

24527

**LABORATORY AND TANK TEST
OF ELASTOL**

Proj. # 114 (c)

LABORATORY AND TANK TEST EVALUATION OF ELASTOL

by

M.A. Bobra and P.I. Kawamura
Consultchem
Ottawa, Ontario

and

M. Fingas and D. Velicogna
Environment Canada
Ottawa, Ontario

Funding for this study was provided by the United States Minerals Management Service and Environmental Emergencies Technology Division of Environment Canada.

This report has not undergone detailed technical review by the Environmental Protection Directorate and the content does not necessarily reflect the views and policies of Environment Canada. Mention of trade names or commercial products does not constitute endorsement for use.

This unedited version is undergoing a limited distribution to transfer the information to people working in related studies. This distribution is not intended to signify publication and, if the report is referenced, the author should cite it as an unpublished report of the Directorate indicated below.

Any comments concerning its content should be directed to:

Environment Canada
Environmental Protection Directorate
River Road Environmental Technology Centre
Ottawa K1A 0H3



ABSTRACT

This study was conducted to determine the performance of a new spill treating agent called Elastol. When applied to oil, Elastol imparts a viscoelastic property, which improves the efficiency of oil spill cleanup. This study focused on the effect of Elastol on selected oil properties and physical processes to which oil slicks are subjected. Experiments were performed in three stages: small-scale laboratory experiments, followed by small, and then large scale wave generating tank tests.

The laboratory tests showed that eight different crude oils as well as diesel exhibited a viscoelastic property when treated with 600 to 6000 ppm of Elastol. In a separate experiment, it was found that the addition of Elastol reduced the extent of spreading. Treated oils also exhibited a slightly lower rate of evaporation but no change in the flash point was observed.

Emulsion studies showed that of the ten oils tested, two exhibited increased emulsion formation tendencies when treated with Elastol while two showed a marked decrease. For the other oils that emulsified, the addition of Elastol lowered the emulsion water content.

In the small-scale tank tests, the addition of 6000 ppm of Elastol imparted significant elasticity to the oils tested. Oil slicks treated with Elastol showed a lower degree of emulsification, dispersion and viscosity increase.

The results from the preliminary large-scale tank tests confirmed the basic trends and results observed in the laboratory testing of Elastol. Moderate wave energy appeared to enhance and speed up the elasticity development. There was evidence that the thickness of the slick increased sufficiently to allow for burning, and the skimmer recovered 93% of the spilled oil. The generally favourable results obtained from this study appear to indicate that Elastol is an effective and useful oil spill treating agent.

RÉSUMÉ

La présente étude avait pour objet de déterminer les caractéristiques d'un nouvel agent de riposte aux marées noires, l'Elastol. Au contact du pétrole, l'Elastol lui confère une certaine visco-élasticité qui améliore la récupération des matières déversées. L'étude a porté surtout sur l'effet qu'exerce l'Elastol sur certaines propriétés du pétrole et sur certains processus physiques auxquels les nappes sont soumises. Les expériences se sont faites en trois temps: à l'échelle réduite de laboratoire, dans un petit bassin à houle, puis dans un gros.

Les résultats des essais en laboratoire montrent que huit bruts de même que du combustible diesel sont devenus visco-élastiques au contact de 600 à $6\ 000 \times 10^{-6}$ d'Elastol. Dans un essai séparé, l'Elastol s'est révélé réduire l'étalement de la nappe. En outre, l'évaporation des huiles traitées se ralentit un peu, mais on n'observe aucune modification du point d'éclair.

Sur dix hydrocarbures, deux sont devenus plus émulsifiables au contact de l'Elastol tandis que deux autres ont montré de façon marquée la caractéristique contraire. Chez les autres hydrocarbures émulsifiés, l'Elastol a eu pour effet d'abaisser la teneur en eau.

L'ajout de $6\ 000 \times 10^{-6}$ d'Elastol, en petit bassin, a conféré une élasticité notable aux hydrocarbures. L'émulsification et la dispersion des nappes ont diminué, et la viscosité a augmenté.

Les résultats des essais préliminaires en gros bassin confirment les résultats et les tendances fondamentales observés en laboratoire. Une houle modérée semble améliorer et accélérer l'accroissement de l'élasticité. Il semble que l'épaisseur des nappes ait augmenté suffisamment pour en permettre le brûlage tandis que, par écrémage, on a récupéré 93 % des matières déversées. Les résultats généralement favorables de l'étude semblent montrer que l'Elastol est un agent efficace et utile de riposte aux déversements d'hydrocarbures.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
RESUME	ii
LIST OF FIGURES	vi
LIST OF TABLES	viii
LIST OF PLATES	ix
ACKNOWLEDGEMENTS	x
1. INTRODUCTION	1
1.1 Objectives of Study	1
1.2 Study Approach	3
1.3 Die Swell Phenomenon and Elasticity	4
2. THE EFFECT OF ELASTOL ON OIL PROPERTIES AND PHYSICAL PROCESSES	6
2.1 Experimental Measurement of Elasticity	6
2.1.1 Die Swell Apparatus	6
2.1.2 Die Swell Measurement	8
2.1.3 Die Swell Ratio Calculation	8
2.2 Effect of Elastol on Viscoelasticity	10
2.2.1 Experimental	10
2.2.2 Results and Discussion	11
2.2.3 Conclusions	12
2.3 Effect of Elastol on Oil Evaporation	28
2.3.1 Experimental	28
2.3.2 Results and Discussion	28
2.3.3 Conclusions	28
2.4 Effect of Elastol on Flash Point	31
2.4.1 Experimental	31
2.4.2 Results	31

	<u>Page</u>
2.5 Effect of Elastol on Slick Thickness	32
2.5.1 Experimental	32
2.5.2 Results and Discussion	32
2.5.2 Conclusions	33
2.6 Effect of Elastol on Spreading of Oil Slicks	34
2.6.1 Experimental	34
2.6.2 Results and Discussion	34
2.6.3 Conclusions	35
2.7 Emulsion Formation Tendency and Stability	37
2.7.1 Experimental	37
2.7.2 Results and Discussion	38
2.7.3 Conclusions	40
3. PERFORMANCE OF ELASTOL IN A SMALL-SCALE WAVE GENERATING TANK	62
3.1 Purpose	62
3.2 Experimental	62
3.3 Results and Discussion	64
3.3.1 Effect of Elastol on Weathering	64
3.3.2 Effect of Elastol on Dispersion	65
3.3.3 Effect of Elastol on Emulsification	65
3.3.4 Viscosity of Surface Slick	67
3.3.5 Evaluation of the Performance of the Die Swell Apparatus	68
3.3.6 Elasticity of Surface Oil	70
3.4 Conclusions	85
4. EFFECT OF ELASTOL ON OTHER SPILL TREATING AGENTS	86
4.1 Objectives	86
4.2 Experimental	86
4.3 Results and Discussion	87
4.4 Conclusions	87

	<u>Page</u>
5. PRELIMINARY-LARGE-SCALE TANK TESTS AT ESSO	89
5.1 Purpose	89
5.2 Procedure	89
5.3 Results and Discussion	89
5.4 Conclusions	90
6. CONCLUSIONS	92
7. RECOMMENDATIONS	94
8. REFERENCES	96
APPENDIX I: PHYSICAL-CHEMICAL PROPERTIES OF TEST OILS	97
APPENDIX II: PRODUCT INFORMATION ON ELASTOL	105
APPENDIX III: SHEAR RATES FOR VISCOSITY MEASUREMENTS	108

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1.1	Schematic of Physical, Chemical, and Biological Processes	2
2.1	Schematic of the Die Swell Apparatus	7
2.2	Die Swell Ratio and Viscosity vs. Time for ASMB (15 deg C)	13
2.3	Die Swell Ratio and Viscosity vs. Time for Emulsifying Mix (15 deg C)	14
2.4	Die Swell Ratio and Viscosity vs. Time for Amauligak (15 deg C)	15
2.5	Die Swell Ratio and Viscosity vs. Time for Bent Horn (15 deg C)	16
2.6	Die Swell Ratio and Viscosity vs. Time for Diesel (15 deg C)	17
2.7	Die Swell Ratio and Viscosity vs. Time for Hybernia (15 deg C)	18
2.8	Die Swell Ratio and Viscosity vs. Time for Norman Wells (15 deg C)	19
2.9	Die Swell Ratio and Viscosity vs. Time for Prudhoe Bay (15 deg C)	20
2.10	Die Swell Ratio and Viscosity vs. Time for Tarsiut (15 deg C)	21
2.11	Die Swell Ratio and Viscosity vs. Time for ASMB (0 deg C)	22
2.12	Die Swell Ratio and Viscosity vs. Time for Emulsifying Mix (0 deg C)	23
2.13	Effect of Mixing on the Viscoelastic Properties of ASMB with 6000 ppm of Elastol (15 deg C)	24
2.14	Effect of Mixing on the Viscoelastic Properties of Emulsifying Mix with 6000 ppm of Elastol (15 deg C)	25
2.15	Effect of Mixing Energy on Evaporative Losses vs. Time for ASMB (15 deg C)	29
2.16	Evaporative Losses vs. Time for Amauligak (15 deg C)	29
2.17	Evaporative Losses vs. Time for Bent Horn (15 deg C)	30
2.18	Evaporative Losses vs. Time for Diesel (15 deg C)	30
2.19	The Extent of Spreading vs. Concentration of Elastol for ASMB and the Emulsifying Mix (15 deg C)	36
2.20	The Extent of Spreading vs. Reaction Time for ASMB and the Emulsifying Mix with 6000 ppm of Elastol (15 deg C)	36
2.21	Plots of f and Water Content vs. Time for ASMB (15 deg C)	42
2.22	Plots of f and Water Content vs. Time for 15% Weathered ASMB (15 deg C)	43
2.23	Plots of f and Water Content vs. Time for Emulsifying Mix (15 deg C)	44
2.24	Plots of f and Water Content vs. Time for Hybernia (15 deg C)	45
2.25	Plots of f and Water Content vs. Time for Prudhoe Bay (15 deg C)	46

<u>Figure No.</u>		<u>Page</u>
2.26	Plots of f and Water Content vs. Time for Amauligak (15 deg C)	47
2.27	Plots of f and Water Content vs. Time for Norman Wells (15 deg C)	48
2.28	Plots of f and Water Content vs. Time for Tarsiut (15 deg C)	49
2.29	Plots of f and Water Content vs. Time for ASMB (0 deg C)	50
2.30	Plots of f and Water Content vs. Time for 15% Weathered ASMB (0 deg C)	51
2.31	Plots of f and Water Content vs. Time for Amauligak (0 deg C)	52
2.32	Plots of f and Water Content vs. Time for Emulsifying Mix (0 deg C)	53
2.33	Plots of f and Water Content vs. Time for Hybernia (0 deg C)	54
2.34	Plots of f and Water Content vs. Time for Norman Wells (0 deg C)	55
2.35	Plots of f and Water Content vs. Time for Prudhoe Bay (0 deg C)	56
2.36	Plots of f and Water Content vs. Time for Tarsiut (0 deg C)	57
2.37	Plots of f and Water Content vs. Time for Emulsified ASMB (15 deg C)	58
2.38	Plots of f and Water Content vs. Time for Emulsified Prudhoe Bay (15 deg C)	59
3.1	Small-Scale Tank Tests for ASMB at 15 deg C and 150 RPM	73
3.2	Small-Scale Tank Tests for Emulsifying Mix at 15 deg C and 150 RPM	74
3.3	Effect of Mixing Energy on Small-Scale Tank Tests for ASMB at 15 deg C	75
3.4	Effect of Mixing Energy on Small-Scale Tank Tests for Emulsifying Mix at 15 deg C	76
3.5	Small-Scale Tank Tests for ASMB at 15 deg C and 220 RPM	77
3.6	Small-Scale Tank Tests for Emulsifying Mix at 15 deg C and 220 RPM	78
3.7	Small-Scale Tank Tests for ASMB at 0 deg C and 150 RPM	79
3.8	Small-Scale Tank Tests for Emulsifying Mix at 0 deg C and 150 RPM	80
3.9	Effect of Salinity on Small-Scale Tank Tests for ASMB at 150 RPM	81
3.10	Small-Scale Tank Tests for 15% Weathered ASMB at 15 deg C and 150 RPM	82
3.11	Weathering vs. Time	83
3.12	Weathering vs. Time	84
4.1	Oil Dispersed vs. Time for ASMB with 1:100 Corexit at 15 deg C	88
5.1	Viscosity vs. Time for Large-Scale Tank Tests	91

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
2.1	Degree of Elasticity of Test Oils	26
2.2	Elastol Reaction Time of Test Oils	27
2.3	Spill Contraction Results	33
2.4	Emulsion Formation Tendency, Stability and Water Content of Test Oils at 15 deg C	60
2.5	Emulsion Formation Tendency, Stability and Water Content of Test Oils at 0 deg C	61

LIST OF PLATES

<u>Plate No.</u>		<u>Page</u>
1	Die Swell of Untreated Oil	9
2	Die Swell of Elastol-Treated Oil	9
3	Alberta Sweet Mixed Blend Emulsions	41
4	Oscillating Hoop Tank Apparatus	63

ACKNOWLEDGEMENTS

This report was prepared for and funded by Environment Canada and the United States Minerals Management Service. The authors would like to thank General Technology Applications Inc. for providing the Elastol required for this study, the Esso Research facility in Calgary for their assistance and cooperation during the preliminary large-scale tank tests and S.L.Ross Environmental Research Ltd., for the use of their oscillating hoop apparatus.

1. INTRODUCTION

When spilled on water, oil is subjected to a complex array of physical, chemical and biological processes. Figure 1.1 illustrates these processes. When feasible, the primary objectives of spill response are containment and collection of the spill (Waters and Hadermann, 1987). Recently, a new spill treating agent called Elastol has been developed, which when applied to oil, imparts a viscoelastic property. It is claimed that this viscoelastic enhancing agent increases the oil slick's resistance to spreading and breakup, and improves the performance of skimmers, other collection devices, and containment barriers.

Elastol is manufactured in the form of a white powder, 100 to 1000 microns in size, by General Technology Applications Inc. It is composed of a simple, nominally non-toxic polymer coated with a water-insoluble salt. To date, the product has shown promise in small-scale field demonstrations but the effect of many important variables has not been addressed.

The bulk of this study was undertaken on a small scale to determine the effect of Elastol on selected oil properties and physical processes to which oil slicks are subjected. The results of this study will be used as a guide towards future large-scale testing of this product.

1.1 Objectives of Study

The main objectives of this study were:

- i. to determine the effect of various parameters (oil type, temperature, Elastol dose, mixing energy, water salinity) on Elastol's performance
- ii. to determine the effect of Elastol on selected physical properties of oils and on the physical processes to which oil spills are subjected
- iii. explore any factors of interest arising out of i or ii of the foregoing.

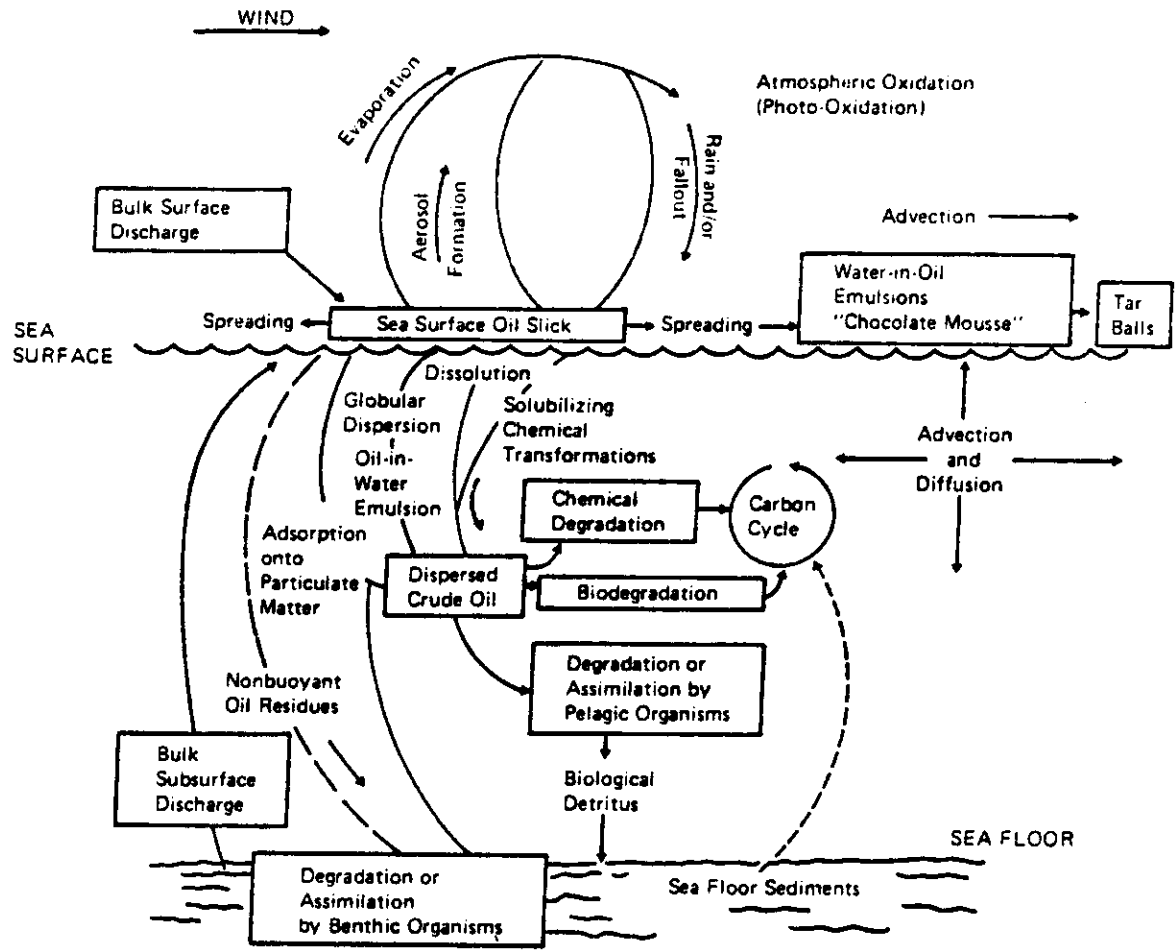


FIGURE 1.1 Schematic of physical, chemical, and biological processes.

SOURCE: Adapted from Burwood and Speers (1974).

1.2 Study Approach

Although the viscosity and elasticity of a viscoelastic fluid are related, these properties were treated and measured separately throughout this study. All viscosity measurements were performed using the Brookfield viscometer, and a novel "die swell" apparatus was constructed to measure the elasticity.

This apparatus was constructed based on the swelling behaviour of viscoelastic fluids when forced through a small opening (die). This behaviour, which is called the die swell phenomenon, is described further in Section 1.3.

This study was divided into four phases. The first phase studied the effect of Elastol on selected oil properties and processes, such as: flash point, evaporation, change in slick thickness, spreading, emulsification and increase in viscoelasticity. Separate experiments were performed for each variable. In each experiment, a control test was also conducted. A description of these experiments and the results are presented in Section 2.

The second phase studied the combined, simultaneous processes of weathering, dispersion, emulsification and increase in viscoelasticity of oil slicks subjected to wave action in a small tank. This work is described in Section 3.

The third phase involved the study of the effect of Elastol on the performance of two surfactant-based oil spill treating agents, Corexit 9527 oil dispersant, and Brand S emulsion inhibitor. This work is reported in Section 4.

Section 5 reports the findings of a preliminary large-scale tank test performed by M.Fingas.

1.3 Die Swell Phenomenon and Elasticity

Fluids exhibiting viscoelastic property such as polymer solutions are of particular interest to the plastic industry. This rheological property, as the name suggests, includes both viscous and elastic components. Viscous properties have been extensively studied for many years, and are relatively easy to characterize and specify. On the other hand, elastic properties have received less attention, although it is now recognized that elastic properties play an important role in rheological behaviour.

When a polymeric solution exhibiting an elastic nature is forced through a small opening (die), the diameter of the extrudate (exiting fluid) is greater than the diameter of the die opening. This swelling effect is known as the die swell phenomenon. The degree of swelling depends on several factors: the fundamental properties of the solution, such as the polymer's molecular structure, concentration and distribution; the presence of fillers; the flow conditions, such as shear rate and the length to diameter ratio of the capillary tube; and temperature.

Die swell ratio, which is defined as the ratio of the fluid extrudate diameter to that of the die, is used to quantify this swelling behaviour. Viscoelastic liquids, at high shear rates, may exhibit swells of 2 to 4 times the die diameter (Vlachopoulos, 1981). Die swell is not limited to viscoelastic fluids. At very low (<16) Reynold's numbers, Newtonian liquids exhibit this behaviour (Hill and Chenier, 1984). Middleman (1977) has recorded die swells of about 13% for these fluids. At higher Reynold's numbers, Newtonian fluids may exhibit a negative die swell, in which the extrudate flow diameter can be as much as 13% less than the die opening (Bird et.al. 1977).

Die swell is a very complex phenomenon. Despite active research in this area, there is still disagreement regarding the contributions of molecular, rheological and geometrical effects on die swell and there is also a lack of a comprehensive theory. Attempts to explain the die swell phenomenon have been neither completely clear nor successful. None of the long and involved theories are presented here but are well summarized in Samara (1985). However, experiments utilizing the die swell behaviour have been used in many

studies in the comparison and classification of materials in specific applications and in the characterization of the degree of elasticity of viscoelastic fluids (Samara 1985, Bird et.al. 1977 and Mannheimer, 1986).

