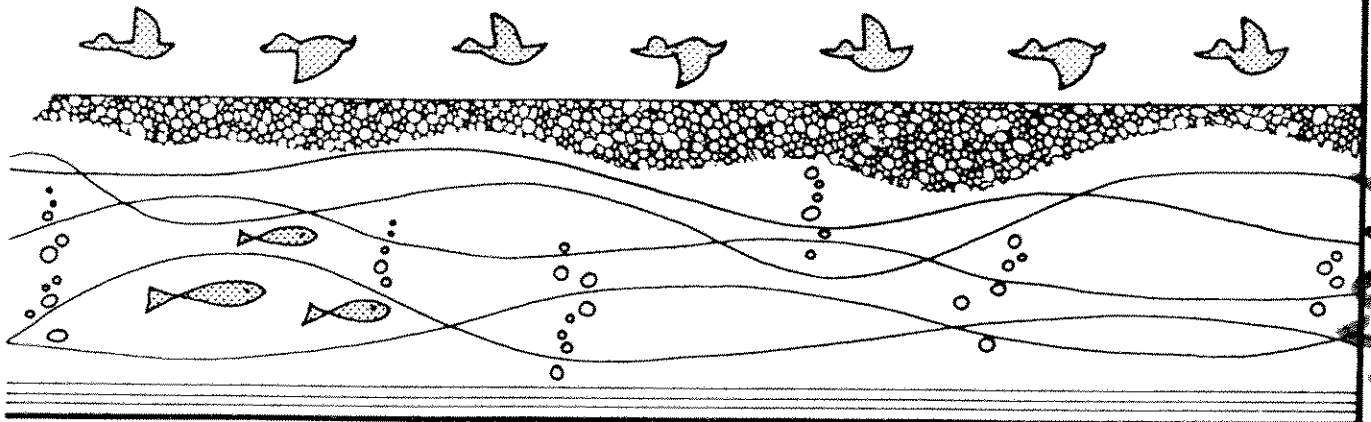




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# SPILL TECHNOLOGY NEWSLETTER



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## EVALUATION OF TWO NEW OIL SPILL CHEMICAL ADDITIVES: ELASTOL AND DEMOUSSIFIER

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### Introduction

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

At the same time, another new spill treating agent, demoussifier, was tested in large outdoor tanks and 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 breaks up water-in-oil emulsions and prevents their formation.

### Laboratory Testing of Elastol

The laboratory work on Elastol involved several different tests. The effect on a suite of different oils was determined by measuring the time to initiate change and the degree of elasticity formed. These oils included: Prudhoe Bay, Alberta Sweet Mix Blend, Norman Wells, Bent Horn, Hibernia, Tarsiut, Atkinson, Amauligak crudes, diesel fuel 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 elasticity than non-viscous oils, but did so over a longer period of time. No simple correlation could be established between an oil property and Elastol effectiveness. Elastol effectiveness is enhanced by mixing and by higher temperatures, although the latter may be the effect of decreasing 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 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 benefit by itself in real applications. When Elastol is applied in very large doses, >1%, the slick would actually contract somewhat, but again, the effect would not be beneficial in a field situation.

The addition of Elastol either had no effect or an inhibiting effect on the formation of water-in-oil emulsions, except in the case of the Amauligak and Tarsiut oils from the Beaufort Sea region. In two cases, the application of Elastol to emulsified oil actually led to measurable de-emulsification. Application of Elastol to stable water-in-oil emulsions sometimes had little effect. Testing with commercial de-emulsifiers and the Environment Canada "demoussifier", showed that Elastol had no effect on the operation of these chemicals and that they could be used together.

Elastol reduces chemical dispersant effectiveness by as much as one 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 to threshold levels.

Elasticity was measured using a die swell apparatus in which oil is pushed through a small opening and the fluid responds by swelling to a size corresponding to its elasticity. This is measured by photographing the swell, measuring it with a vernier caliper and comparing untreated versus treated oil to yield a ratio which is described as "elasticity" in this paper. The instrument displayed good sensitivity to polymer concentration and to the degree of observed elasticity. This instrument could also be used in field conditions and is relatively insensitive to debris and water in the oil.

