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EVALUATION OF OIL SPILL CHEMICAL ADDITIVES

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Objective To evaluate two new oil spill treating agents in the laboratory and field situations. One agent is Elastol, a recovery-enhancer that renders oil visco-elastic and the other agent is Demoussifier, which prevents the formation of and breaks water-in-oil emulsions.

A new oil spill treating agent, Elastol, has been developed for enhancing the recovery potential of oil. When added to oil, the polymer powder renders oil visco-elastic and thus makes it adhesive to oil spill recovery equipment. Elastol is composed of a non-toxic polymer, polyisobutylene and is not water soluble and hydrophobic. A major study was undertaken jointly by the U.S. Minerals Management Service and Environment Canada to evaluate this new spill additive. Studies were conducted in the laboratory, large scale test tanks and in a major field exercise off Canada's East coast.

At the same time as the above tests were done, another new spill product, demoussifier, was tested in the large outdoor test tanks and also at sea. This product, which also consists of a mixture of long-chain polymers which have no measurable toxicity to humans or to aquatic life, was developed at Environment Canada's River Road Labs. The product prevents the formation of water-in-oil emulsions and breaks the same. A similar product was tested by Environment Canada in earlier tests as well (S.L. Ross, 1986).

Laboratory Testing of Elastol

The laboratory tests on Elastol involved several different tests. The effect of a suite of different oils was test by measuring the time to effect and the degree of elasticity formed. These oils included Prudhoe Bay Crude, Alberta Sweet Mix Blend, Norman Wells, Bent Horn, Hybernia, Diesel Fuel, Tarsiut, Atkinson, Amauligak and a Bunker C mix. All oils displayed viscoelastic properties when treated with doses of 600 to 6000 ppm Elastol. In general, more viscous oils tended to attain a higher degree of elasticicity than non-viscous oils, but did so over a longer period of time. No simple correlation between an oil property and Elastol effectiveness could be established. Elastol effectiveness is enhanced by mixing and by higher temperatures, although the latter may be the effect of increasing oil viscosity.

Under low mixing energy conditions, oils exhibited some degree of elasticity within 15 minutes of Elastol application. A high degree of elasticity was not observed until after one hour. Less viscous oils took less time to reach maximum elasticity and viscous oils more time. If left to weather, Elastol-treated oil became more elastic with the increasing viscosity of the oil. In fact some samples left for 30-day periods became as elastic as rubber bands sold for stationery purposes. This effect has been ascribed to the effect of the increasing viscosity of the oil with weathering (evaporation) and not the progressive reaction of the Elastol.

Elastol causes a minor reduction in the rate of oil evaporation, but not significant enough to reduce its flash point. Elastol reduces slick spreading to a limited degree, especially at high concentrations. This effect, about 20%, is not believed to have a significant useful result by itself in real applications. When Elastol is applied in very large doses, >1%, the slick would actually contract somewhat, but again, probably not to a field usable degree.

The addition of Elastol had no effect or an inhibiting effect on the formation of water-in-oil emulsions, except in the case of Amauligak and Tarsiut oils, both from the Beaufort Sea region. In a couple of cases, the application of Elastol to emulsified oil actually led to measurable de-emulsification. Application of Elastol to stable water-in oil emulsions sometimes did not result in significant effectiveness. Testing with commercial de-emulsifiers and the Environment Canada Demoussifier, showed that Elastol had no effect on the operation of these chemicals and thus these products could be used together.

Elastol reduces chemical dispersant effectiveness by as much as an order-of magnitude. Elastol also reduces natural dispersion of oil into water by as much as three orders of magnitude. This property, while superficially appearing negative, is actually quite useful. If Elastol was used in situations where the aquatic life is very sensitive and important, it could reduce water concentrations of the oil in the water sufficiently to minimize damage.

A die swell apparatus was developed to provide measurement of elasticity. The instrument displayed good sensitivity to polymer concentration and to the degree of observed elasticity. The instrument could also be used in field conditions and displays relative insensitivity to debris and water in the oil.