2. THE EFFECT OF ELASTOL ON OIL PROPERTIES AND PHYSICAL PROCESSES

Objectives

The objective of this phase of the study was to investigate the effects of Elastol on the physical behaviour of oils and petroleum products under controlled laboratory conditions. In particular, the studies in this section focused on the following:

- i. the development of a method to measure the elasticity of Elastol-treated oil samples
- ii. the change in viscoelastic properties as a function of time for a variety of oils under various conditions
- iii. the effect of Elastol on oil flash point and evaporation
- iv. the increase in slick thickness following Elastol application
- v. the effect of Elastol on slick spreading
- vi. Elastol's effect on emulsion formation and stability.

2.1 Experimental Measurement of Elasticity

2.1.1 Die Swell Apparatus

A novel apparatus was constructed to measure the elasticity of Elastol-treated oils based on the die swell phenomenon.

The assembly consists of two 10 mL syringes, one acting as a piston, the other as a sample holder. The piston is driven by air pressure, set at 90 kPa (13 psi) by an in-line regulator. The system is activated by an on-off shut-off valve. The downward force of the piston is directly transmitted to the plunger of the sample syringe (which contains the oil sample), and ejects the sample through a 12 gauge (0.22 cm ID), no. 3 point (90 deg cut) needle. A schematic diagram of this apparatus is illustrated in Figure 2.1.

The swelling of the oil as it flowed from the needle was photographed with an instant Polaroid camera connected to a Leitz microscope. The photographs were then used to calculate the die swell ratios.

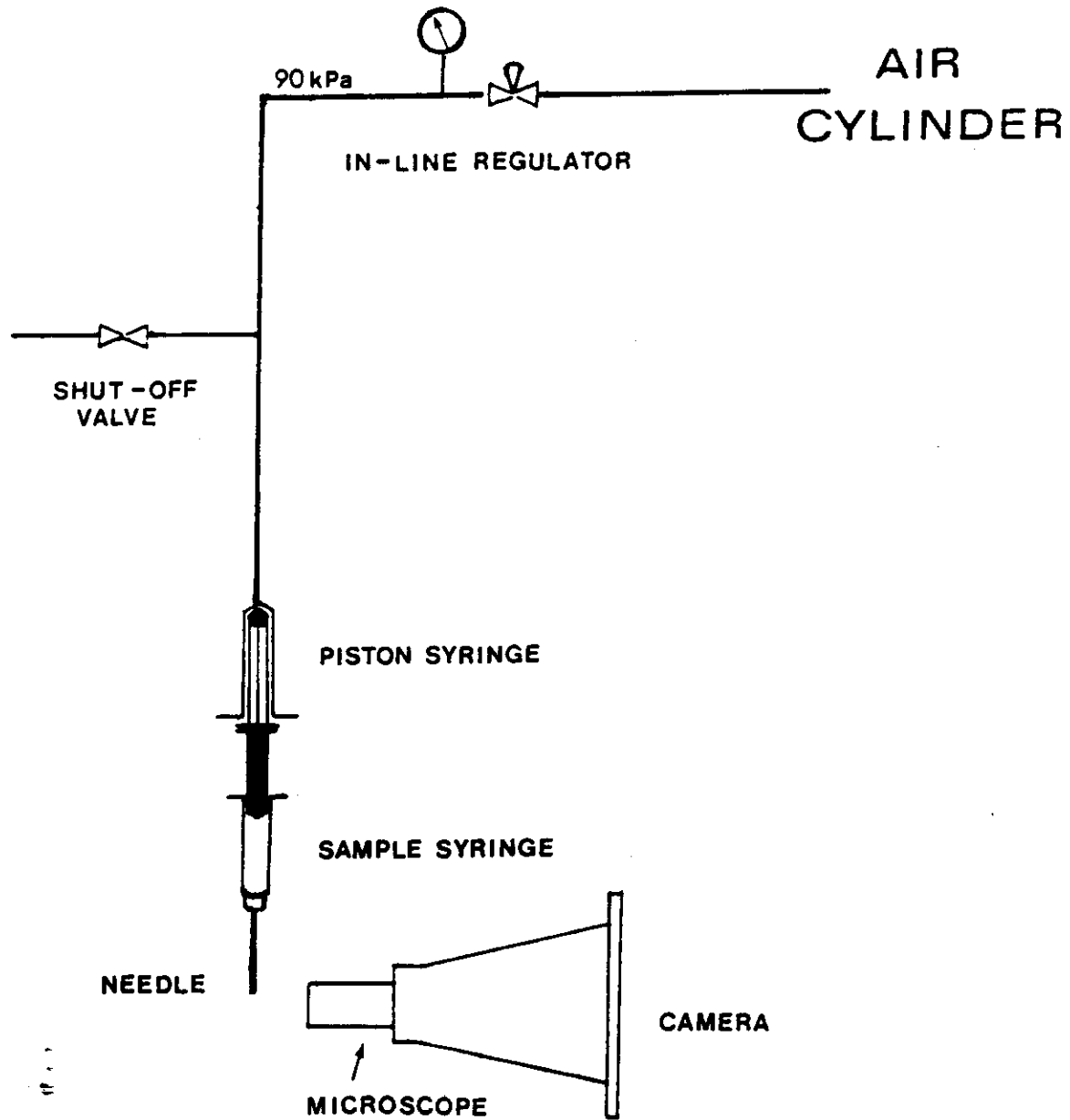


FIGURE 2-1. SCHEMATIC OF THE DIE SWELL APPARATUS.

2.1.2 Die Swell Measurement

The air in the system was set to 90 kPa gauge pressure. Approximately 10 mL of the oil sample was poured into the sample syringe and the syringes and plungers were set in place as shown in Figure 2.1. (It was found that the sample syringe required a little lubrication in the form of grease or liquid detergent.) With the microscope and the camera focused at the tip of the needle, the shut-off valve was closed, which forced the oil sample through the needle by the action of the two plungers. To allow for steady flow to be established, photographs were taken after one third to one half of the oil was dispensed from the syringe.

2.1.3 Die Swell Ratio Calculation

Die swell ratios were determined directly from the photographs. Sample photographs are shown in Plates 1 and 2. The extrudate diameter required in the die-swell ratio calculation was measured from the picture at the point of maximum swell.

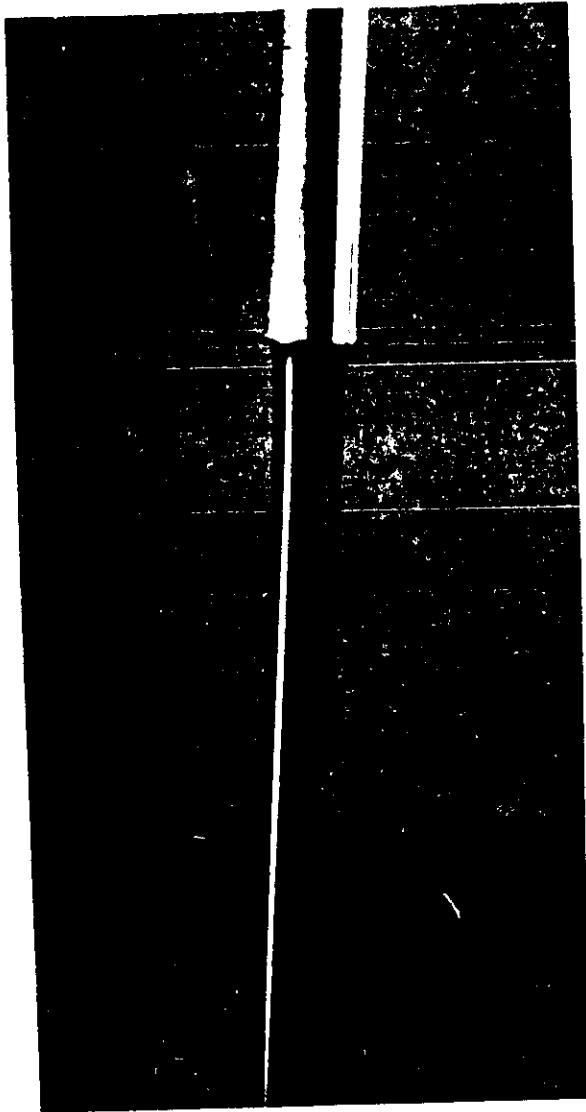


Plate 1: Die Swell of Untreated Oil

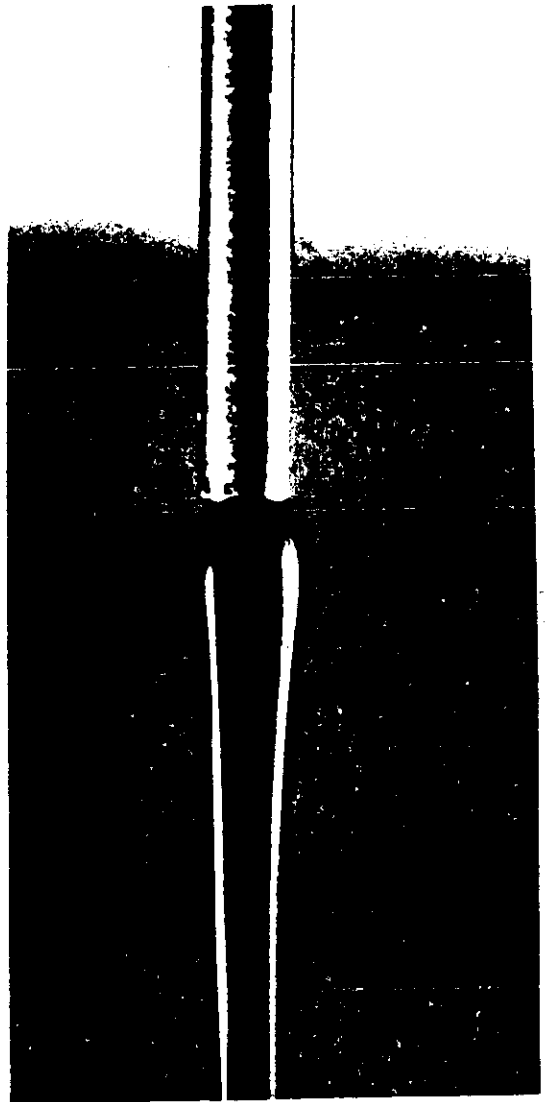


Plate 2: Die Swell of Elastol-Treated Oil

2.2 Effect of Elastol on Viscoelasticity

A series of bench-scale experiments were performed to determine the viscosity and elasticity of Elastol-treated oils at different concentrations, temperatures and mixing times.

2.2.1 Experimental

This study was conducted in a New Brunswick Shaker/Incubator which mixed the Elastol-treated oil samples contained in 18.5 cm crystallizing dishes at a controlled temperature. This apparatus was chosen for its ideal mode and speed of mixing since other equipment/techniques, such as magnetic bar stirrers and rotating mixers failed to produce a homogeneous oil sample of consistent elasticity.

For each experiment, 200 mL of oil was treated with 600 ppm (approximately 0.45 mg Elastol/ cm² of oil surface area) or 6000 ppm (4.5 mg/cm²) of Elastol. A simple dispenser was constructed out of a tea strainer which dispensed the Elastol powder from 1.5 mm diameter holes in a manner similar to that of a salt shaker. A watch glass was placed over the dish to prevent evaporation. The dish was then mixed at a speed of 80 RPM.

Nine different oils were used in this study: Alberta Sweet Mixed Blend (ASMB), Amauligak, Bent Horn, Diesel, Hybernia, Norman Wells, Prudhoe Bay, Tarsiut, and Emulsifying Mix which is a 50-50 mixture of ASMB and Bunker C fuel oil. All oils were tested at 15 deg C; ASMB and Emulsifying Mix were studied at both 15 and 0 deg C. In addition, these two oils were tested at 15 deg C with no mixing at the higher Elastol concentration. Oil samples were taken at time intervals of 5 min.; 1, 4, 24, and 48 hours.

The viscosity and elasticity of each sample were measured using the Brookfield viscometer and the die swell apparatus, respectively.

2.2.2 Results and Discussion

All oils tested exhibited viscoelastic properties when treated with Elastol. Untreated oils, on the other hand, showed no elastic behaviour. As Figures 2.2 to 2.12 illustrate, each Elastol-treated oil displays a unique rheological behaviour in terms of increase in viscoelasticity and reaction time. For most experiments, the dynamic viscosity and die swell ratio curves paralleled each other. As expected, a higher dose of Elastol imparted a greater increase in viscosity (and elasticity): at a concentration of 6000 ppm, viscosity increased by a factor of 6.2 to 35.4 after 48 hours; at 600 ppm, the increase was only 1.1 to 4.0 (except for Bent Horn Crude, which had a 18.3 fold increase).

Personnel performing the tests and subsequent cleaning of the apparatus had adequate opportunity to observe the physical nature of Elastol-treated oil samples. In their opinion, the measured die swell was indicative of the relative degree of observed elasticity.

In an attempt to present the results in a simplified form, each oil treated at a particular concentration and temperature was classified into one of three groups under two categories: degree of elasticity and reaction time. The criteria for classification was arbitrarily chosen as follows:

<u>Die Swell Ratio After 48 Hours</u>	<u>Degree of Elasticity</u>
> 1.75	High
1.25 to 1.75	Moderate
< 1.25	Low

<u>Time to Reach 50% of Total Die Swell Increase</u>	<u>Reaction Time</u>
0 to 1 hour	Fast
1 to 4 hours	Moderate
> 4 hours	Slow

The grouping of oils under both categories is tabulated in Tables 2.1 and 2.2. It is important to note that the classifications only provide a relative measure of the degree of elasticity and reaction times for the nine oils tested. Since the experiments were performed without the presence of water and under ideal laboratory conditions, the magnitude of the elasticities and

reaction times are not necessarily indicative of values expected in actual spill conditions.

i) Effect of Mixing

Figures 2.13 and 2.14 show that Elastol-treated oils exhibited greater viscoelasticity and faster reaction times when the oils were subjected to mixing. However, even under static conditions, a significant increase in elasticity was observed.

ii) Effect of Temperature

Two oils, ASMB and the Emulsifying Mix were tested at both 0 and 15 deg C. As shown in Figures 2.2, 2.3, 2.11, and 2.12, temperature had a noticeable effect on reaction times. Lowering the temperature increased the reaction time for both oils. A lower degree of elasticity was also observed at the lower temperature for the Emulsifying Mix experiments and ASMB treated with 600 ppm of Elastol but ASMB treated at the higher concentration exhibited approximately the same die swell ratio at both temperatures.

The two oils also exhibited different behaviour with respect to the effect of temperature on the viscosity of Elastol-treated oils. The relative increase in dynamic viscosity was approximately the same for Emulsifying Mix at both temperatures but was significantly higher for ASMB at 0 deg than at 15 degrees.

2.2.3 Conclusions

The die swell apparatus developed for this study provides a quantitative measure of elasticity, which appears to be indicative of the visually observed degree of elasticity.

Oils tested with 600 and 6000 ppm of Elastol exhibited an increase in viscoelastic properties. The magnitude of this increase varied with Elastol concentration, temperature and mixing energy. In general, a higher viscoelasticity was observed for oils subjected to mixing at the higher concentration and temperature.

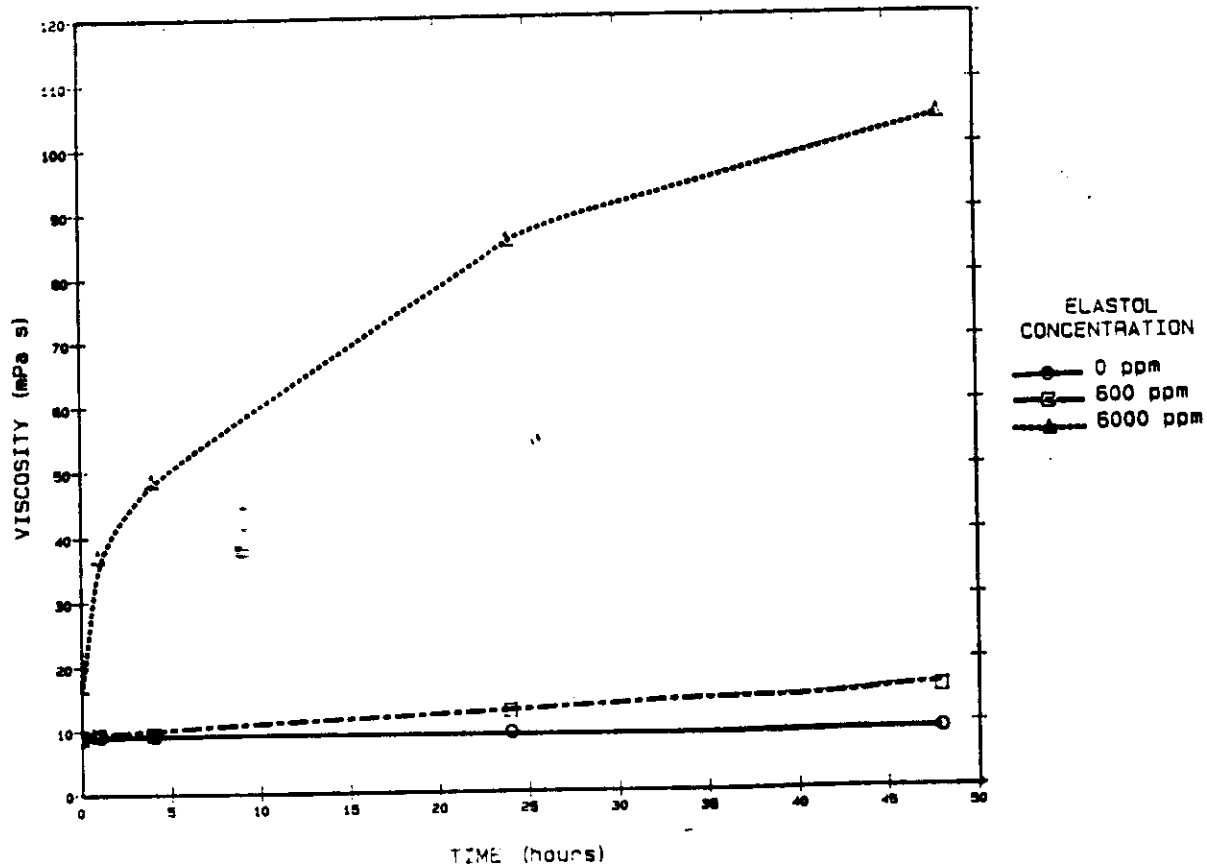
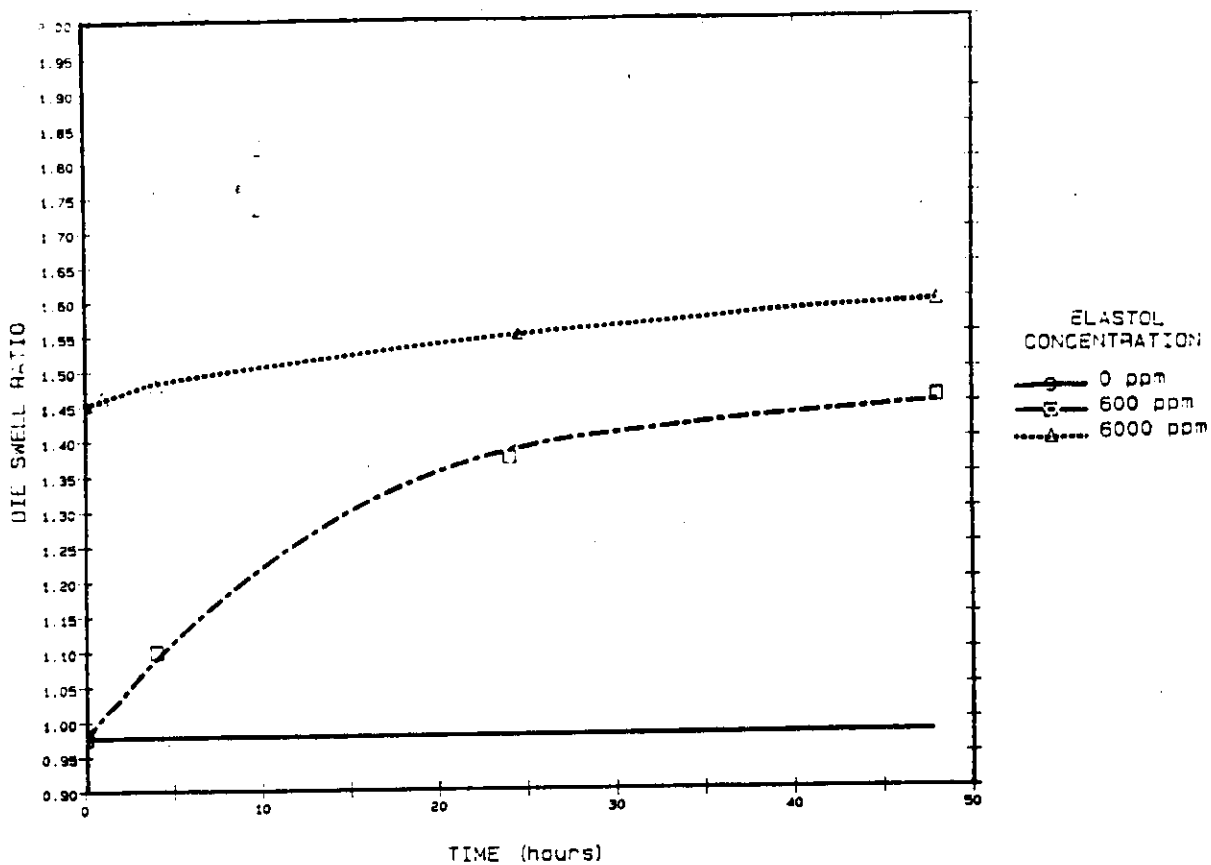


Figure 2-2. Die swell ratio and viscosity versus time for ASMB at 15 deg C.

