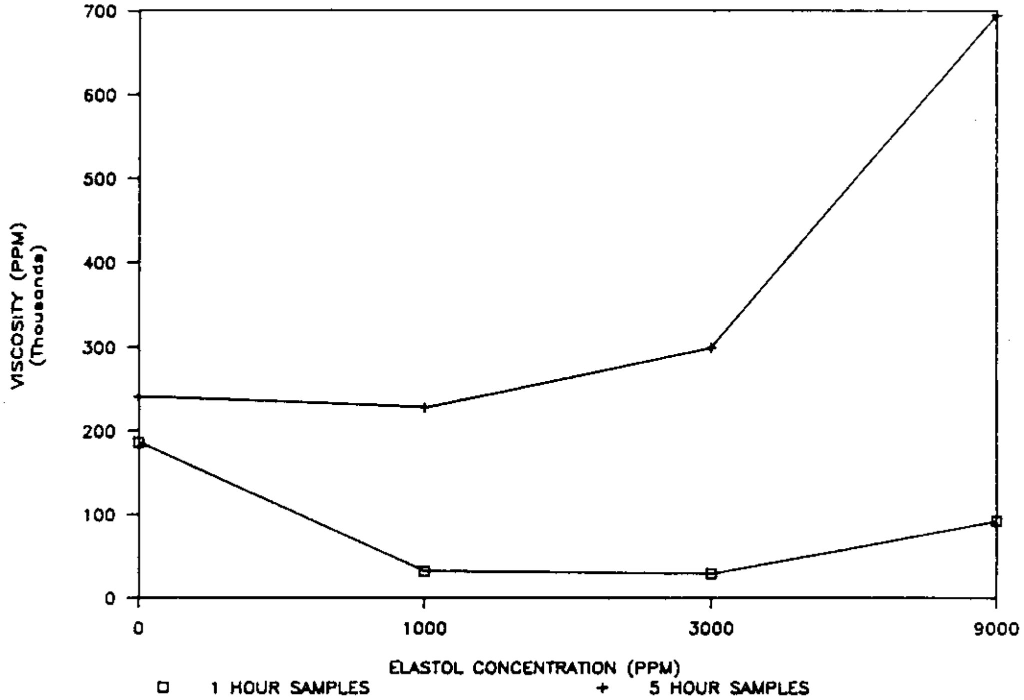
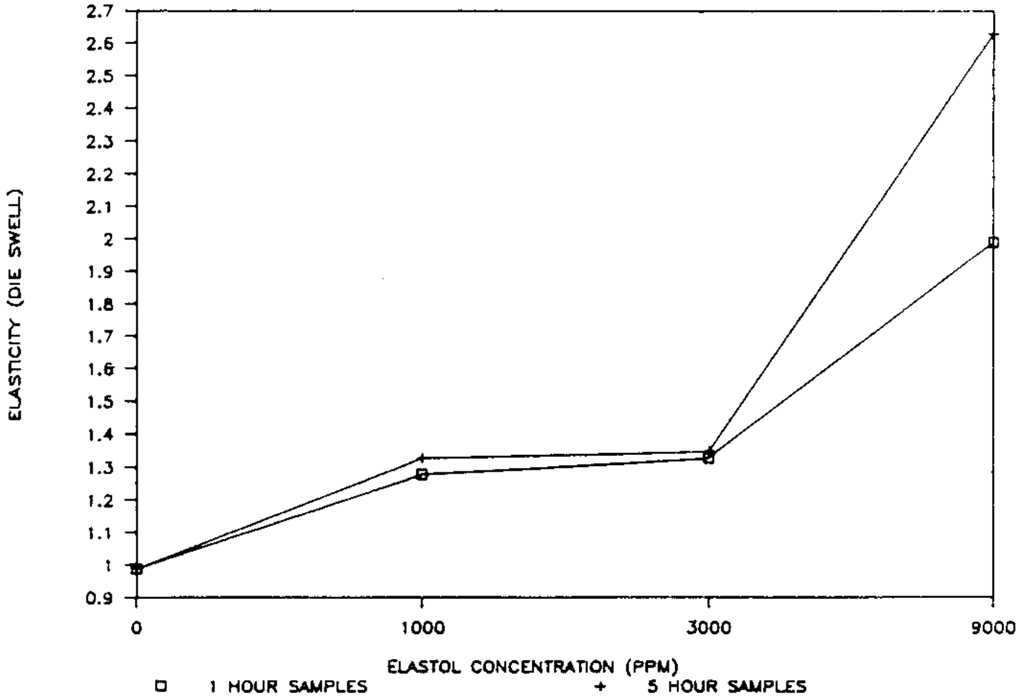