Tank Scale Testing of Elastol and Demoussifier

An application device for each of the two products was designed, as commercial devices do not exist for delivering treatments at ratios as low as necessary. Elastol would be tested at treatments from 500 to 5000 ppm and Demoussifier would tested from 150 to 2000 ppm. After a search of commercial devices revealed that no suitable devices could be found but that sandblaster-type devices could be modified. A commercial blaster (Sears) was modified so that it could spray low quantities, one modification was necessary for the solid Elastol, and another for the liquid Demoussifier. The applicator operation was tested on each product to ensure that uniform spacial distribution was achieved and that application rates could be controlled over the necessary range by adjusting the air pressure and applying the product from a boat travelling at approximately 3 knots. A series of test tank runs were performed with the new applicators to ensure that results obtained previously with hand distribution techniques and with pre-mixing were the same as the present results. Success was achieved in all cases, and no detrimental effects were noted during application of either product, such as had been noted with dispersants where herding and other phenomena decreased measured effectiveness very dramatically (Bobra et al, 1988).

Part of this study involved large-scale tank testing of both products. The Esso test tank in Calgary, Alberta, was used for these tests. The tank has dimensions of 15m by 19m with a depth of .8 to 2m. Two test days were devoted to Demoussifier and two to Elastol. Testing was conducted in two boomed areas inside the tank. This permitted the simultaneous testing of a control and a treated slick at the same time. The Demoussifier prevented the formation of water-in-oil emulsions in both test days and did so at ratios as low as 1:2000 or at 500 ppm.

Elastol was added to a test crude oil at the 4000 ppm level and the test slick released several hours later when the oil was highly elastic. Despite this high elasticity, the oil was of insufficient thickness to burn. The oil was recovered by a rotating disk skimmer and increased the recovery rate of this unit significantly, in fact the pump could not pump all the oil being recovered. On the fourth day of testing, crude oil was treated with 2000 ppm Elastol and recovered with a skimmer. The recovery rate was again high and exceeded the capacity of the pump to remove it from the skimmer head. On this particular day, the oil in the untreated boom had formed an emulsion. This was treated with Demoussifier as was the Elastol-treated slick, to ensure that this did not affect the test results. The Demoussifier broke the emulsion in the untreated slick and no emulsion formed in the treated slick, nor were any other effects noted. During the first two trial days, the use of Demoussifier reduced the effectiveness of the recovery operation significantly. Thus it was concluded that on a preliminary basis, Demoussifier and Elastol could be used together productively.

The large scale tests showed that there were no scaling effects for either the Elastol or the Demoussifier. Both products worked well for the purpose intended. Elastol increased the visco-elasticity of the oil and greatly increased the recovery potential of the oil skimmer. Elastol did not however reduce the spreading or increase the thickness of the slick sufficiently to allow direct burning on open water. Demoussifier prevented the formation of water-in-oil emulsions and could also break emulsions already formed. Demoussifier, however does cause the oil to be less adhesive and lowers the recovery rate of skimmers. The products can be applied together to achieve both positive results.

Large Scale Field Testing

The tests conducted in the tank were repeated on 5-barrel slicks during a field trail 50 miles offshore Nova Scotia (Seakem, 1988). Five slicks were laid to test each of the products and each product was tested both in a premixed and an application -at-sea mode, to ensure that application effects were not important. , Table 1 summarizes the treatments and results of the trial.

The Demoussifier trials were performed by laying down a five-barrel oil slick, treating it with the product at the ratio designated, taking samples at subsequent times and measuring the water content and the viscosity of the product. One slick was left untreated throughout as a control and another slick was left to form mousse (water-in-oil emulsion) and then treated at the 240 minute interval to test Demoussifier's ability to break emulsion at sea. As can be seen by the dramatic reduction in viscosity (105000 to 22600 cSt) over the 30-minute period between samples, the product worked well to break the emulsion. The product also worked well over the five hour test period to prevent the formation of emulsions. This is also illustrated in Figure 1 which shows that there is a strong correlation between the viscosity and the amount of treatment. The greater the treatment, the less the viscosity, because of the lesser water content. The water content was also measured and was universally high, including in those slicks that visibly did not form water in-oil emulsions. Although water content is indicative of the formation of water-in-oil emulsification, the stability of the emulsion would have to be measured since the non-emulsified oil did loose water slowly. The water content of the slicks is interesting in that all the slicks laid out over the two day test period, rapidly took up water, including those slicks that were treated with Elastol. This was noted despite the fact that the oil viscosity was higher, but not as high as that expected from an emulsion and the oil did not have the appearance of an emulsion. The appearance of the unemulsified oil is also significant, the water droplets were often of sufficient size to be seen in this oil. Emulsion appears reddish-brown, has a high viscosity and the water droplets are too small to be seen.