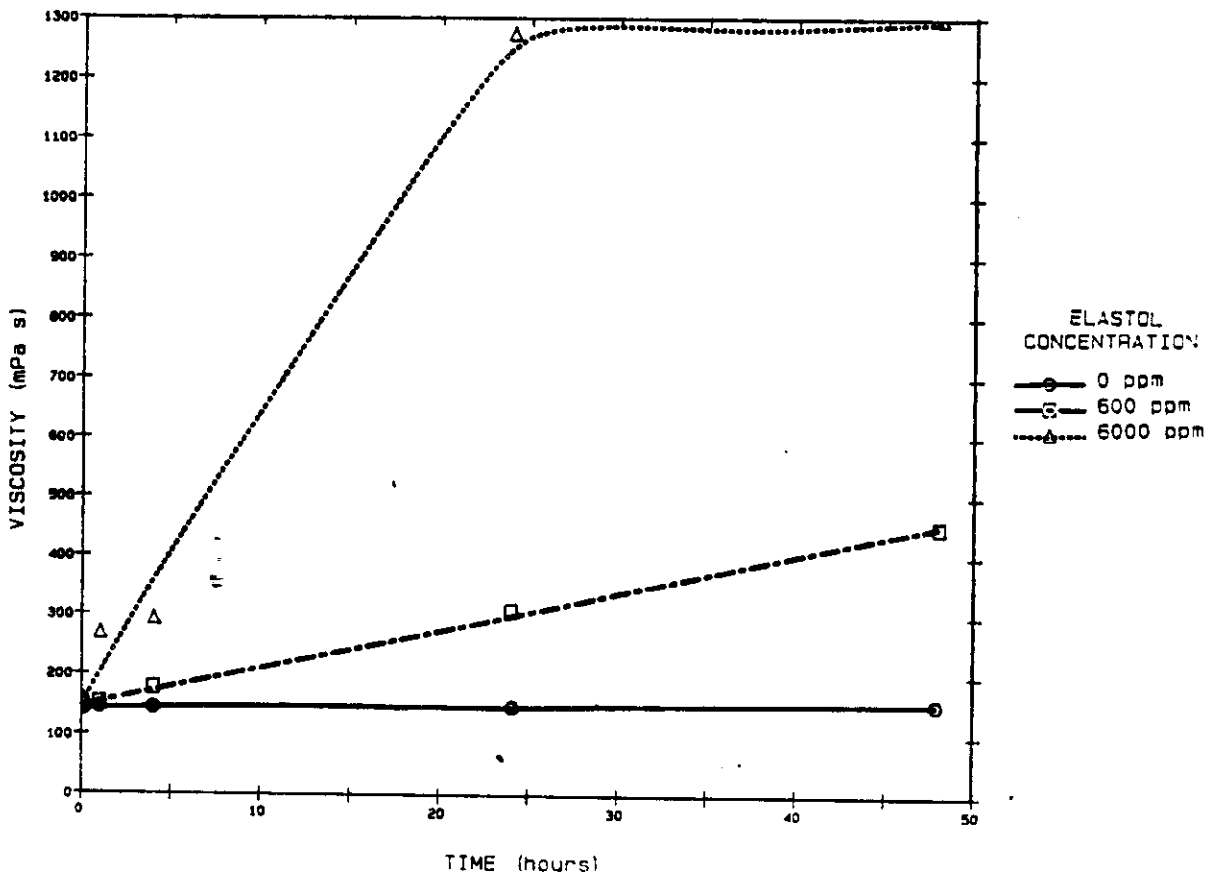
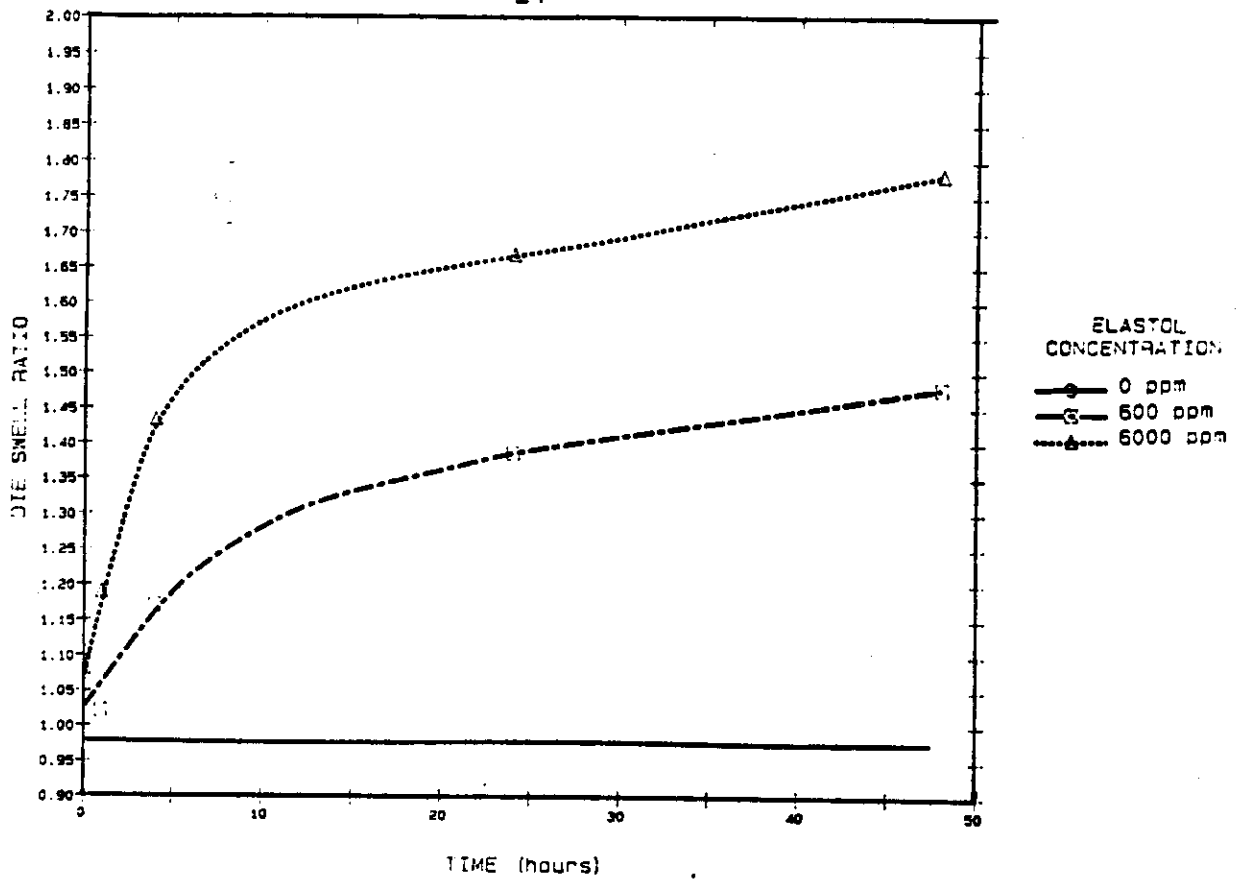


Figure 2-3. Die swell ratio and viscosity versus time for Emulsifying Mix at 15 deg. C.

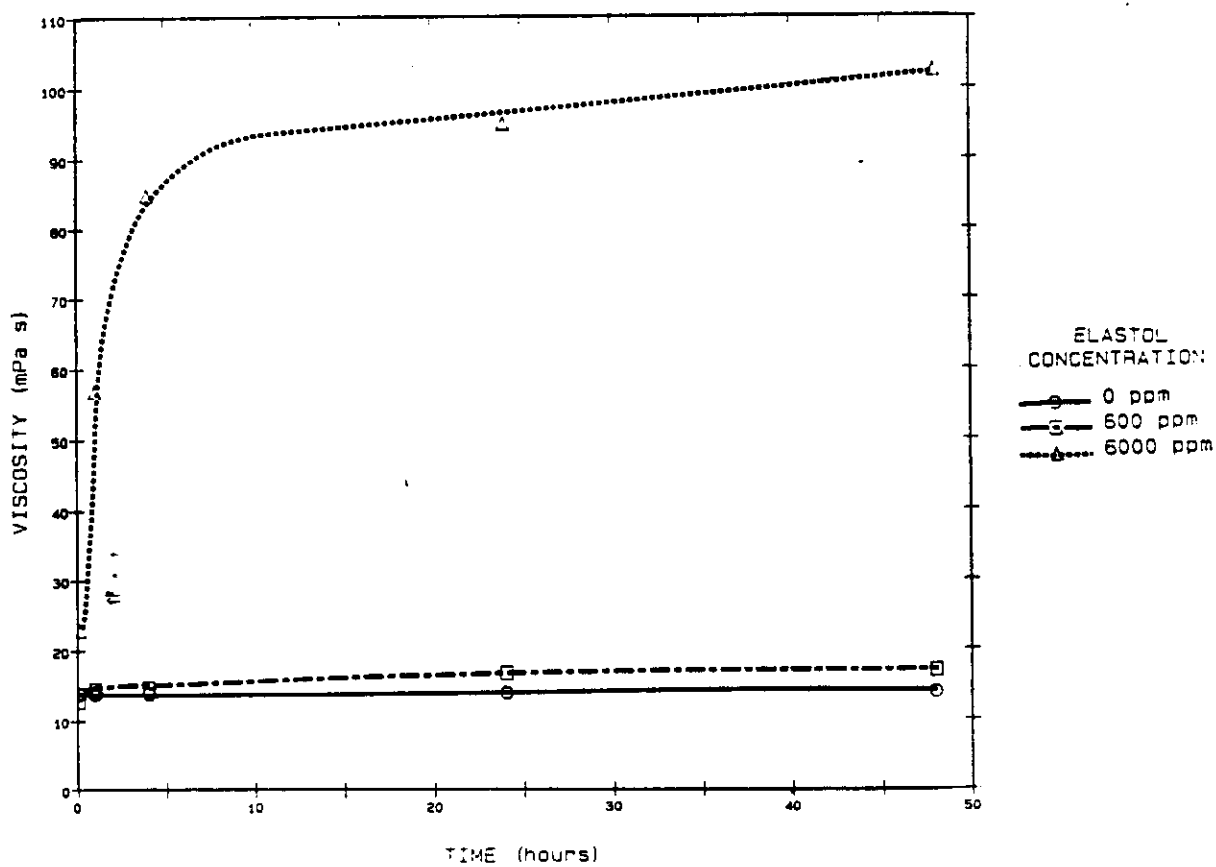
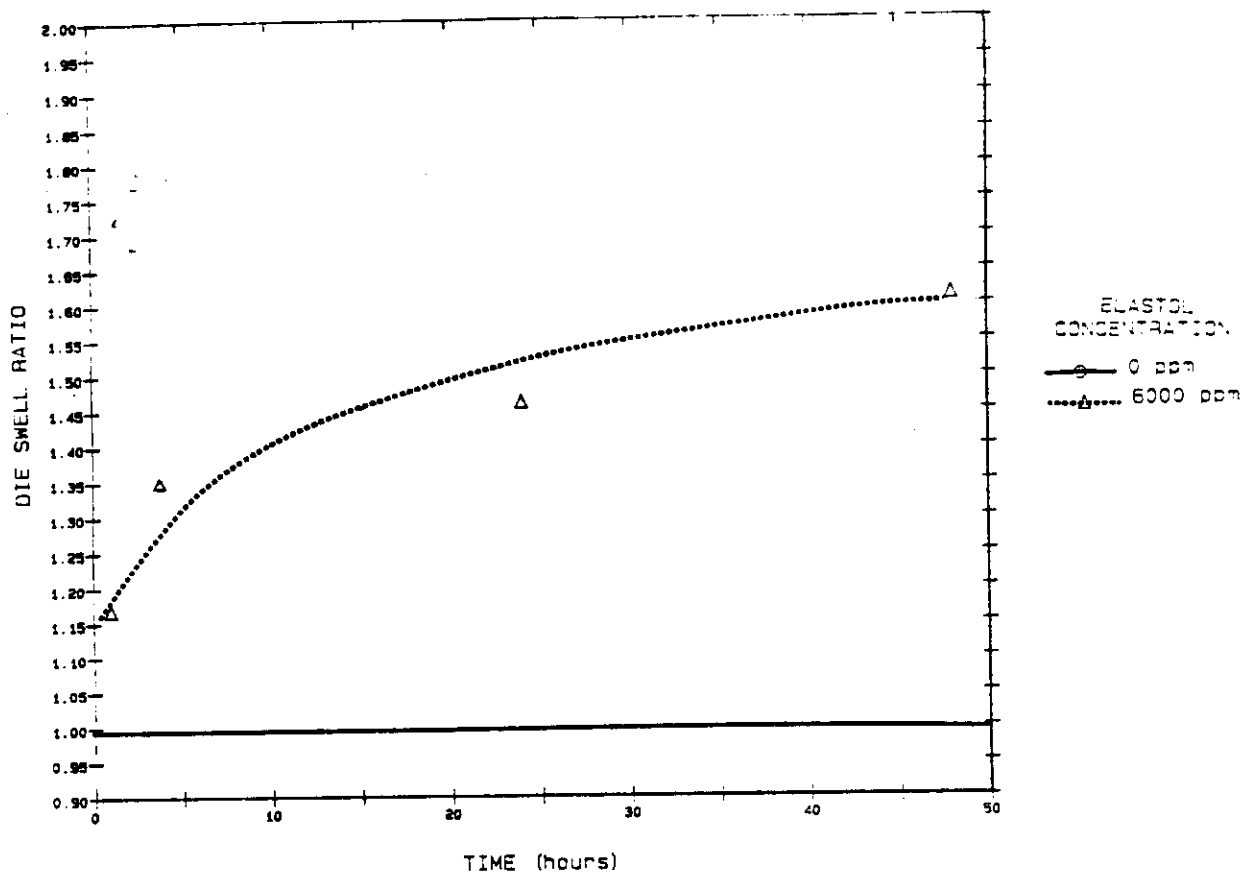


Figure 2-4. Die swell ratio and viscosity versus time for Amauligak at 15 deg. C.

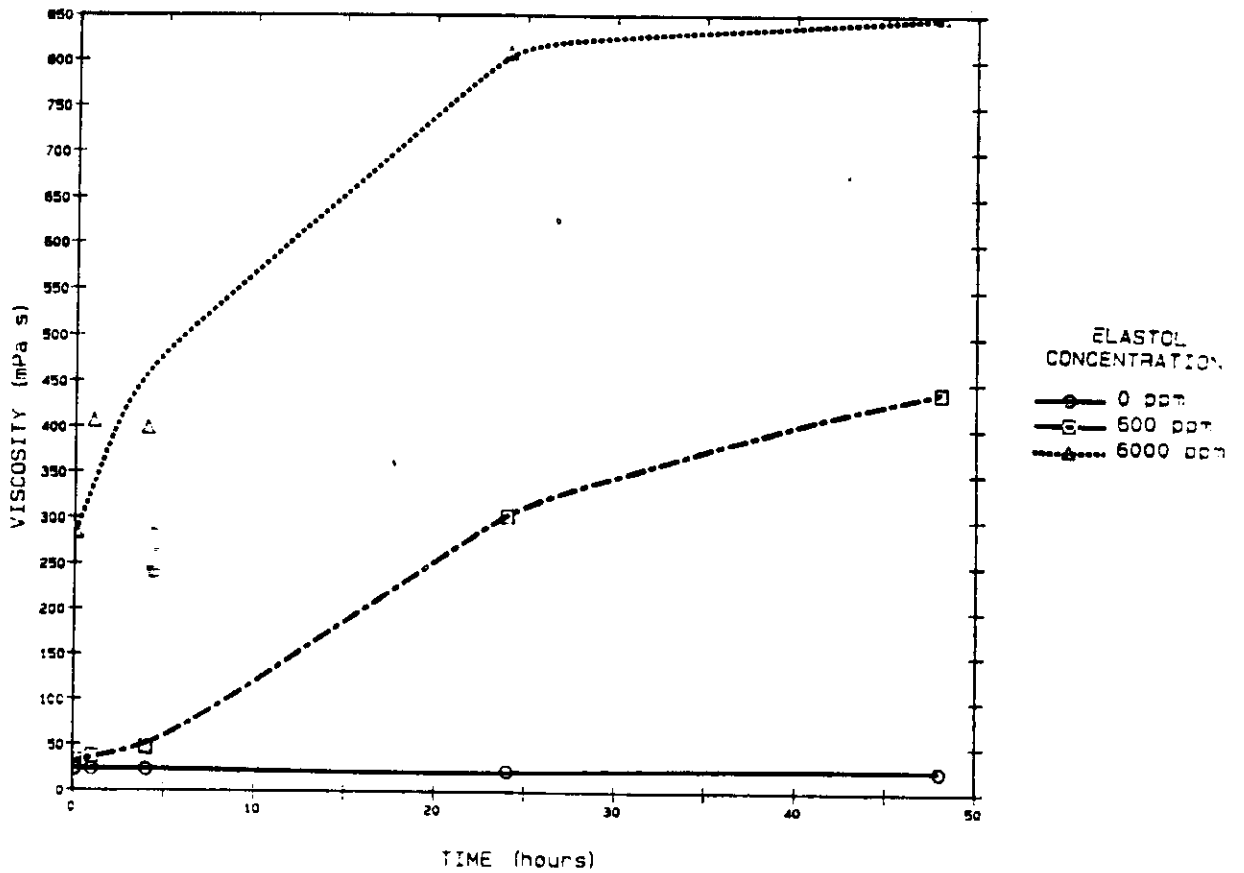
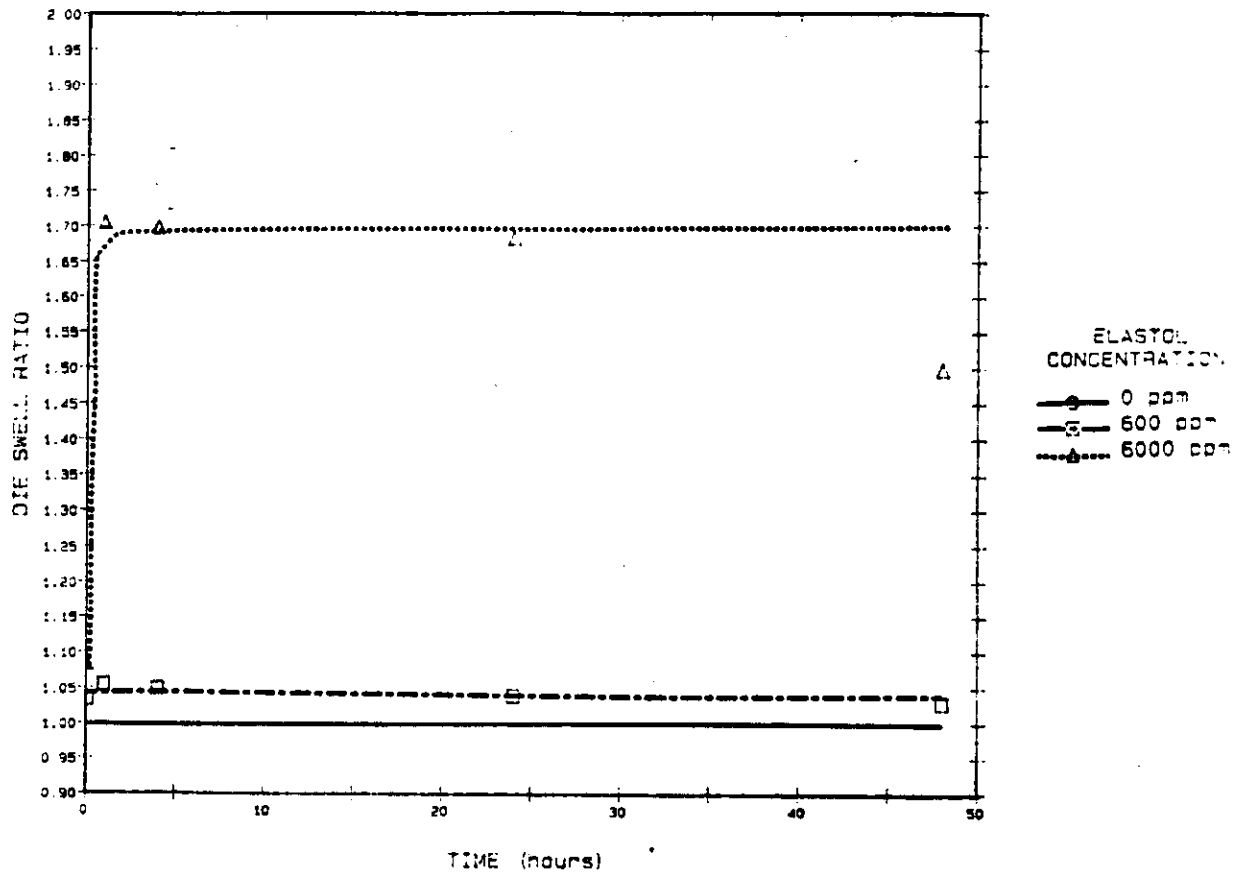


Figure 2-5. Die swell ratio and viscosity versus time for Bent Horn at 15 deg. C.