FIGURE 6: ELASTICITY OF SLICKS 6-10



increasing the viscoelasticity of the oil. As shown in table 5 and figure 5, the viscosity of the Elastol-treated slicks increased 7.5-10 fold over a five hour period. The untreated slick, though having a high viscosity at the one-hour interval, increased by only 20% over the same interval, presumably as a result of uptake of water and/or emulsion formation (Bobra 1987a). The growth of viscosity in the treated slicks, on the other hand, shows a clear relationship to the concentration of Elastol applied (figure 5).

The die swell measurements show more distinctly the effects of the treatment on the visco-elasticity of the oil. Samples taken from the control slick at one and five hours had die-swell ratios of unity (no elasticity) while those from the slicks treated with low and medium concentrations of Elastol had ratios of about 1.35. These ratios are as high or higher than the results obtained by Bobra (1987a) from laboratory tank tests in which similar concentrations of Elastol were used. It is also interesting to note that the maximum die swell ratios were reached before the one-hour sampling time and remained essentially unchanged at the five-hour sampling time.

The slick treated with the highest dose (9000 ppm) of Elastol showed the highest elasticity with the die swell ratio increasing from 2 to 2.6 over the five-hour interval between samples. While all of the samples taken from the treated slicks were obviously elastic at sampling time, the five-hour sample collected from the slick treated with 9000 ppm Elastol appeared to be almost semi-solid (super-elastic - table 5). This slick showed a higher elasticity than any of the samples from the laboratory tests of Elastol (Bobra 1987a), presumably as a result of the high mixing energy prevalent at the time of the field trials.

In summary, Elastol worked as well or better than expected under the conditions of an actual spill. High elasticities were observed at all treatment concentrations.

CONCLUSIONS

The period over which the trials were run was characterized by high wave energy and this tended to disperse the test slicks only a relatively short time (ca. 12 hours) after they were laid. Thus the long-term effects of the treating agents can not be assessed from the data collected during this study. However, the following observations were made on the physical behaviour of the slicks over a four to six hour period after the treatment agents were applied:

- Brand M demoussifier worked well. The formation of water-in-oil emulsions was inhibited in the slicks treated with demoussifier.
- The direct application of the demulsifier to patches of mousse in the untreated slicks had the immediate effect of breaking up the emulsion (10-15 seconds).
- Mousse in areas of the slick not directly sprayed appeared to break up when the agent migrated from sprayed areas (ca. 10 minutes).

- Water content did not appear to be a good indicator of mousse formation; all slicks accumulated a large quantity of water whether mousse was present or not.

- Elastol increased the viscoelasticity of the oil in the treated slicks to a greater extent than expected from previous laboratory studies.

- The manner in which either of the agents was applied did not seem to particularly critical, i.e. if the agents were applied in a non-uniform manner, they appeared to migrate to all portions of the slick through the mixing action of the waves.

REFERENCES

Bobra, M.A., P.I. Kawamura, M. Fingas and D. Velicogna, "Laboratory and tank test evaluation of Elastol", Proceedings of the tenth Arctic Marine Oilspill Program Technical Seminar, Edmonton, Alta., June 9-11, 1987, pp. 223-241, (1987a)

Bobra, M.A., P.I. Kawamura, M. Fingas and D. Velicogna, "Mesoscale application and testing of an oil spill demulsifying agent and Elastol", Preprint prepared for U.S. Minerals Management Service, September, 1987, (1987b)

National Research Council, Oil In the Sea: Inputs, Fates and Effects, National Academy Press, Washington, D.C., pp. 279-281, 1985

Waters, P. and A.F. Haderman, "The efficiency of elastomers in oil spill cleanup", 1987 Oil Spill Conference, Baltimore, MD, pp. 231-233, (1987)

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