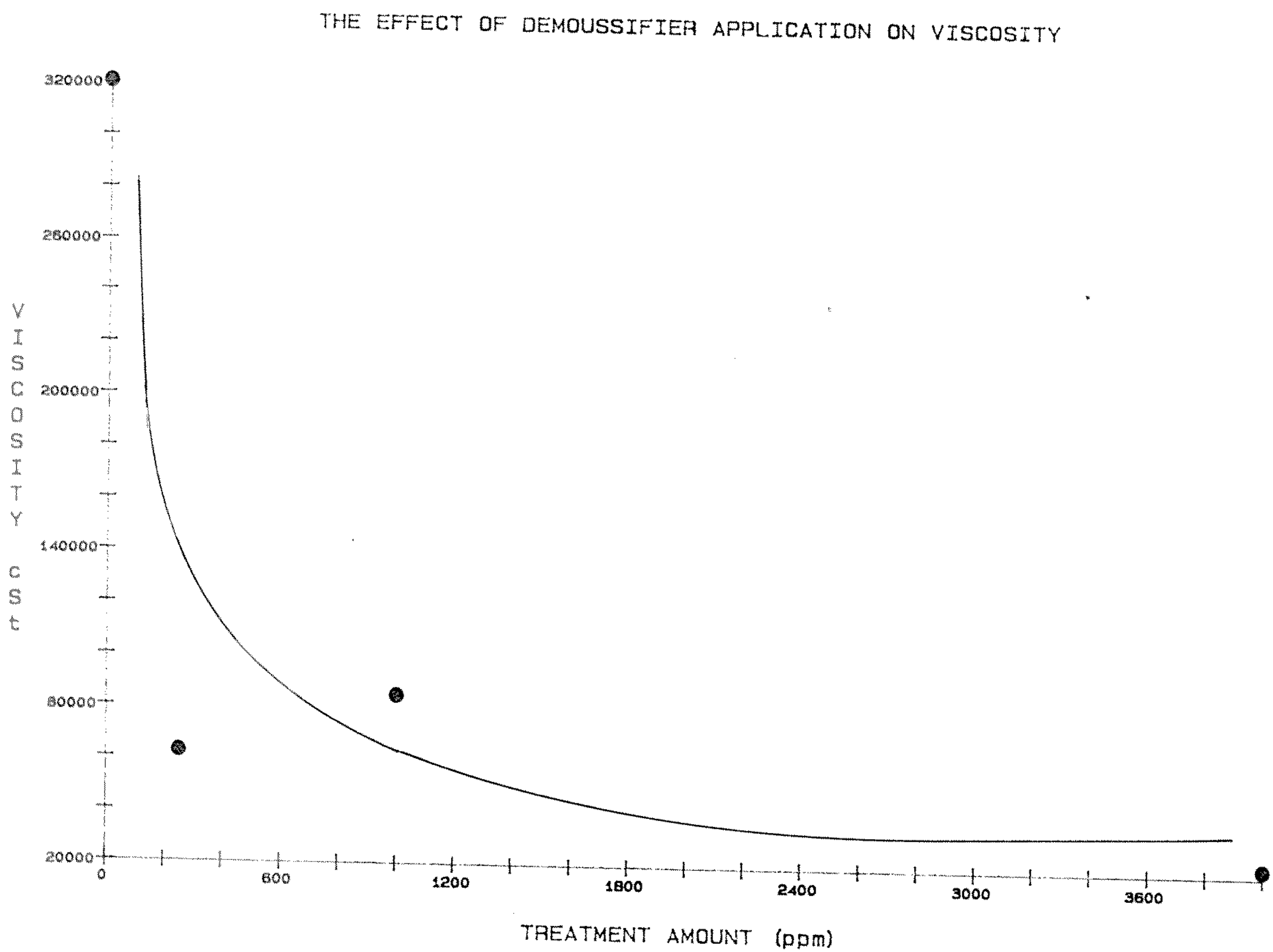
The Elastol tests were performed in an analogous manner, with one control slick laid and one slick being pretreated to test the effect of at-sea treatment. The slicks were sampled periodically, and both viscosity and elasticity measured immediately on board the ship. Elasticity was measured using the die swell technique in which oil is pushed through a small opening and the fluid responds to this by swelling to a size corresponding to it elasticity. This is measured by photographing the swell, measuring with a vernier caliper and comparing untreated versus treated oil to yield a ratio which is described as "elasticity" in this paper.