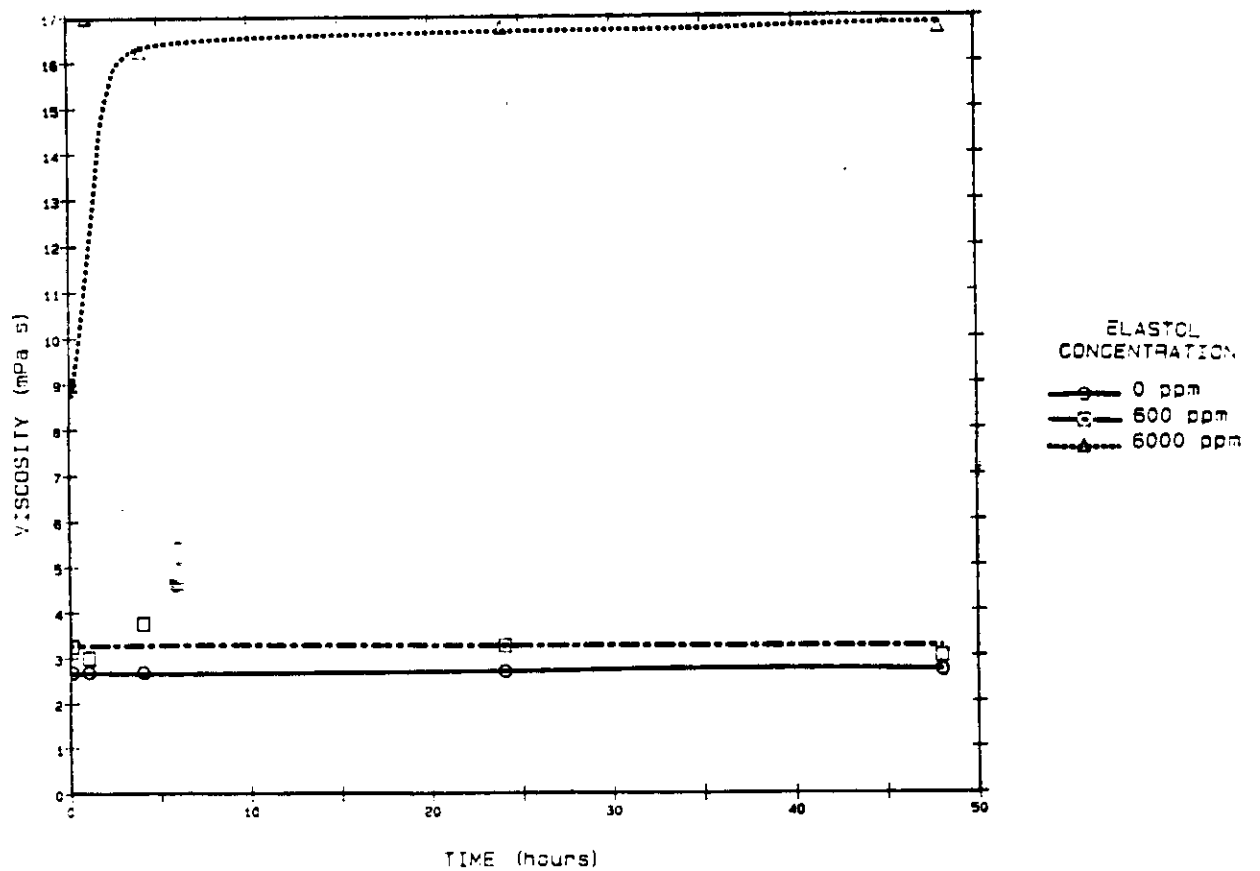
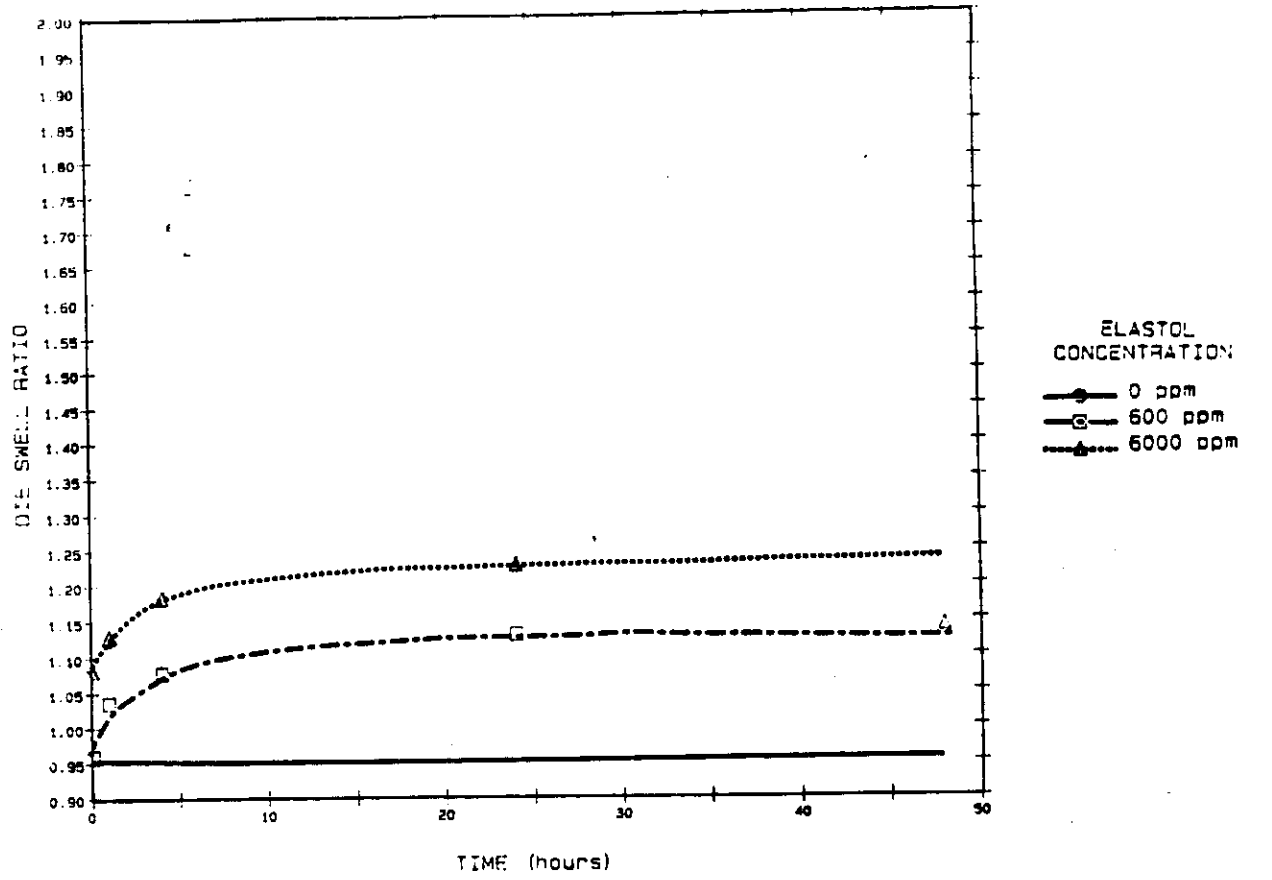


Figure 2-6. Die swell ratio and viscosity versus time for Diesel at 15 deg. C.

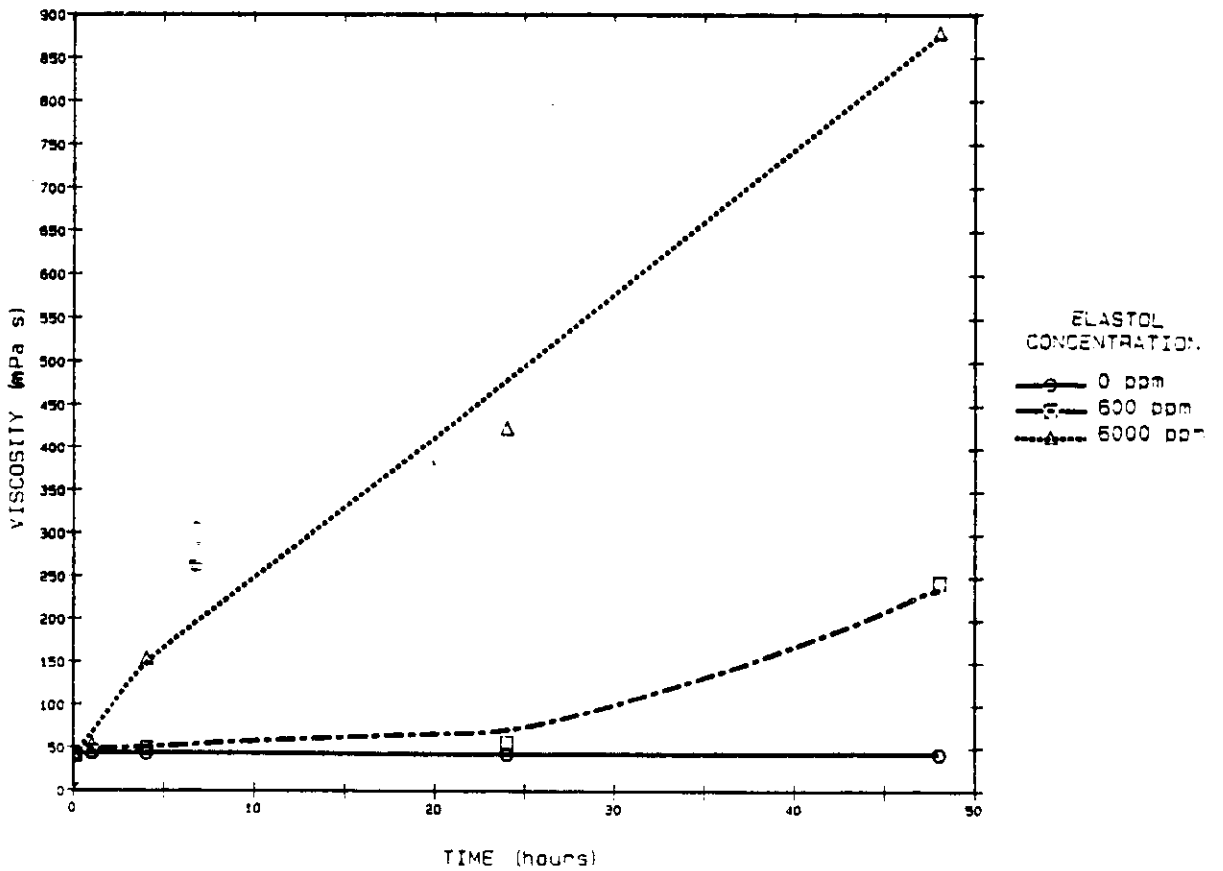
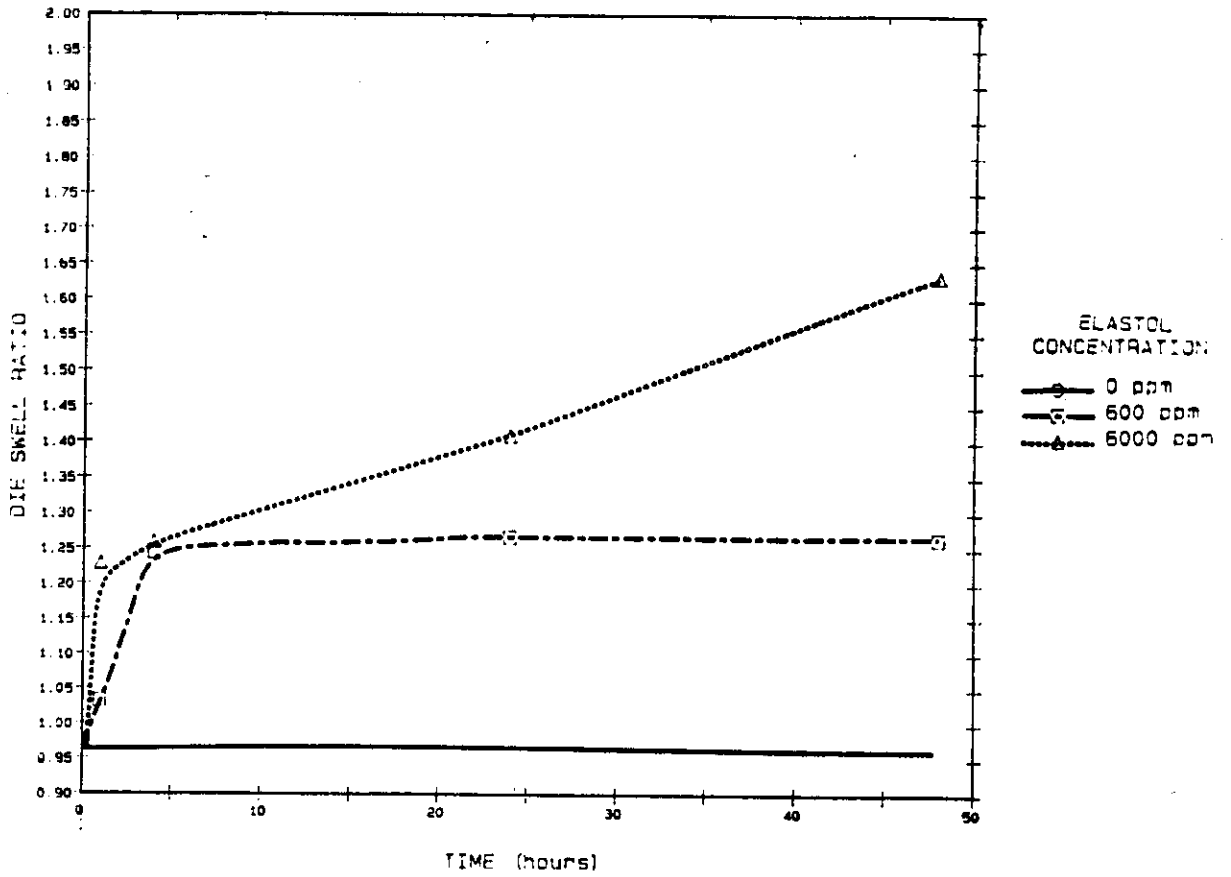


Figure 2-7. Die swell ratio and viscosity versus time for Hybernia at 15 deg. C.

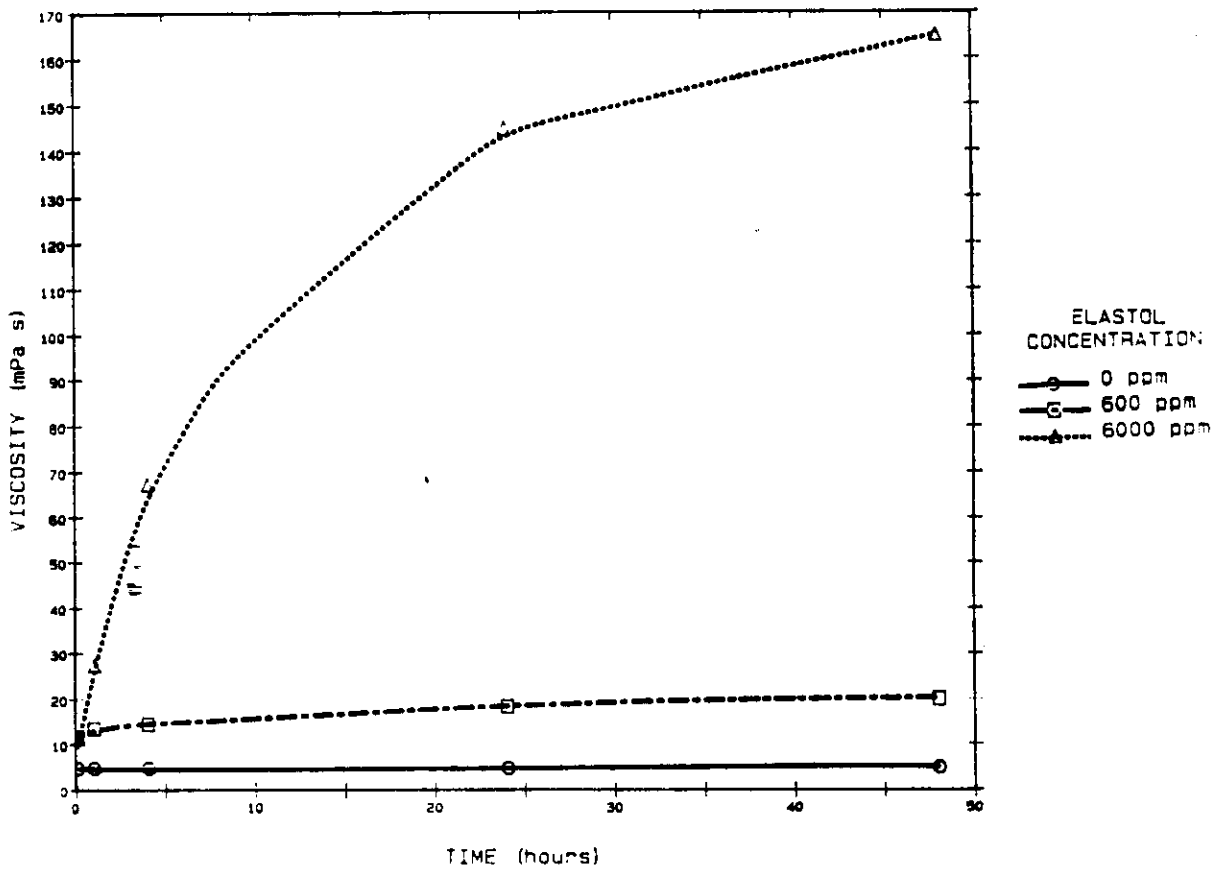
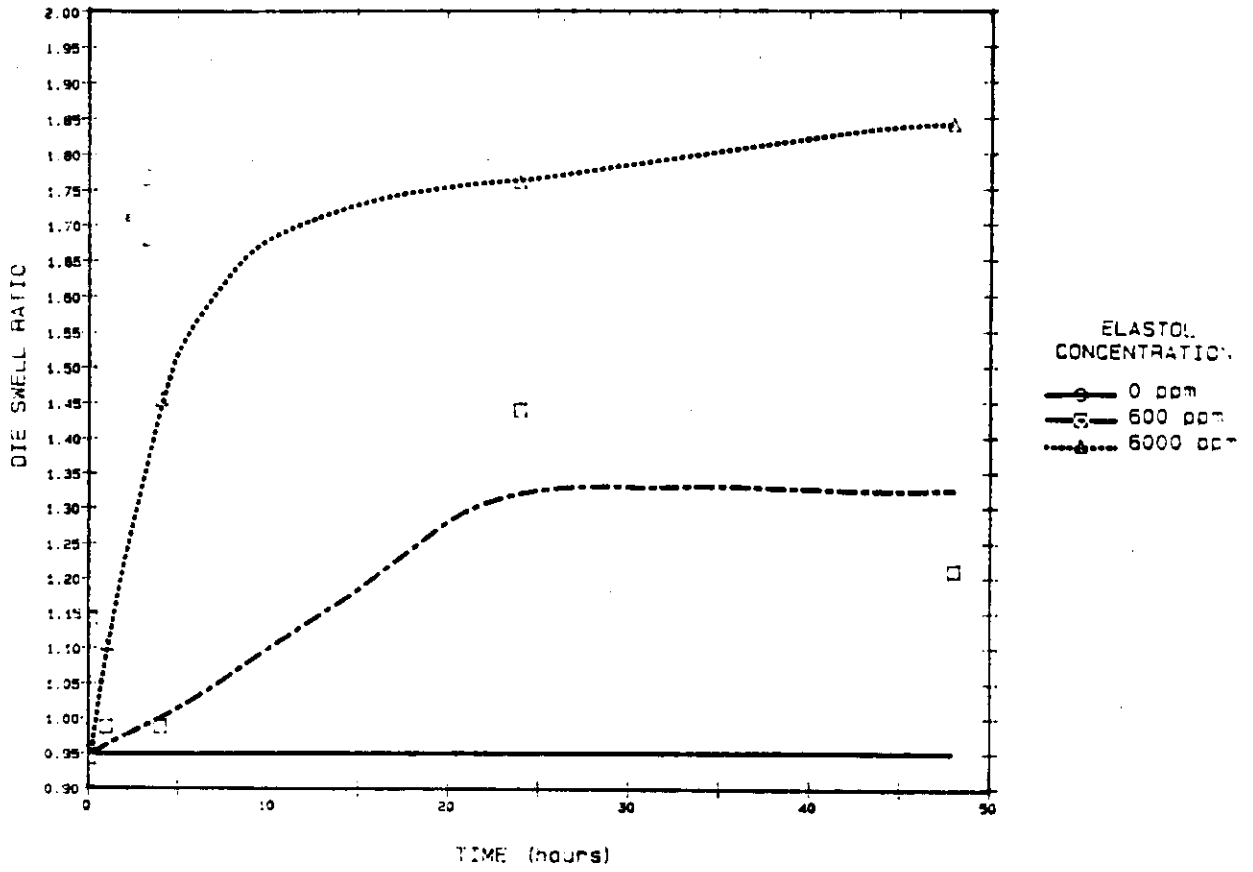


Figure 2-8. Die swell ratio and viscosity versus time for Norman Wells at 15 deg. C.