### **Tank Scale Testing of Elastol and Demoussifier**

An application device was developed for each of the two products, as commercial devices do not exist for delivering treatments at the low ratios required. Elastol would be tested at 500 to 5000 ppm and demoussifier would be tested at 150 to 2000 ppm. A search of commercial devices revealed that nothing suitable was available off-the-shelf but that sandblaster-type equipment could be satisfactorily 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 modified applicator 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 when applying the product from a boat travelling at approximately 3 knots. A series of test tank runs were performed to ensure that results obtained previously with hand distribution techniques and with pre-mixing were duplicated with the new applicators. Success was achieved in all cases, and no detrimental effects were observed during application of either product, such as herding and other phenomena that have decreased the field effectiveness of dispersants so dramatically (Bobra et al., 1988).

Part of this study involved large-scale tank testing of both products using the Esso tank in Calgary, Alberta. The tank measures 15 x 19 m with a depth of 0.8 to 2 m. Two test days were devoted to demoussifier and two to Elastol. Testing was performed in two boomed areas inside the tank. This permitted the simultaneous testing of a control and a treated slick under identical conditions. The demoussifier prevented the formation of water-in-oil emulsions on both test days and did so at ratios as low as 1:2000 (500 ppm).

Elastol was added to a test crude oil at 4000 ppm and the test slick was released several hours later when the oil was highly elastic. Despite this high elasticity, the oil was not thick enough to burn. The oil was recovered by a rotating disk skimmer and the effect of Elastol was to increase the recovery rate of this unit significantly. In fact, the pump could not keep pace with all the oil being recovered. On the fourth day of testing, crude oil was treated with 2000 ppm of Elastol and recovered with a skimmer. The recovery rate was again high and exceeded the capacity of the pump to remove it. 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. 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. It was concluded, therefore, that on a preliminary basis, demoussifier and Elastol could be used together to enhance recovery and eliminate emulsion.

The tank scale tests showed that there were no scaling effects for either the Elastol or the demoussifier. Both products worked well for the intended purpose. Elastol increased the visco-elasticity of the oil and greatly increased the recovery by the oil skimmer. Elastol, however, did not reduce the spreading or increase the thickness of the slick sufficiently to allow in-situ burning. Demoussifier prevented the formation of water-in-oil emulsion and also broke emulsion already formed. Although demoussifier causes the oil to be less adhesive and lowers the recovery rate of skimmers, the two products can be applied together to achieve positive results.

### Large-scale Field Testing

The tests conducted in the tank were repeated on five-barrel slicks during a field trial 50 miles offshore of Nova Scotia (Seakem, 1988). Five slicks were laid for each of the products and each product was tested both premixed and by application-at-sea, to confirm that application effects were not a factor. The treatments and results of the trial are summarized in Table 1.

The demoussifier trials were performed by laying down a five-barrel oil slick, treating it with the product at the specified ratio, taking samples at subsequent intervals and measuring the water content and the viscosity. 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 the demoussifier's ability to break emulsion at sea. As can be seen by dramatic reduction in viscosity (105 000 to 22 600 cSt; 1050 to 226 cm<sup>2</sup>/s) over the 30-minute period between samples, the product worked well in breaking up the emulsion.

The product also worked well over the five-hour test period to prevent the formation of emulsions. This is illustrated in Figure 1 which also shows that there is a

TABLE 1 TREATMENTS AND RESULTS OF TRIALS

Trials	Slick	Treatment (ppm)	Sample 1				Sample 2					
			Time (min.)	Viscosity (cSt)*	Water Content	Elasticity	Comments	Time (min.)	Viscosity (cSt)*	Water Content	Elasticity	Comments
Demoussifier	1	1000	60	10 000	84%						No mousse formed	
	2	250	60	2 700	54%						No mousse formed	
	3	control	60	6 350	88%						Heavy mousse	
	4	post-4000	60	2 200	72%						Moderate mousse	
	5	pre-1000	15	970	32%						No mousse formed	
Elastol	6	3000	130	29 300		1.33		280	300 000		1.35	Highly elastic
	7	1000	145	32 250		1.28		280	228 000		1.33	Moderately elastic
	8	control	135	187 000		0.99		290	242 000		0.99	No elasticity, widespread
	9	9000	120	93 000		1.99		330	696 000		2.63	Super elastic
	10	pre-3000	115	170 500		1.35		315	156 000		1.57	Highly elastic

\* 1 cSt =  $1 \times 10^{-2}$  cm<sup>2</sup>/s

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 universally high, even 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 determined because the unstable emulsions lost water slowly. The water content of the slicks is interesting in that all the slicks laid 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, although 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. An emulsion is reddish-brown in colour, 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 were measured immediately on board the ship.