DEMOUSSIFIER TRIALS

SLICK	TREATMENT	SAMPLE 1 TIME	VISCOSITY	WATER CONTENT	COMMENTS	SAMPLE 2 TIME	VISCOSITY	WATER CONTENT	COMMENTS
1	1000-PPM	60	10000	84%	NO MOUSSE FORMED	300	84250	90%	NO MOUSSE NOTED
2	250-PPM	60	2700	54%	NO MOUSSE FORMED	300	62250	93%	NO MOUSSE NOTED
3	CONTROL	60	6550	88%	HEAVY MOUSSE	270	320000	95%	HEAVY MOUSSE
[illegible]	PRE-4000PPM	60	2200	72%	MODERATE MOUSSE	PRE-240	105000	90%	HEAVY MOUSSE
						POST-270	22600	78%	TREATMENT BROKE MOUSSE
[illegible]	PRE-1000PPM	.5	970	32%	NO MOUSSE OBSERVED	280	38500	80%	NO MOUSSE FORMED

ELASTICITY TRIALS

SLICK	TREATMENT	SAMPLE 1 TIME	VISCOSITY	ELASTICITY	COMMENTS	SAMPLE 2 TIME	VISCOSITY	ELASTICITY	COMMENTS
[illegible]	3000-PPM	130	23300	1.33	MODERATELY ELASTIC	280	300000	1.35	HIGHLY ELASTIC
[illegible]	1000 PPM	145	32250	1.28	LOW ELASTICITY	280	228000	1.33	MODERATLEY ELASTIC
[illegible]	CONTROL	135	187000	0.99	NO ELASTICITY,WIDESPREAD	290	242000	0.99	NO ELASTICITY,WIDESPREA
[illegible]	3000 PPM	120	93000	1.99	HIGH ELASTICITY	330	696000	2.63	SUPER ELASTIC
[illegible]	PRE-1000PPM	125	170500	1.35	MODERATE ELASTICITY	315	156000	1.57	HIGHLY ELASTIC


THE EFFECT OF DEMOUSSIFIER APPLICATION ON VISCOSITY
VISCOSITY cSt
320000
260000
200000
140000
80000
20000
0
600
1200
1800
2400
3000
3600
TREATMENT AMOUNT (ppm)

The elasticity of the treated slicks was significantly higher that untreated slicks and corresponded to that expected in the laboratory, in fact in the case of the higher doses, actually exceeded laboratory results. This unexpected result is probably due to the better mixing achieved in the field situation. This is shown in Figure 2. Interestingly the dose and elasticity in the field appear tq be linear, a phenomenon that has not been noted before.