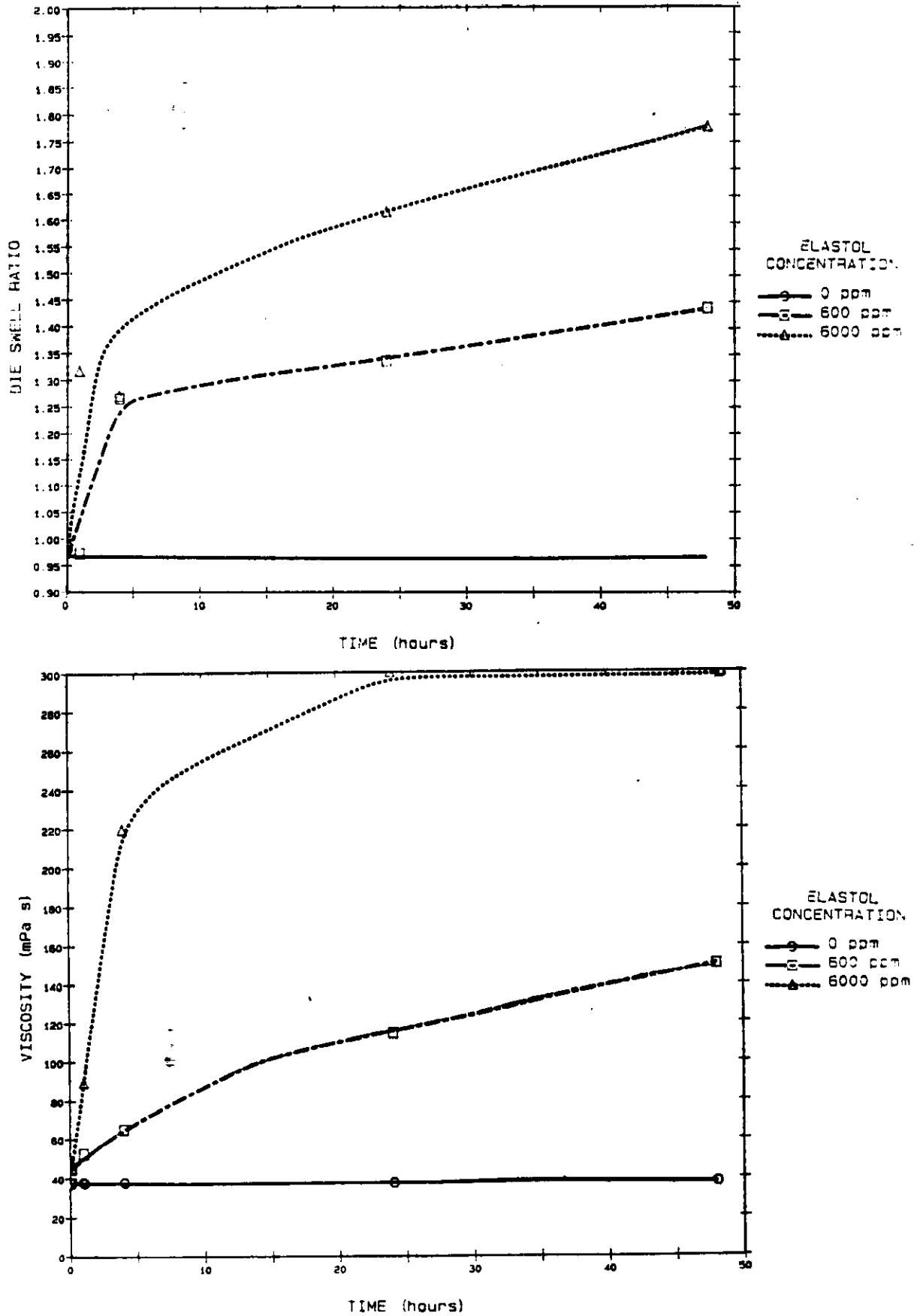


Figure 2-9. Die swell ratio and viscosity versus time for Prudhoe Bay at 15 deg. C.

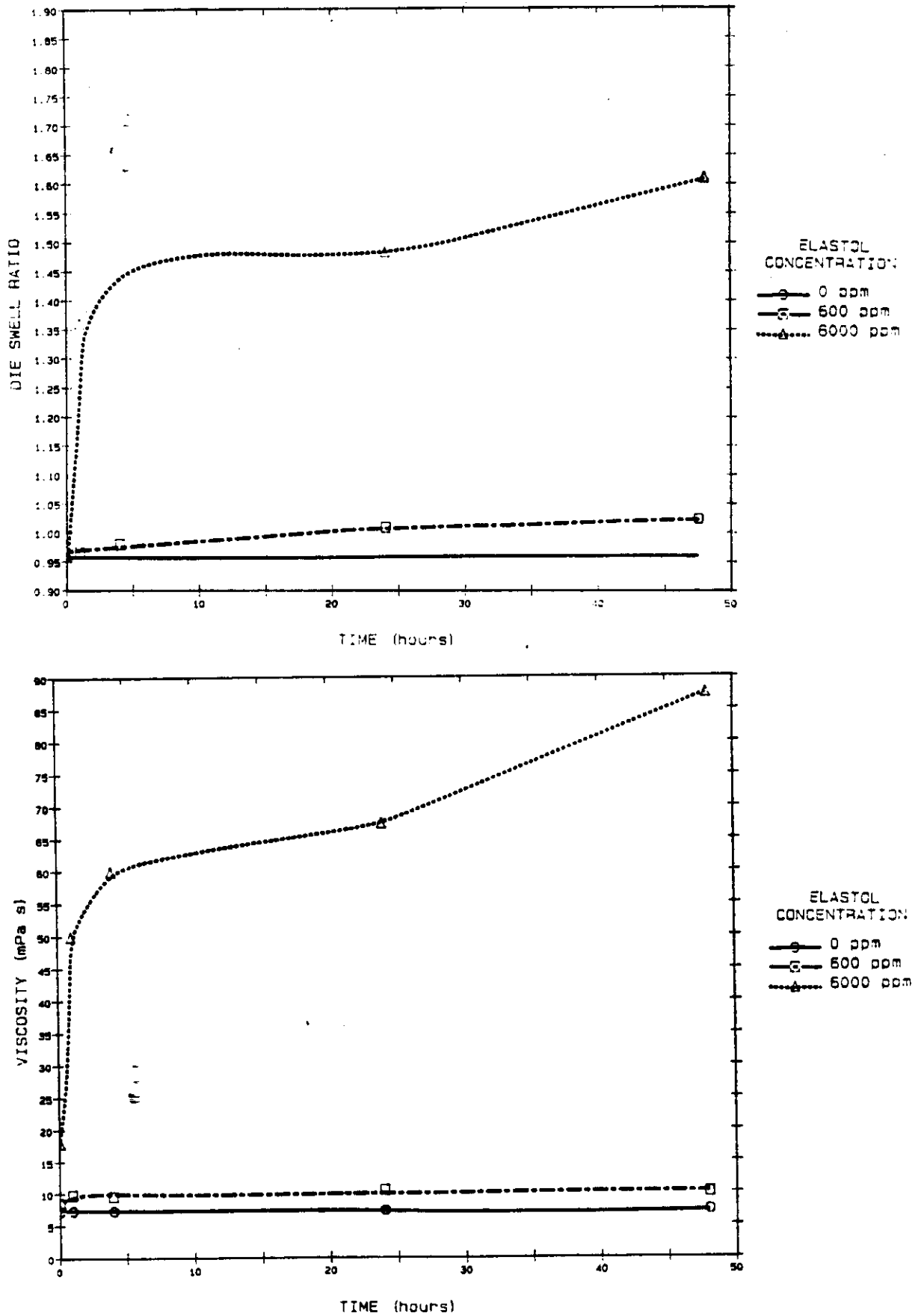


Figure 2-10. Die swell ratio and viscosity versus time for Tarsiut at 15 deg. C.

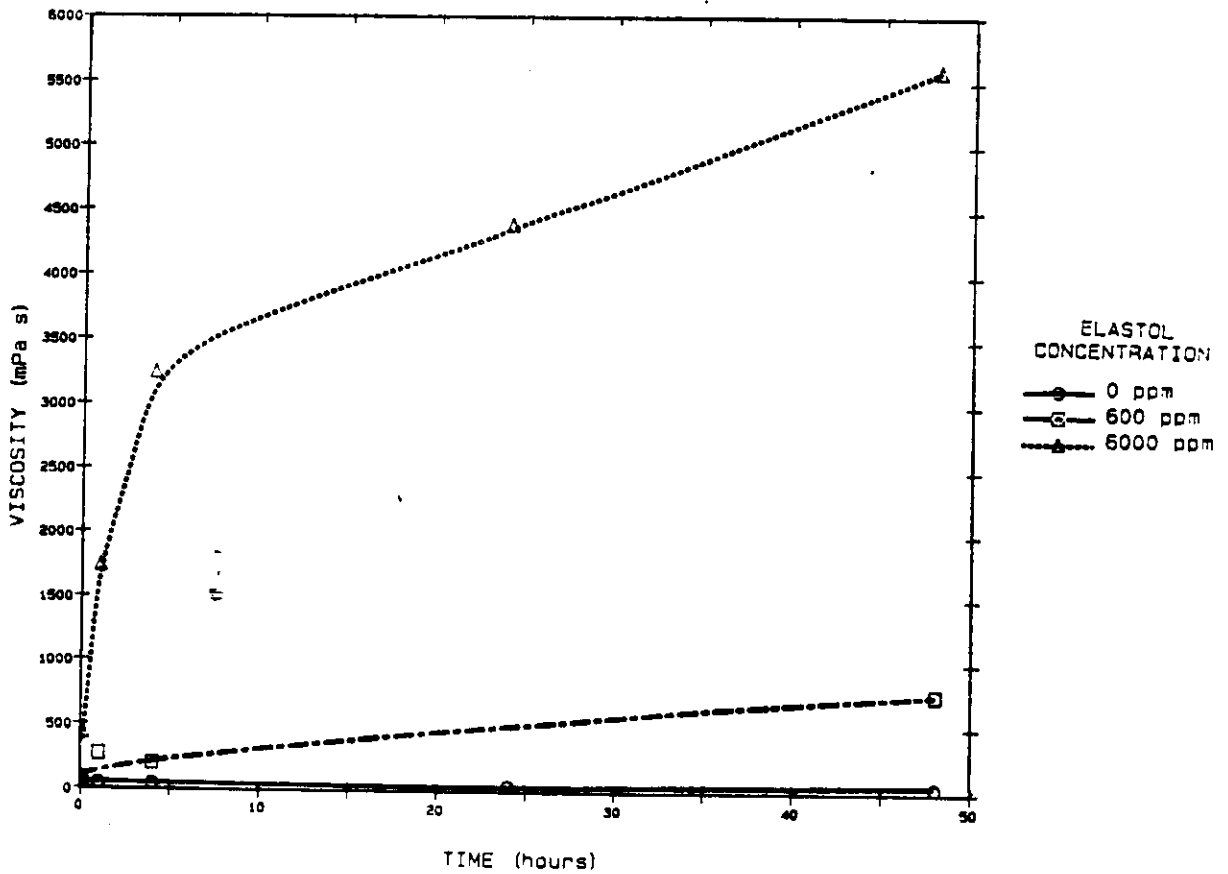
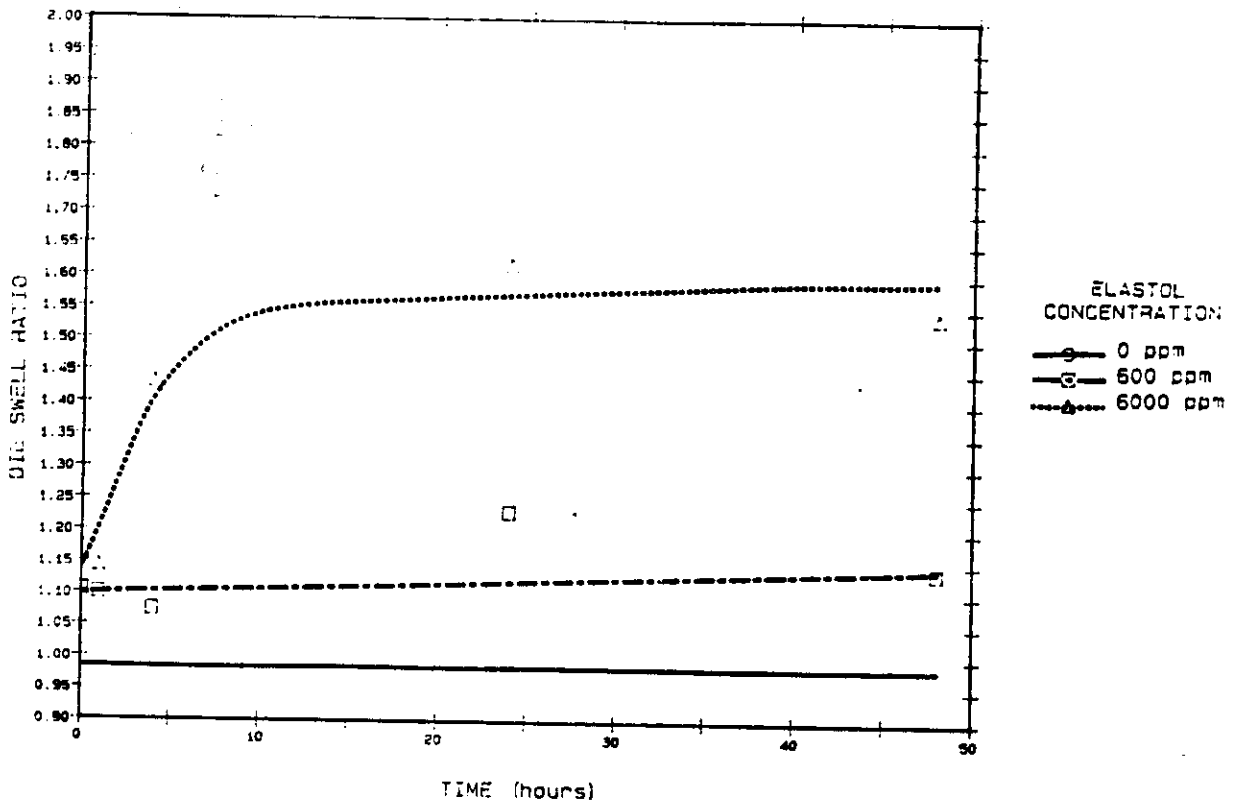


Figure 2-11. Die swell ratio and viscosity versus time for ASMB at 0 deg. C.

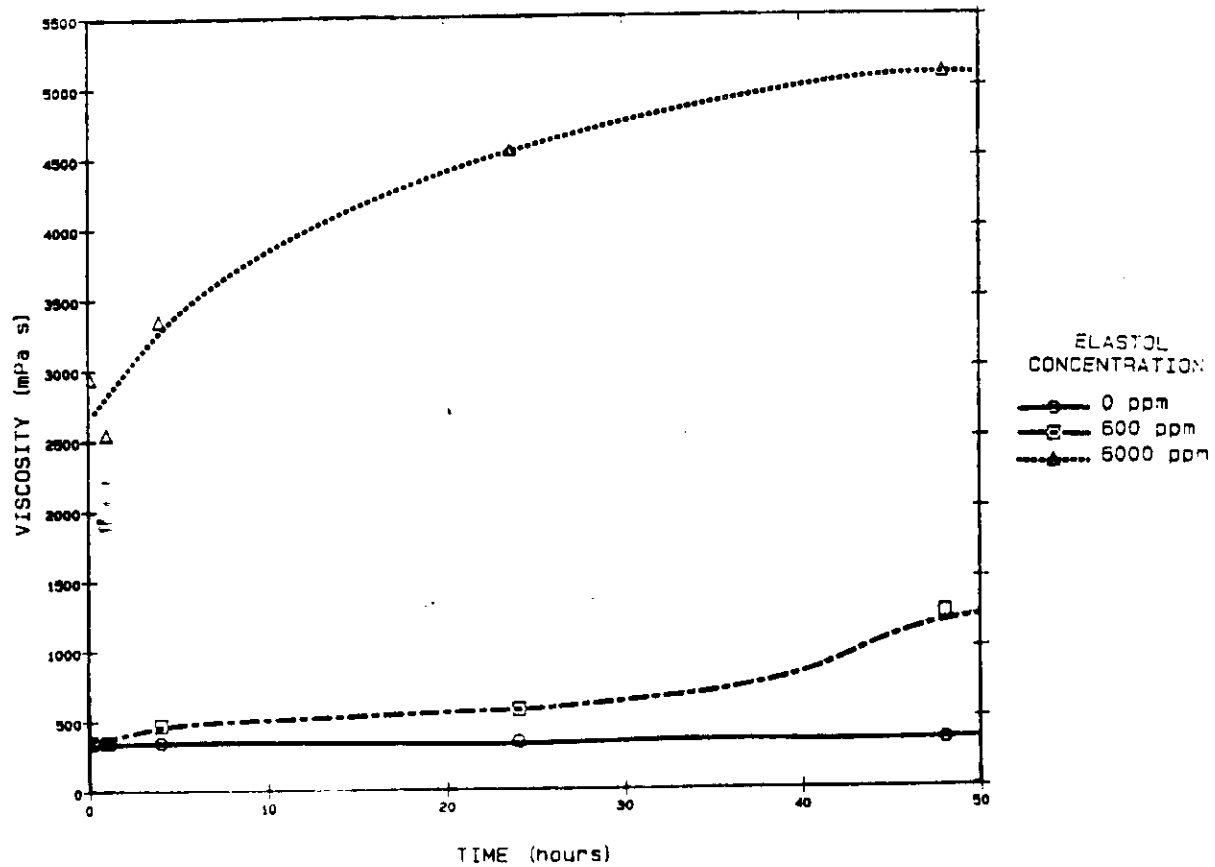
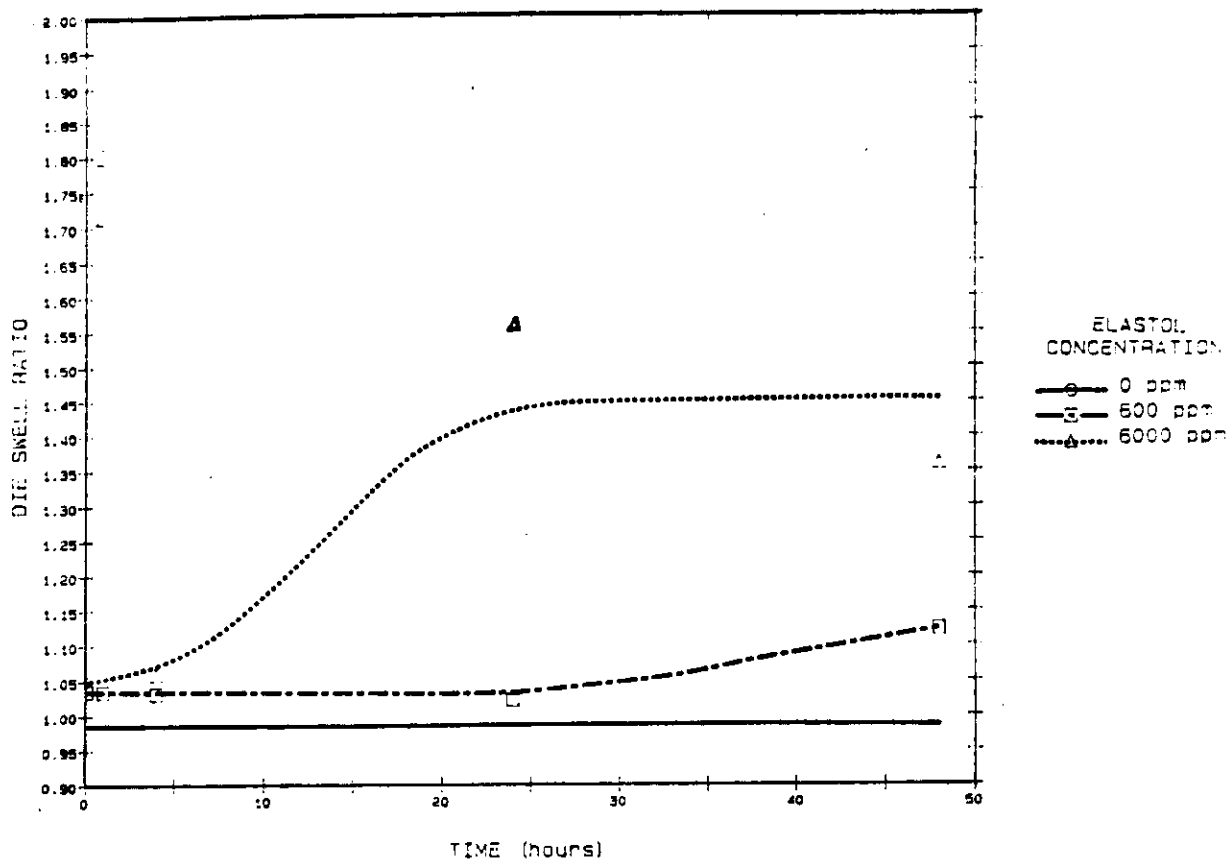


Figure 2-12. Die swell ratio and viscosity versus time for Emulsifying Mix at 0 deg. C.