The high elasticity of the treated slicks was significantly higher than that of the untreated slicks and corresponded to that experienced in the laboratory, in fact, as shown in Figure 2, it actually exceeded laboratory results at the higher doses. This unexpected result is probably due to the better mixing achieved in the field situation. Interestingly, the dose and elasticity in the field appear to be linear, a phenomenon that had not been noted previously.

The elasticity of the oil was sufficient to cause 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 uneven distribution of treating agent at sea.

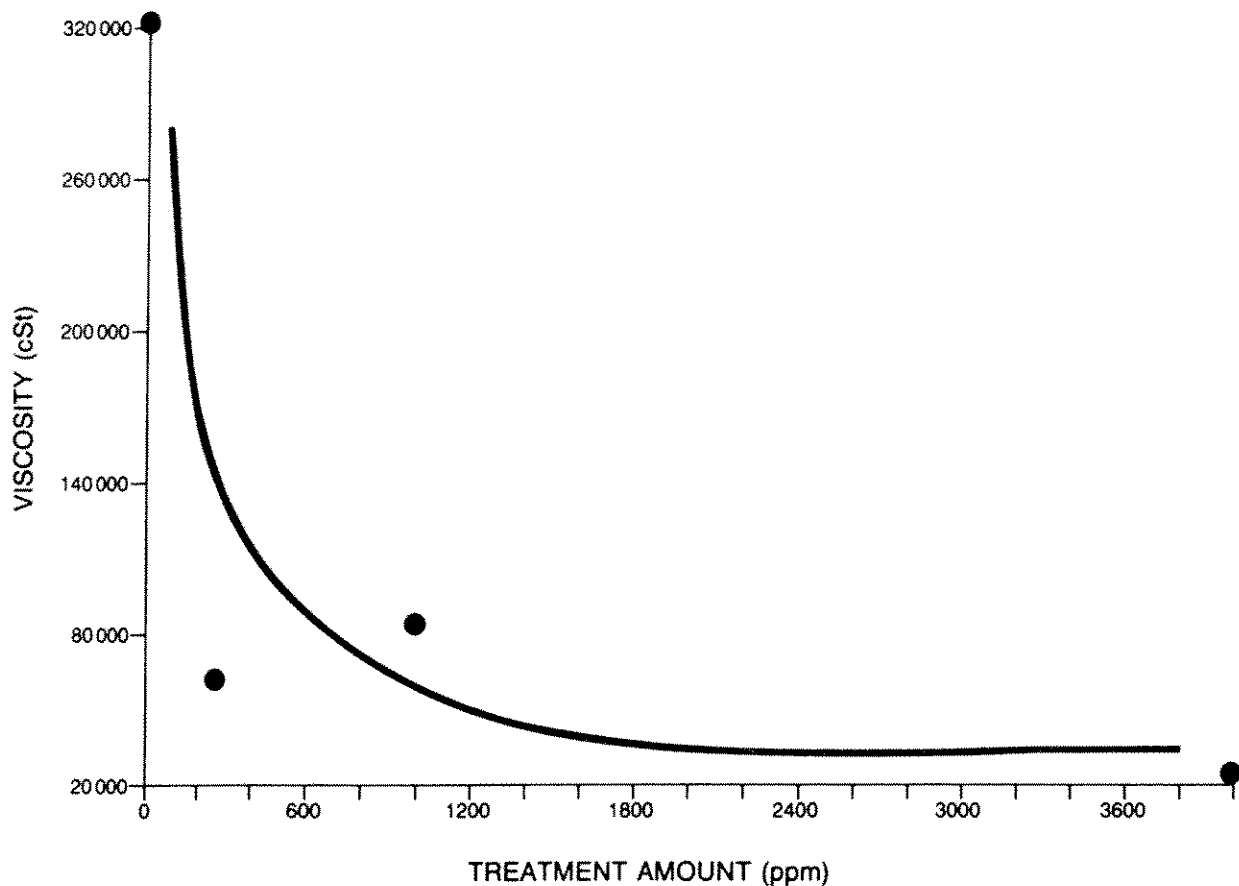


FIGURE 1 THE EFFECT OF DEMOUSSIFIER APPLICATION ON VISCOSITY

The slicks were monitored by a remote sensing aircraft, but the analysis of slick areas was not complete at the time of writing. Slicks treated with Elastol, however, appeared to be smaller to