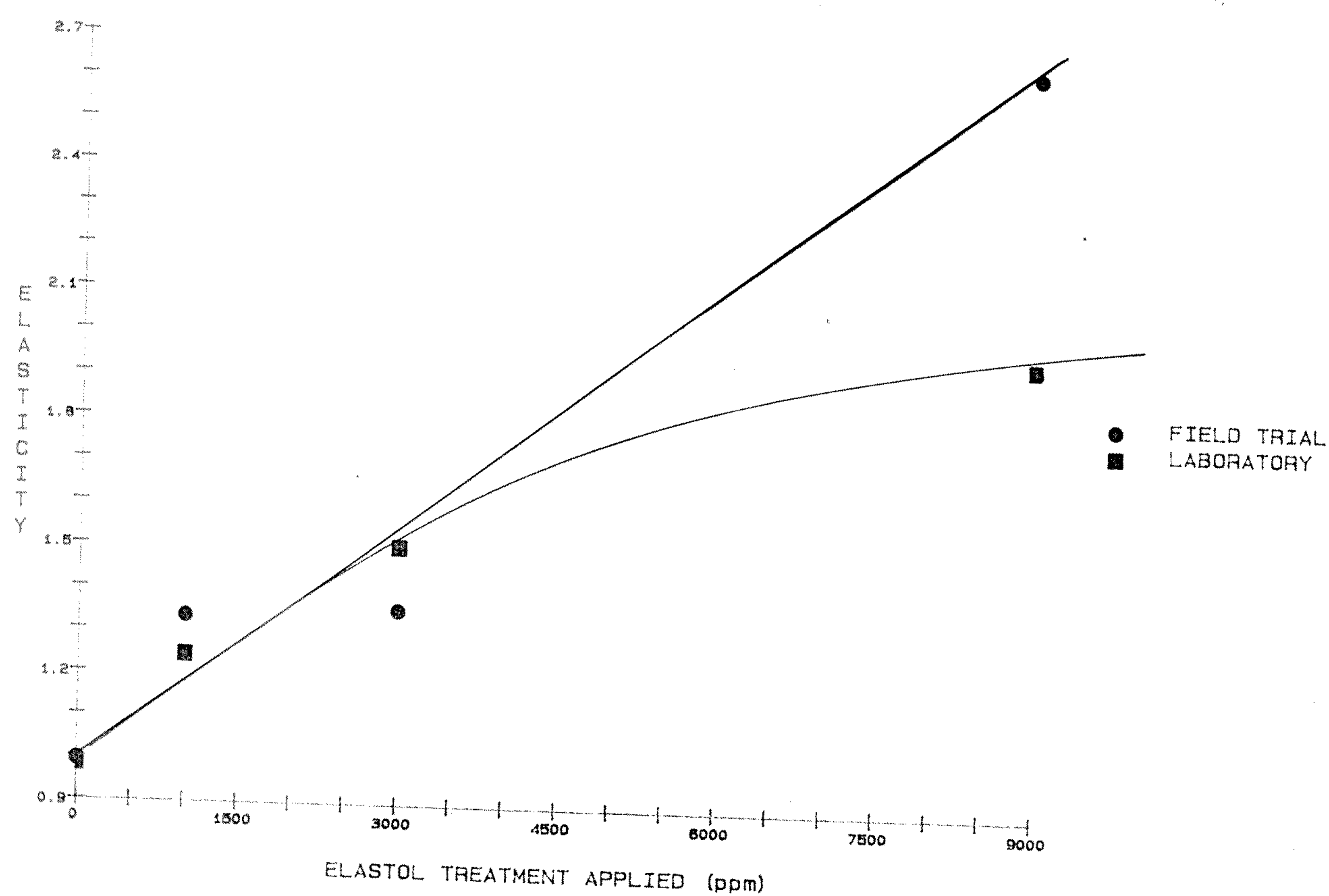
The elasticity of the oil was sufficient to cause the stringing of the product when samples were recovered. This is indicative of a very high state of elasticity and would result in high oil recovery rates if a skimmer was used. The elasticity appeared to be uniform throughout the slicks despite the typical poor distribution of treating agent at sea.

The slicks were monitored by a remote sensing airplane, the analysis of slick areas is not complete at time of writing, however those slicks treated with Elastol appeared to be smaller on the surface of the sea and the size of the slick appeared to correlate well with the amount of Elastol. In fact, one was able to immediately distinguish slicks by their size, with the 9000-ppm-treated slick being the smallest.

<u>Summary and Conclusions</u>

1. Elastol functioned well in the laboratory, test tank and in field situations; it caused oil to become viscoelastic in all applications,
2. Elastol is able to float with and mix with oil so that application is not critical as it is with dispersants,
3. Demoussifier has the same application insensitivity as does Elastol,
4. Elastol functions well to improve oil skimmer recovery,
5. Elastol does slow down and retard slick spreading, however this effect, for physical reasons, is not sufficient for countermeasures purposes such as direct ignition of oil on water,
6. The Demoussifier prevented emulsion in the test slicks over the five hour test period,
7. The Demoussifier broke water-in-oil emulsions in 10 to 15 seconds after application,
8. Application effects, such as herding, loss effectiveness, etc, often noted with dispersants, were not noted at all with either product, and
9. Water content is not a good indicator of mousse formation as all slicks at the offshore trial accumulated a large amount of water. Stable mousse formation is indicated by a stable water content, small water droplet size, red colouring and a very high viscosity.

ELASTICITY OF OILS AFTER ELASTOL TREATMENT



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