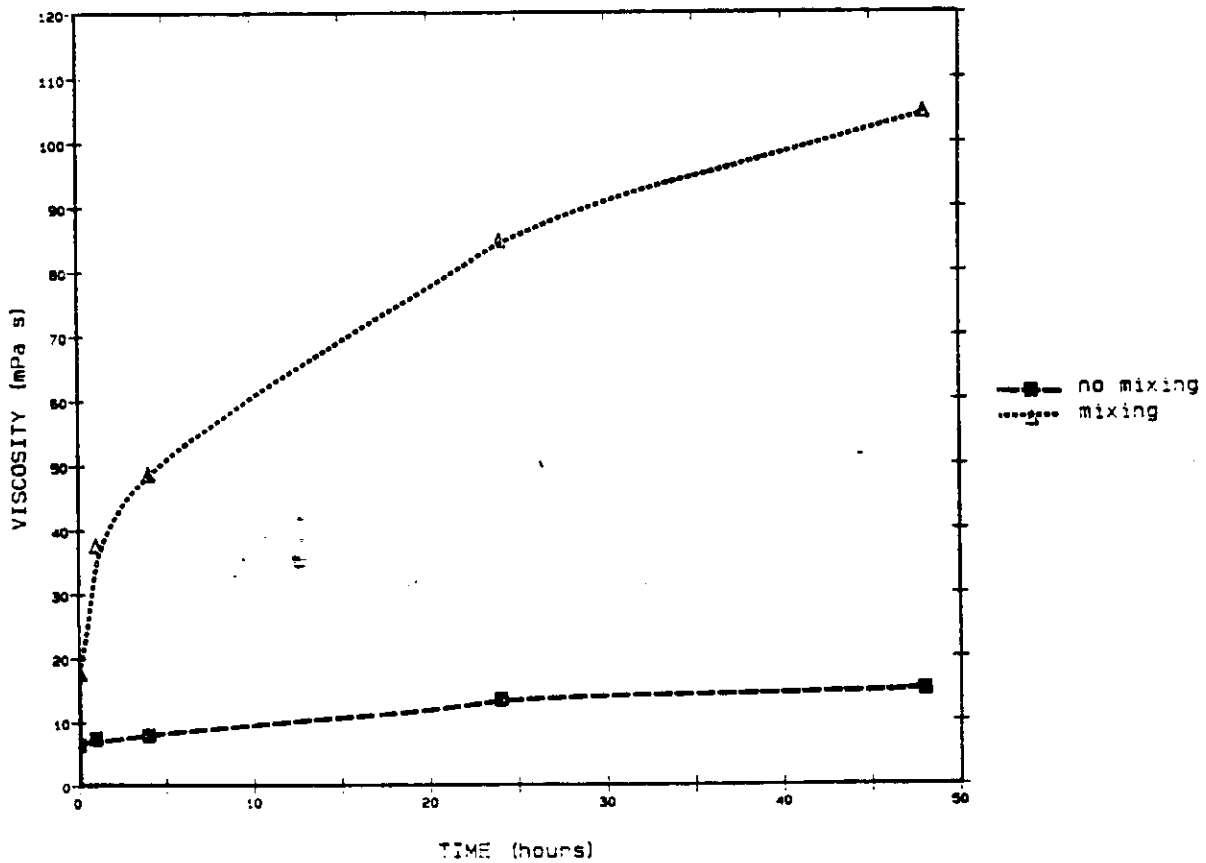
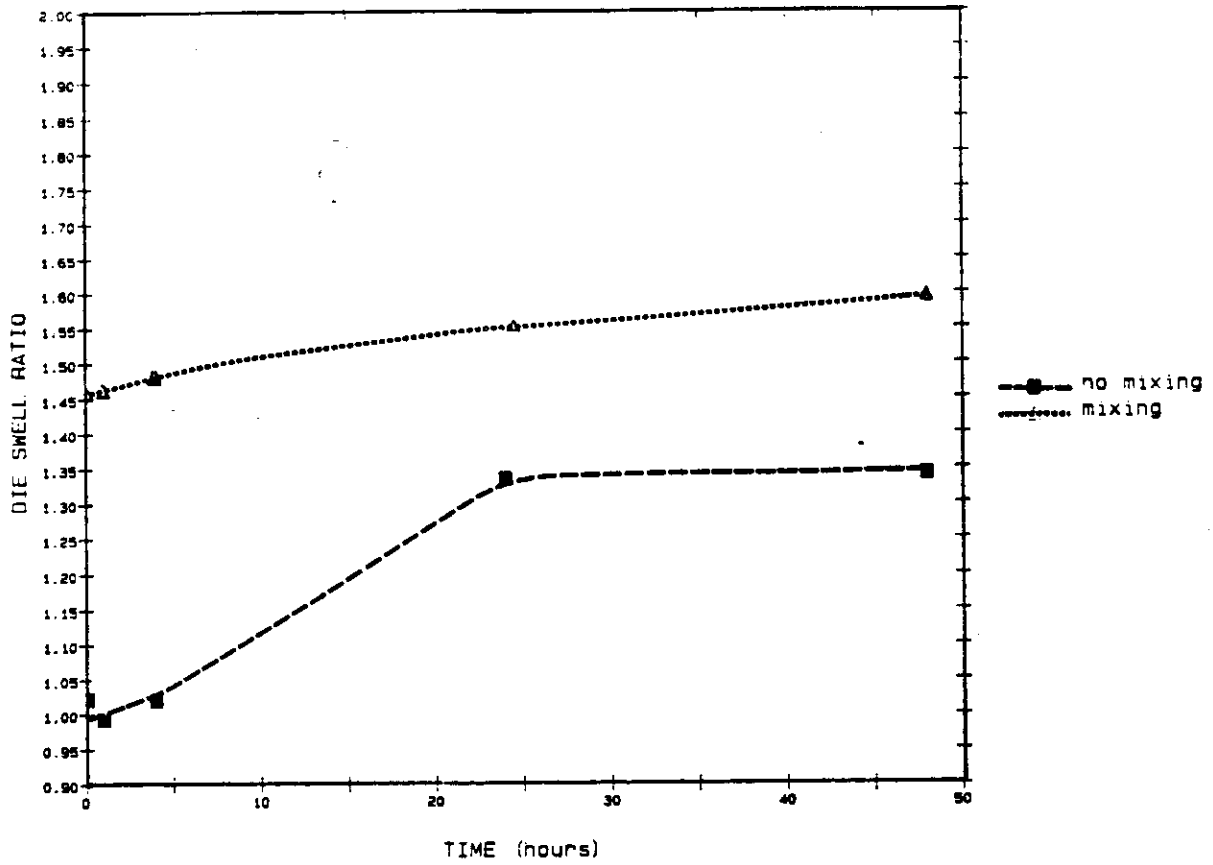


Figure 2-13. Effect of mixing on the viscoelastic properties of ASMB with 6000 ppm of Elastol at 15 deg. C.

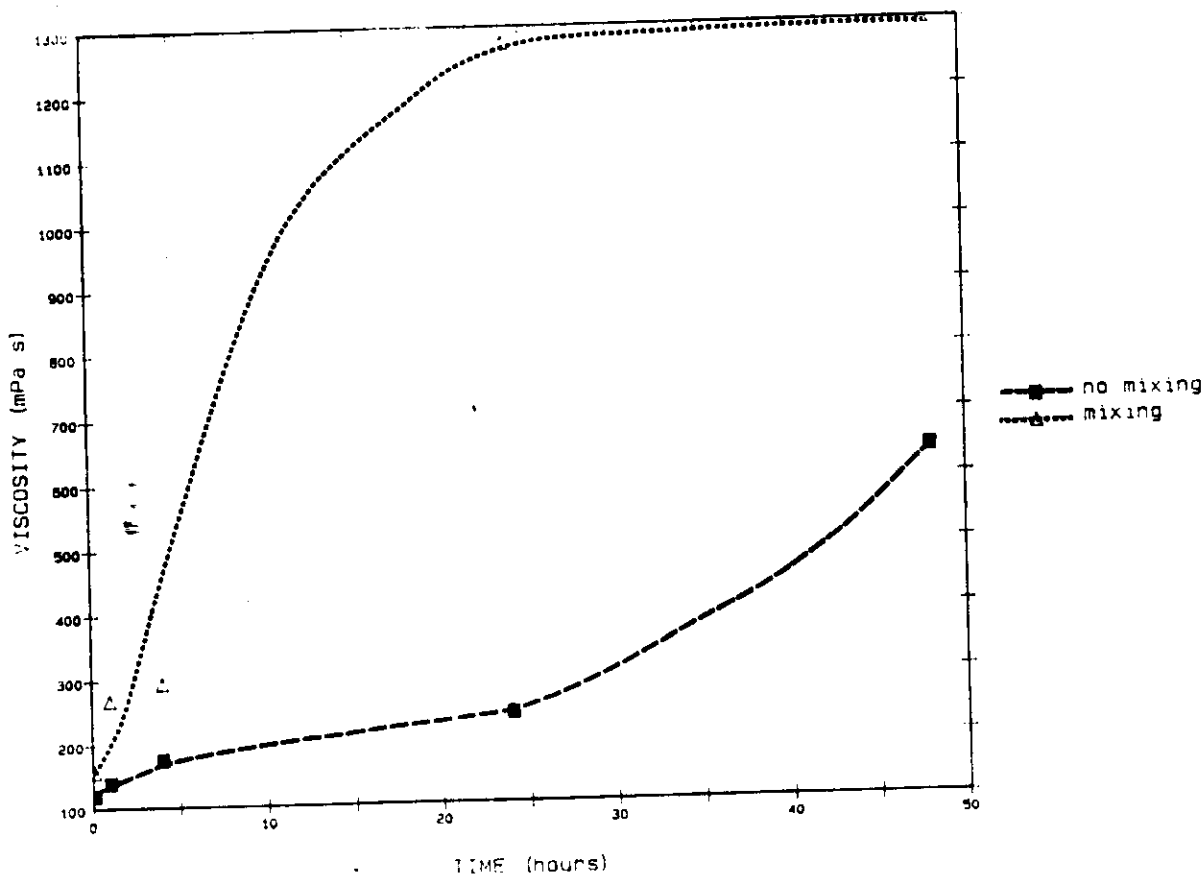
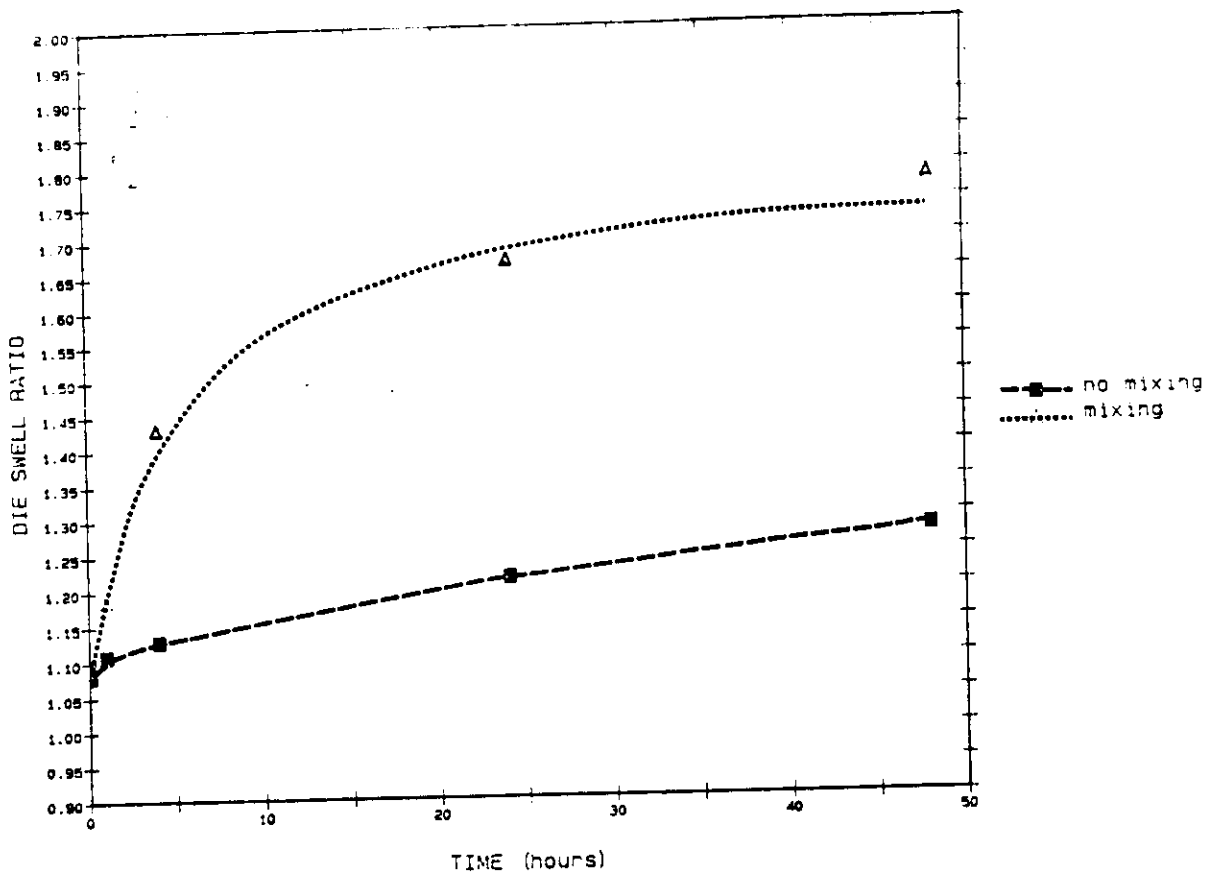


Figure 2-14. Effect of mixing on the viscoelastic properties of Emulsifying Mix with 6000 ppm of Elastol at 15 deg. C.

Table 2.1: Degree of Elasticity of Test Oils

Temperature: 15 deg C

DEGREE OF ELASTICITY	ELASTOL CONCENTRATION	
	6000 PPM	600 PPM
HIGH	Emulsifying Mix Norman Wells Prudhoe Bay	----
MODERATE	ASMB ASMB (no mixing) Amauligak Bent Horn Emulsifying Mix (no mixing) Hybernia Tarsiut	ASMB Emulsifying Mix Hybernia Norman Wells Prudhoe Bay
LOW	Diesel	Bent Horn Diesel Tarsiut

Temperature: 0 deg C

HIGH	----	----
MODERATE	ASMB Emulsifying Mix	----
LOW	----	ASMB Emulsifying Mix

All samples subjected to mixing at 80 RPM unless otherwise stated.

Table 2.2: Elastol Reaction Time for Test Oils

Temperature: 15 deg C

REACTION TIME	ELASTOL CONCENTRATION	
	6000 PPM	600 PPM
FAST	ASMB Bent Horn Diesel Tarsiut	Bent Horn
MODERATE	ASMB (no mixing) Amauligak Emulsifying Mix Hybernia Norman Wells Prudhoe Bay	Diesel Prudhoe Bay
SLOW	Emulsifying Mix (no mixing)	ASMB Emulsifying Mix Hybernia Norman Wells Tarsiut

Temperature: 0 deg C

FAST	----	----
MODERATE	ASMB	----
SLOW	Emulsifying Mix	ASMB Emulsifying Mix

All samples subjected to mixing at 80 RPM unless otherwise stated.

2.3 Effect of Elastol on Evaporation

This study examined the effect of Elastol on the oil evaporation rate.

2.3.1 Experimental

The evaporation experiments were performed in a laboratory fume-hood at room temperature (21 +/- 1 deg C). Pans measuring 22.2 x 22.2 cm were filled with oil to a depth of 5 mm. The test oils were treated with 6000 ppm of Elastol, which was evenly distributed over the oil surface. For each oil, a pan of untreated oil was aged at the same time and location to ensure that the two pans were subjected to the same weathering conditions. The induced air velocity above the oil surface was measured at 0.7 m/s. The oils were either left to stand undisturbed (no mixing) during the aging interval or were continually stirred by magnetic stirrers set at 285 RPM.

The oils tested in this study were: ASMB, Amauligak, Bent Horn and diesel. Evaporative losses were measured gravimetrically.

2.3.2 Results and Discussion

Graphs of evaporative loss versus time are presented in Figures 2.15 to 2.18. Both Elastol-treated and untreated oils were found to follow the same basic weathering trends. It can also be seen that during the initial stages, treated oils have a slightly lower rate of evaporation than the untreated oils. As Figure 2.15 shows, this reduced rate of evaporation is more significant when the oil is subjected to mixing. However, over extended time intervals, no noticeable difference in the overall evaporation was observed.

2.3.3 Conclusions

The addition of Elastol did not significantly affect the evaporation rate.

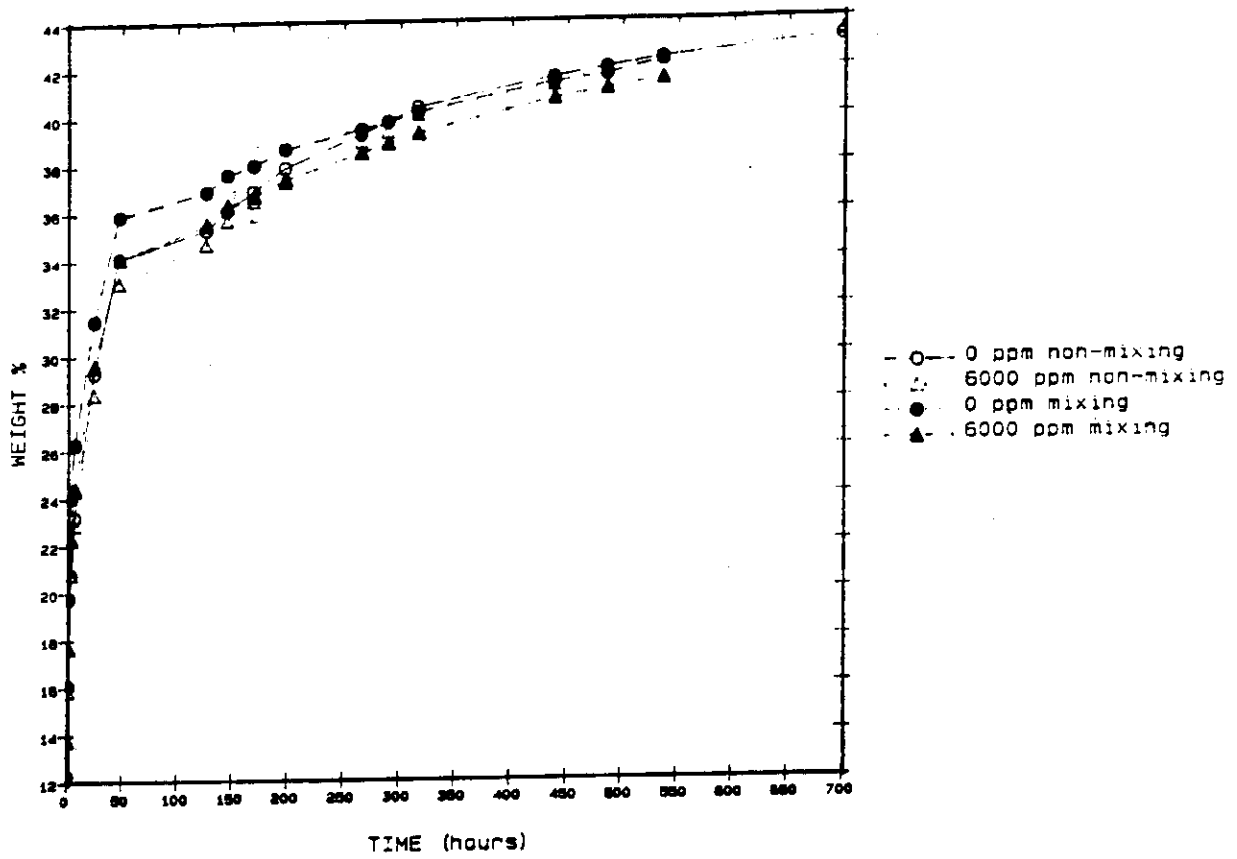


Figure 2-15. Effect of mixing energy on evaporative losses versus time for ASMB at 15 deg. C.