shipboard observers and the size of the slick appeared to correlate well with the amount of Elastol. In fact, one was able to distinguish slicks by their size, with the 9 000-ppm-treated slick being the smallest.

#### Summary and Conclusions

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 Elastol.

4. The effects of Elastol improves oil skimmer recovery.
5. Elastol retards slick spreading; however, this effect, for physical reasons, is not sufficient for countermeasures purposes such as in-situ burning 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. Results of field application such as herding and loss of effectiveness, seen with dispersants, were not noted at all with either product.
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.

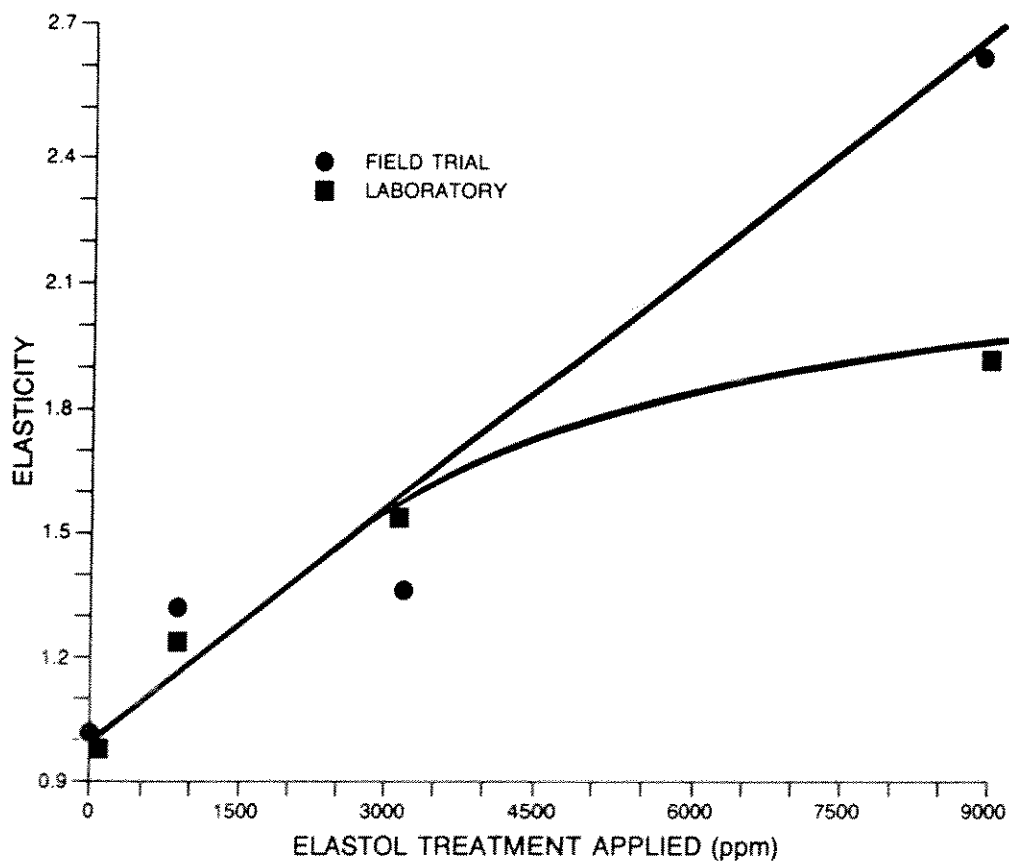


FIGURE 2 ELASTICITY OF OILS AFTER ELASTOL TREATMENT

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