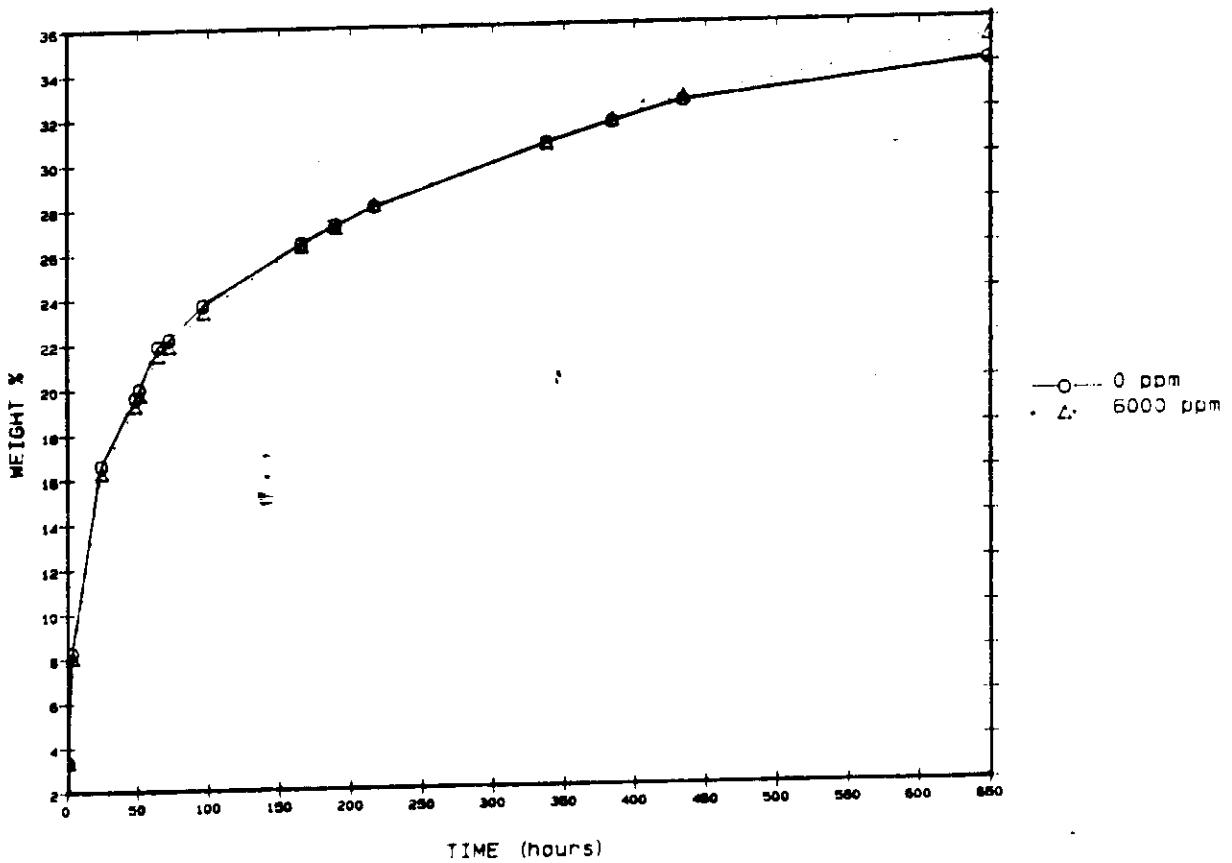


Figure 2-16. Evaporative losses versus time for Amauligak at 15 deg. C.

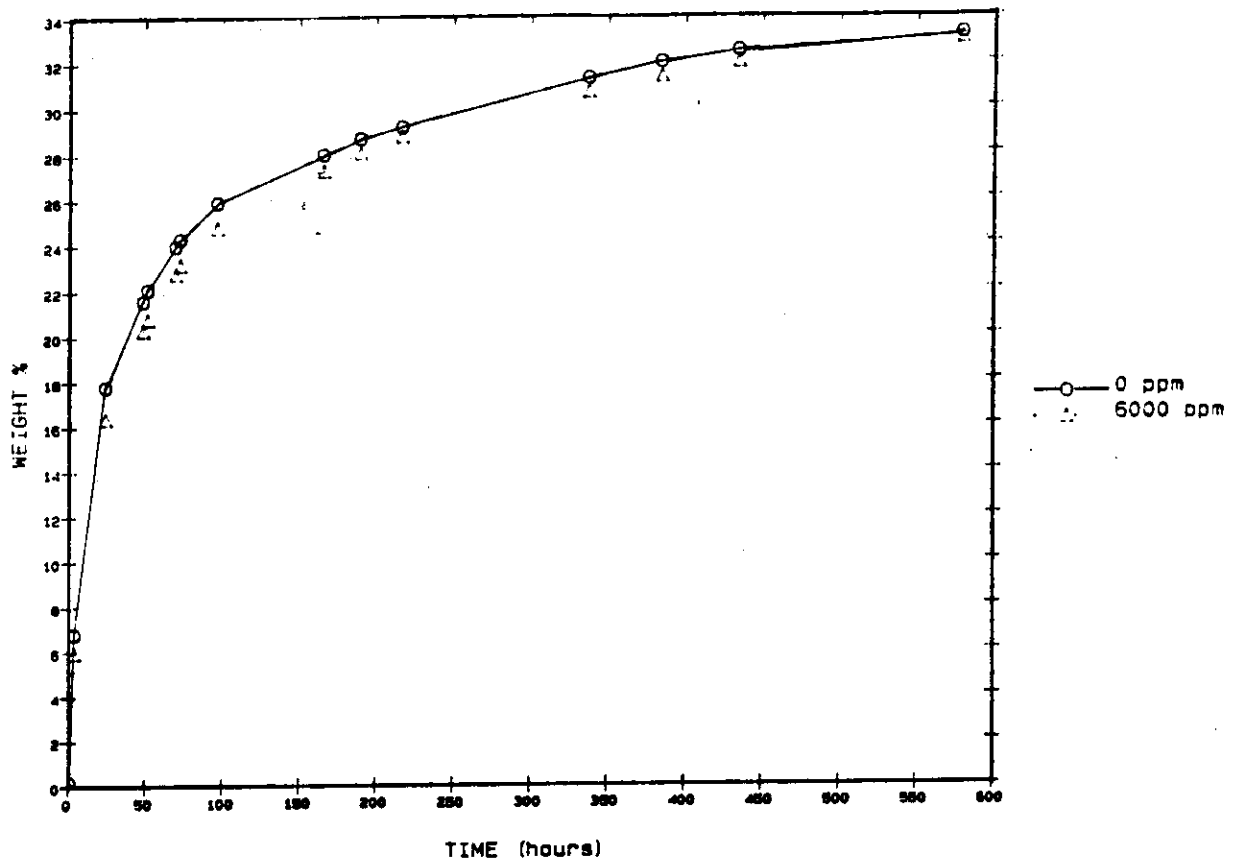


Figure 2-17. Evaporative losses versus time for Bent Horn

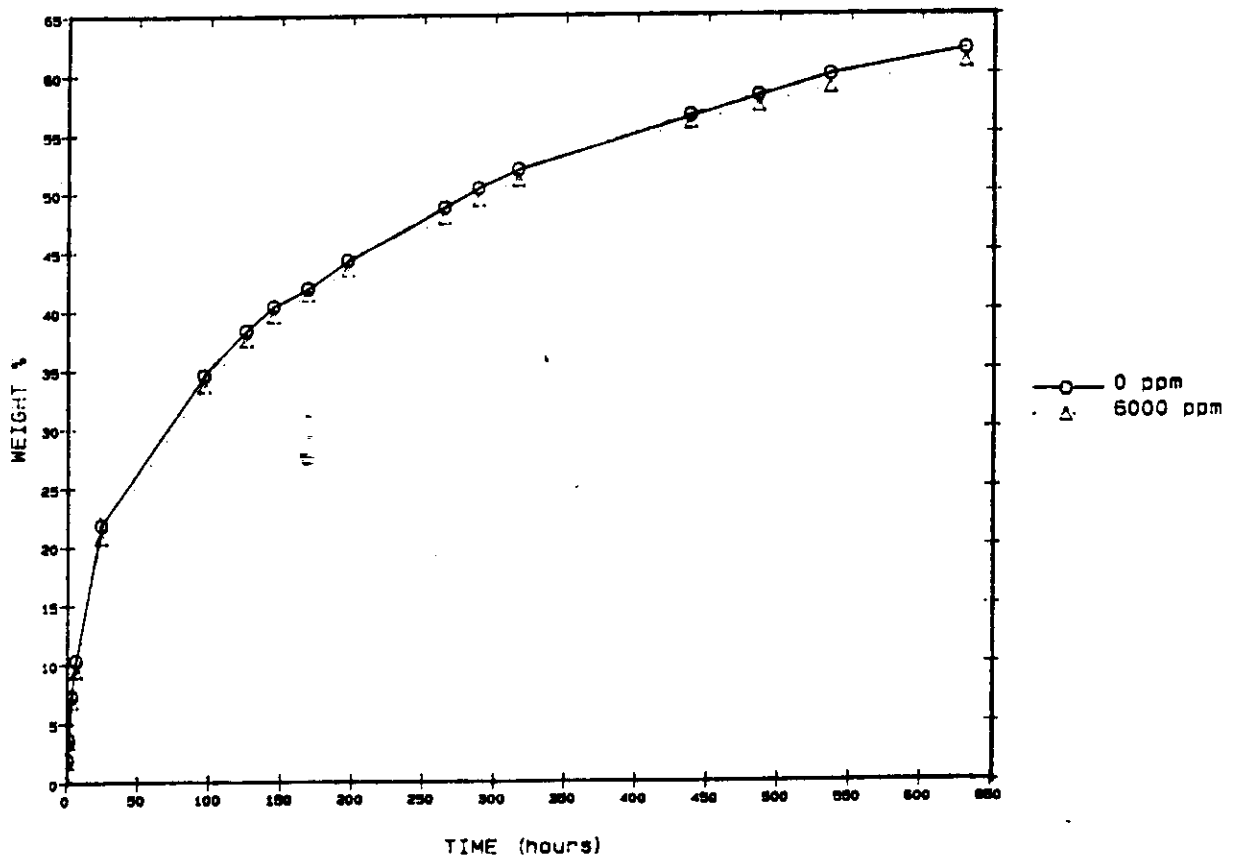


Figure 2-18. Evaporative losses versus time for Diesel.

2.4 Effect of Elastol on Flash Point

Measurements were made to determine the effect of Elastol on the flash point of various oils. Flash point is the lowest temperature at which vapours above a sample ignite when exposed to a flame.

2.4.1 Experimental

Petroleum samples at 15 deg C were treated with Elastol at concentrations of 600 and 6000 ppm and were allowed to mix for 48 hours, as outlined in Section 2.2. Flash points were determined using the ASTM D 93 test procedure for the Pensky-Martens closed tester.

Three samples were tested: regular unleaded gasoline (flash point -43 deg C); Alberta Sweet Mixed Blend crude oil (7 deg C); automotive diesel (52 deg C).

2.4.2 Results

Flash point measurements showed that Elastol had no effect on this property.

2.5 Effect of Elastol on Slick Thickness

A set of small-scale experiments was performed to determine Elastol's ability (if any) to increase oil slick thickness. The procedure involved applying a specified amount of Elastol to a terminal unconfined oil slick and observing the change in the slick area before and after the addition of Elastol.

2.5.1 Experimental

The experiments were conducted at 15 deg C in a 45 x 32 cm container filled with 33 ppt salt water. Two oils, Hybernia and ASMB were used in the study. Initially, 1 to 1.5 mL of the oil was applied on the water to produce a light sheen. This was followed by the addition of 1/2 mL of oil, which spread and formed a distinct slick surrounded by the sheen. The initial slick thickness ranged from 0.02 to 0.04 mm. This slick was allowed to spread to completion before Elastol, in concentrations ranging from 6000 ppm to 10%, was added.

The area of the Elastol-treated oil slick was compared to the area prior to the Elastol addition to determine the change in slick thickness.

2.5.2 Results and Discussion

The results for the area contraction experiments for the two oils studied are tabulated in Table 2.3. The results indicate that there was little or no decrease in spill area at the concentrations studied for ASMB and at the two lower concentrations for Hybernia. The only significant shrinkage occurred for the Hybernia slick at concentrations of 6 and 10%.

Table 2.3 lists the Elastol concentration based on both volume (ppm) and area (mg/cm^2). For both oils, it was found that the concentration of Elastol must exceed $0.02 \text{ mg}/\text{cm}^2$ of slick area to achieve measurable spill contraction. It should be noted that these results only apply to very thin slicks. Further study in this area was not conducted since attempts to produce thicker unconfined spills in the laboratory were unsuccessful.

Table 2.3: Spill Contraction Results

HYBERNIA

Elastol Concentration (mg/cm ²)*		Area Contraction (%)
-----		-----
6000 ppm	0.01	0
1%	0.02	0
6%	0.15	51
10%	0.19	61

ALBERTA SWEET MIXED BLEND CRUDE

Elastol Concentration (mg/cm ²)*		Area Contraction (%)
-----		-----
6000 ppm	0.02	0
1%	0.03	12
6%	0.24	13
10%	0.38	18

* based on the spill area before Elastol application.

2.5.3 Conclusions

Significant increase in slick thickness was observed only by the addition of very large doses of Elastol. The threshold Elastol concentration was found to be 6% (0.15 mg/cm²) for Hybernia and 1% (0.03 mg/cm²) for ASMB.

2.6 Effect of Elastol on Spreading of Oil Slicks

This study was performed to determine Elastol's effectiveness in retarding the spreading of oil slicks. The effect of two variables on this property, concentration and reaction time were studied.

2.6.1 Experimental

The approach taken was to confine the oil and a specified amount of Elastol in a tube, which was positioned in the centre of a salt-water-filled 0.91 m diameter shallow pan. The top of the tube was sealed to prevent evaporation and the Elastol was allowed to dissolve in the oil. After a defined time interval, the tube was lifted, thus allowing the oil to spread out on the water. The final spill areas for each experiment were then recorded. It was the extent of this spreading that was used as the criteria for the effectiveness of Elastol to retard the spread of an oil slick.

The oils used were ASMB and Emulsifying Mix. An oil volume of 4.4 mL which produced a 2 mm "slick" in the tube, was used in all experiments. To determine the effect of different concentrations, Elastol was added at doses of 0, 600, 6000 ppm and 6%, and left to react for 30 minutes for ASMB and 6.5 hours for the 50-50 mixture. With the reaction time as the variable, 6000 ppm of Elastol was allowed to dissolve in the oil for 0.5, 2, 16.5, 24 and 48 hours for ASMB and 0.5, 4, 16.5, 24 and 65 hours for the 50-50 blend. In addition, a control experiment was performed for each reaction time for the two oils.

2.6.2 Results and Discussion

The results from these experiments were expressed as a ratio of the final spill area of the Elastol-treated oil slick to the area of the control slick. These ratios were plotted against concentration in Figure 2.19 and against reaction time, in Figure 2.20.

In the study in which Elastol concentration was varied, it is clear from Figure 2.19 that the greater the concentration, the smaller the extent of spreading. This is due to a greater increase in viscoelasticity of the oils treated at the higher concentrations.

In the reaction time study, it can be seen from Figure 2.20 that the effectiveness of Elastol at a given concentration increases with greater reaction time for both oils. However, the time required for Elastol to dissolve and "take effect" was found to be much shorter for ASMB than for the Emulsifying Mix.

2.6.3 Conclusions

Elastol was effective in reducing the extent of spreading of oil slicks. This effectiveness increased at greater doses of Elastol and reaction times.

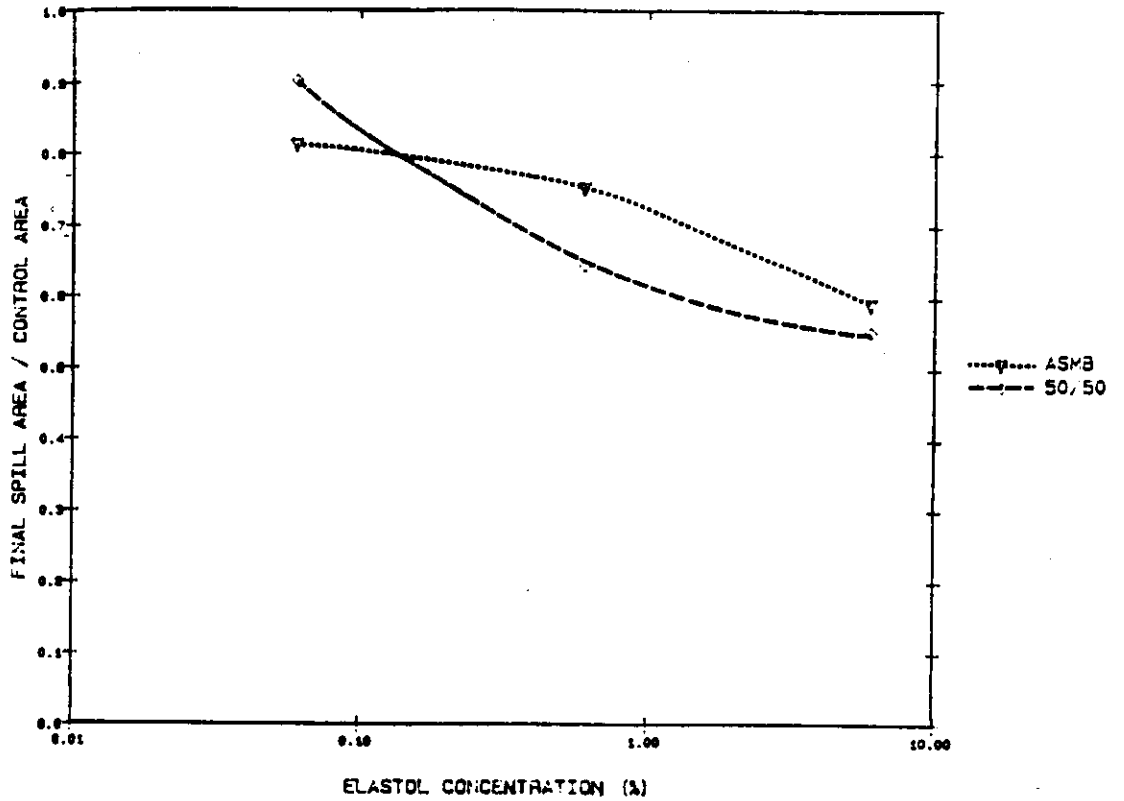


Figure 2-19. The extent of spreading versus concentration of Elastol for ASMB and the Emulsifying Mix at 15 deg. C.

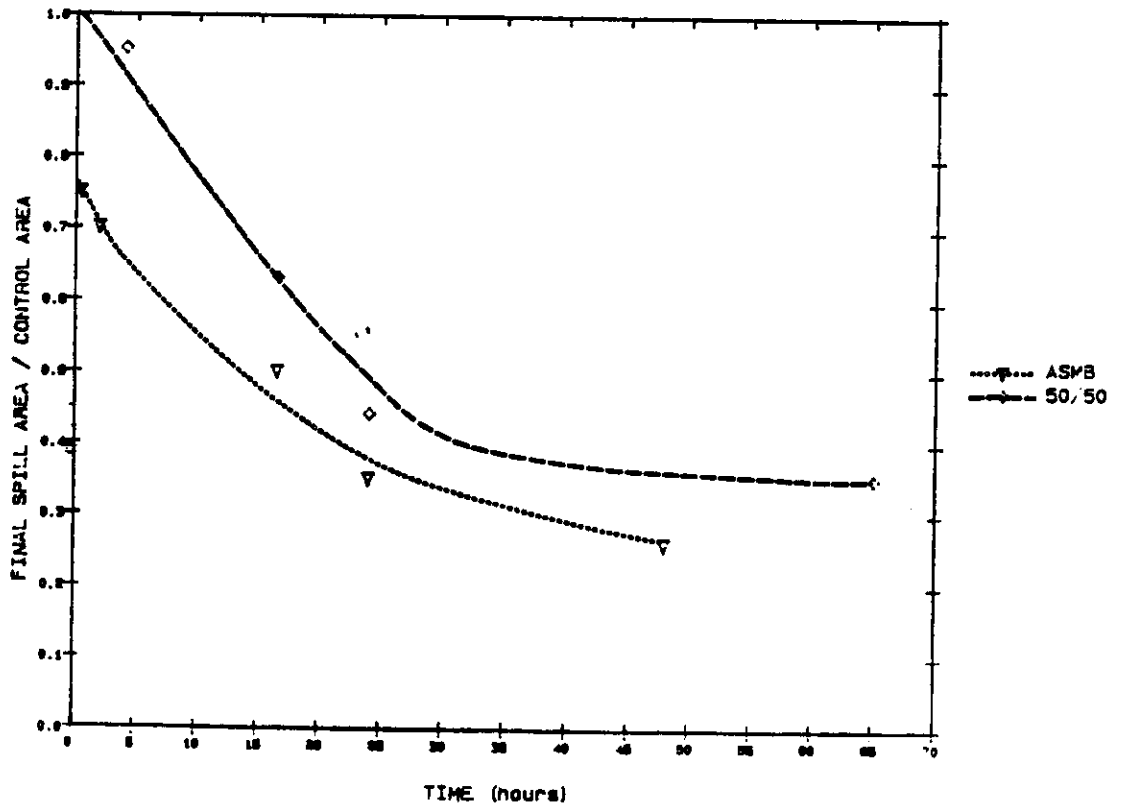


Figure 2-20. The extent of spreading versus reaction time for ASMB and the Emulsifying Mix with 6000 ppm of Elastol at 15 deg. C.

2.7 Emulsion-Formation Tendency and Stability

The purpose of this phase of the study was to examine the emulsification behaviour of Elastol-treated oils and petroleum products. Specifically, this involved investigating the effects of Elastol on the following emulsion properties: formation tendency, stability and water-in-oil content.

2.7.1 Experimental

The emulsion study was conducted in an apparatus which consists of a supported aluminum frame holding eight 500 mL fleakers. The frame is attached to a pulley and motor which rotates the frame in a tumbling motion at 65 RPM. The apparatus is shown in Plate 3.

The procedure used was a modification of that of Bobra and Chung (1986) and Mackay and Zagorski (1982). The experimental procedure is summarized below:

1. Keep oil, artificial seawater, Elastol and fleakers at the test temperature for at least 2 to 3 hours prior to testing.
2. Pour 300 mL of seawater into a fleaker; add 30 mL of well-mixed oil sample and distribute Elastol evenly on top of the oil surface.
3. Put stopper on fleaker and repeat step 2 for seven other fleakers.
4. Put fleakers in emulsion apparatus and allow to stand for one hour. Measure the total height (oil and water) and the height of oil.
5. Rotate fleakers for one hour and allow fleakers to stand in vertical position for half an hour. At this time, conduct the following measurements: height of oil, emulsion, and water, ie. the total height of contents; height of oil and emulsion; and height of oil.
6. Repeat step 5 three times.
7. Let fleakers stand for 24 hours and perform the measurements as outlined in step 5.

A variation of the above procedure was also performed in which the Elastol was added to oil already in emulsified form. The following oils were employed in this part: ASMB, Emulsifying Mix, and Prudhoe Bay.

The height measurements were converted to volume fractions. The volume

fraction of the initial amount of oil, f , in the emulsion at any time is given by:

$$f = \frac{\text{initial oil height} - \text{oil height}}{\text{initial oil height}}$$

The f values calculated at two different times, $f(\text{initial})$ and $f(\text{final})$ were used by Mackay and Zagorski (1982) to classify the emulsion formation tendency and stability of oils. $f(\text{initial})$ is obtained by plotting f (from values obtained at 1.5, 3.0, 4.5 and 6.0 hours) versus time and extrapolating the curve to time zero. $f(\text{final})$ is indicated by the fraction of oil in the emulsion after allowing the emulsion to settle for 24 hours after last mixing. The following criteria were used by these authors to classify these two properties:

<u>$f(\text{initial})$</u>	<u>Emulsion Formation Tendency</u>
0.0 to 0.25	Not Likely
0.25 to 0.75	Fairly Likely
0.75 to 1.0	Very Likely

<u>$f(\text{final})$</u>	<u>Emulsion Stability</u>
0.0 to 0.25	Unstable
0.25 to 0.75	Fairly Stable
0.75 to 1.0	Very Stable

2.7.2 Results and Discussion

Figures 2.21 to 2.36 show plots of f (volume fraction of oil emulsified) versus time for untreated and Elastol-treated oils at 0 and 15 deg C. Tables 2.4 and 2.5 give values for $f(\text{initial})$, $f(\text{final})$ and water content of the stable emulsions for untreated oils and oils treated with 600 and 6000 ppm Elastol. A photograph of the ASMB emulsions are presented in Plate 3.

Employing Mackay and Zagorski's criteria, it is seen from the $f(\text{initial})$ values of untreated oils from Table 2.4 that five of the ten oils would be classified as not likely to form an emulsion. The emulsions formed by these oils, if any, would be unstable. Diesel and Bent Horn crude oil had no tendency to form emulsions ($f(\text{initial})$ of zero) and it was found that the

addition of Elastol had no effect on this property. On the other hand, Amauligak and Tarsiut crudes showed an increase in tendency to form an emulsion. The emulsion stability of Tarsiut increased, whereas the Amauligak emulsion decayed completely after 24 hours of settling. The addition of Elastol to Norman Wells crude lowered the emulsion formation tendency from slight to no tendency.

The other five oils tested at 15 deg C would all be classified as very likely to form an emulsion. Three of these oils, 15 % weathered ASMB, Emulsifying Mix and Hybernia crudes formed stable emulsions which did not decay with time. The addition of Elastol to these oils had no effect on their tendencies to emulsify but two of the oils, weathered ASMB and Hybernia, exhibited decreased emulsion stabilities. The Hybernia emulsion was completely unstable at an Elastol dose of 6000 ppm. ASMB crude formed a fairly stable emulsion and the addition of Elastol had no effect on the oil's tendency to emulsify and only slightly decreased the emulsion stability. Prudhoe Bay crude formed an emulsion which could be classified as fairly stable, and the addition of Elastol at 600 ppm resulted in the formation of a completely unstable emulsion, and at 6000 ppm, completely inhibited any emulsion formation.

Figures 2.21 to 2.25 show that for all five of the oils which have a high emulsion formation tendency, the water content of the emulsions formed by the Elastol-treated oils was lower than those of untreated oils. This means that for a given quantity of oil, the volume of emulsion formed is less when treated with Elastol. For example, Elastol had no effect on the Emulsifying Mix's emulsion formation tendency or stability but the water content of the oil treated with 6000 ppm Elastol was 77%, as compared to 90% for the untreated oil. In this case, 1 litre of untreated oil would form 10 litres of stable emulsion while the treated oil would form only 4.3 litres of emulsion, a decrease of 57%.

At 0 deg C, four of the ten oils, Diesel, Bent Horn, Amauligak and Tarsiut would be classified as not likely to form an emulsion. Diesel and Bent Horn crude, whether treated or untreated, showed no emulsification tendencies. The addition of Elastol to Amauligak and Tarsiut crudes greatly

increased their tendencies to form emulsions and the emulsions formed were fairly stable.

The other six oils tested at 0 deg C would be classified as very likely to form an emulsion. With the exception of Norman Wells crude, the remaining five formed highly stable emulsions, irrespective of Elastol concentration. Of the six, only two (Norman Wells and Prudhoe Bay) of these oils' emulsion tendencies and stabilities were lowered by the addition of Elastol. The addition of Elastol at a concentration of 6000 ppm to Norman Wells crude lowered its emulsion formation tendency to unlikely, from very likely. Similarly, the addition of 6000 ppm of Elastol to Prudhoe Bay crude lowered its emulsion formation tendency to fairly likely.

Four oils, ASMB crude, Emulsifying Mix, Norman Wells and Prudhoe Bay crudes formed emulsions with lower water content at 0 deg C when treated with Elastol. These emulsions formed by Elastol-treated oils had 5 to 18% less water than those of untreated oils.

The results of the experiments in which Elastol was added to emulsified oil are presented in Figures 2.37 and 2.38. The application of Elastol to the Emulsifying Mix emulsion had no effect on the existing emulsion. The application of Elastol to the ASMB emulsion was effective in inhibiting the extent of emulsification (Figure 2.37). But the degree of emulsification was greater (f(final) value of 0.63) than in the experiment where Elastol was applied to the fresh oil prior to testing (f(final) of 0.34). As seen in Figure 2.38, the addition of Elastol to the Prudhoe Bay emulsion completely broke the emulsion and prevented any further emulsion formation.

2.7.3 Conclusions

Of the ten oils tested, two oils, Amauligak and Tarsiut crudes, exhibited increased tendencies to form emulsions when treated with Elastol. Among the other eight oils, two, Norman Wells and Prudhoe Bay crudes exhibited lower emulsification tendencies and lower emulsion stabilities when treated. The other oils showed no change in their emulsion formation tendencies and either no change or a decrease in their emulsion stabilities. In general, the emulsions formed by Elastol-treated oils were observed to have lower water

content than those of untreated oils.

The limited tests performed in which Elastol was applied to emulsified oil showed that the effectiveness of Elastol to reduce emulsion formation was still evident.

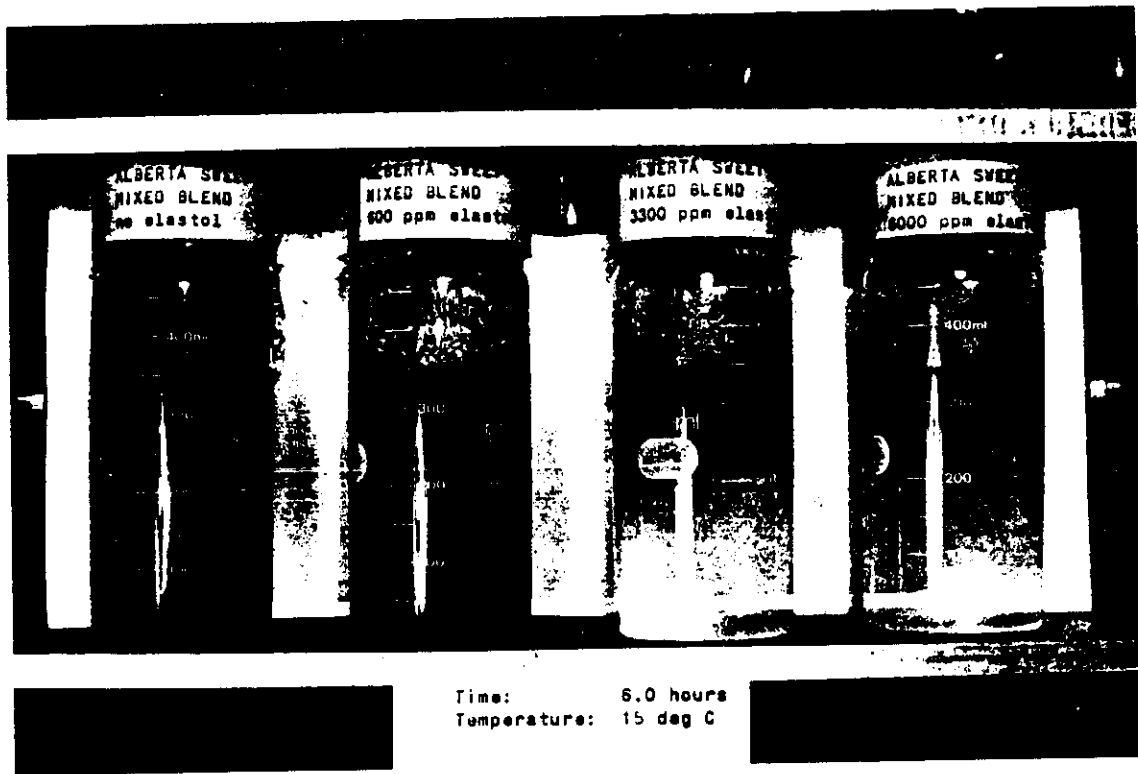


Plate 3: Alberta Sweet Mixed Blend Emulsions

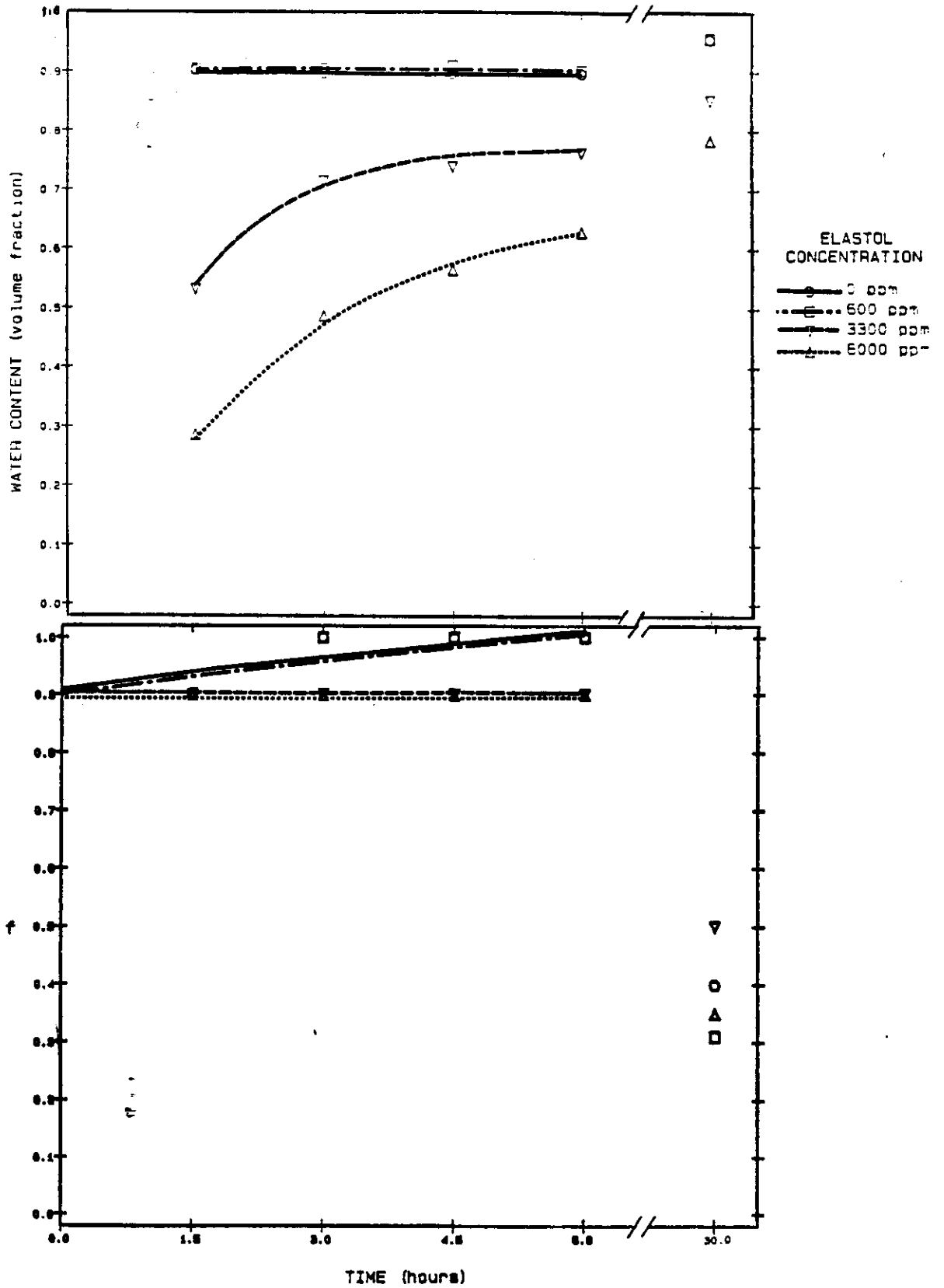


Figure 2-21. Plots of f and water content versus time for ASMB at 15 deg. C.

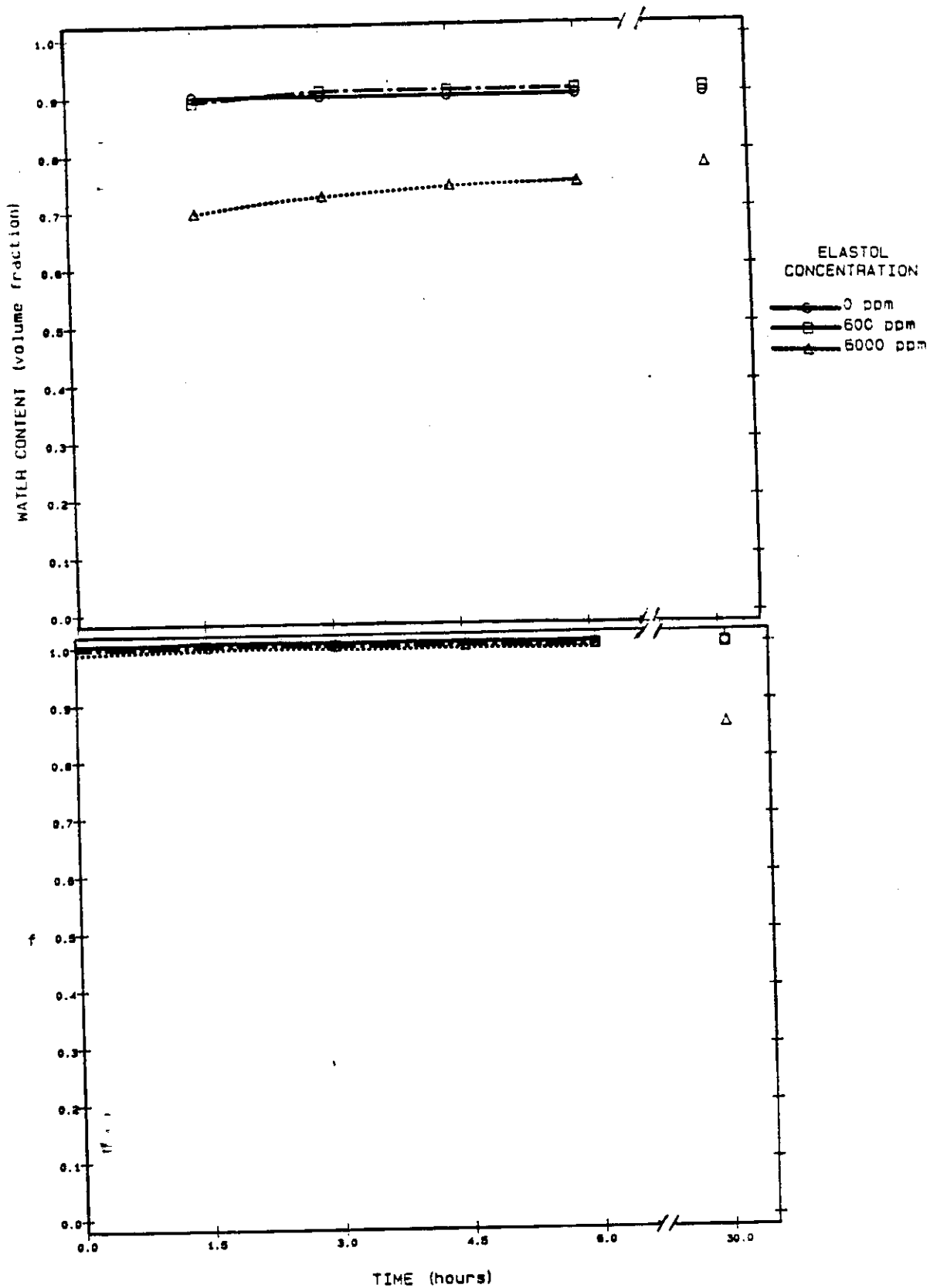


Figure 2-22. Plots of f and water content versus time for ASMB 15% weathered at 15 deg. C.

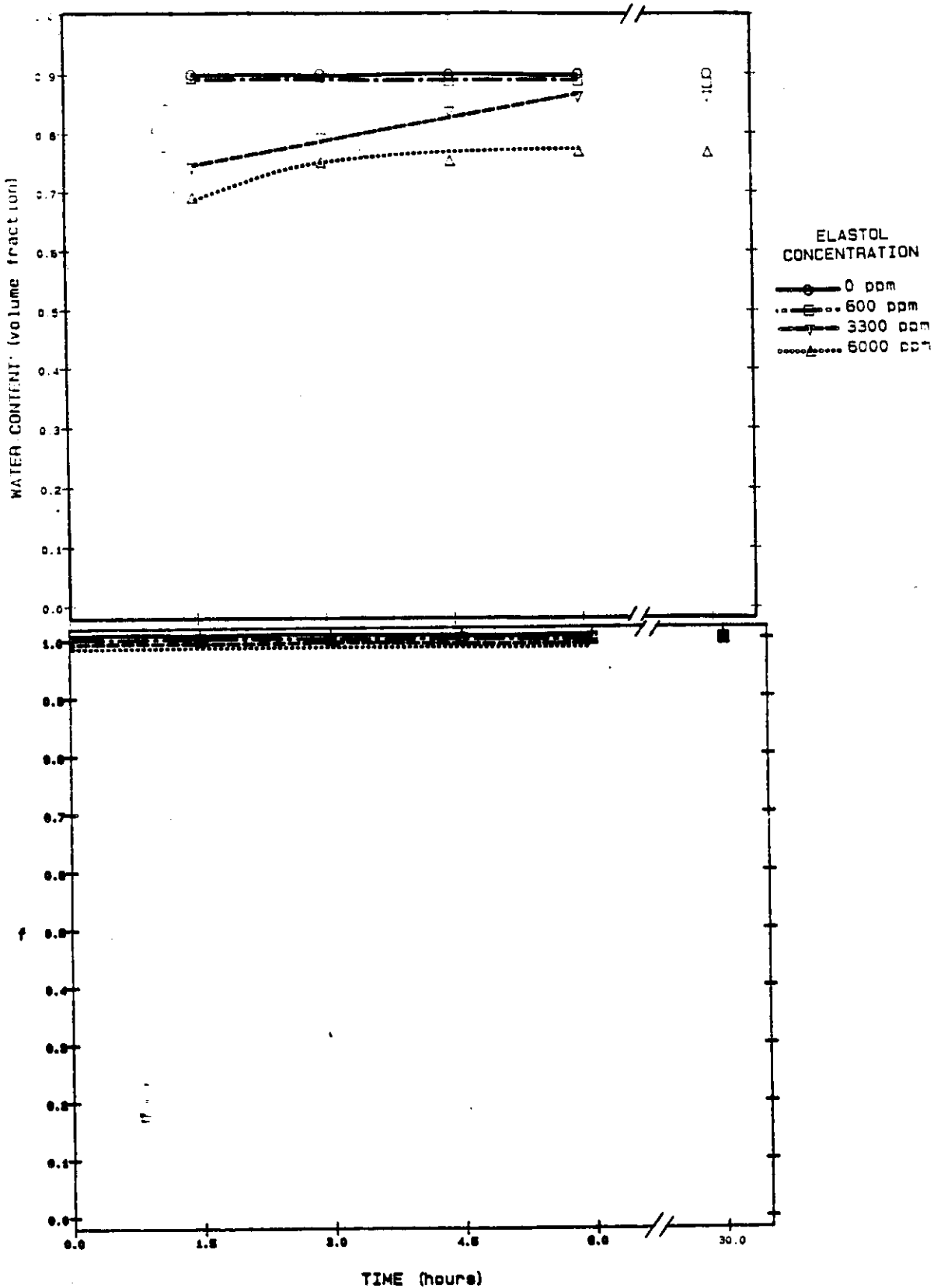


Figure 2-23. Plots of f and water content versus time for the Emulsifying Mix at 15 deg. C.

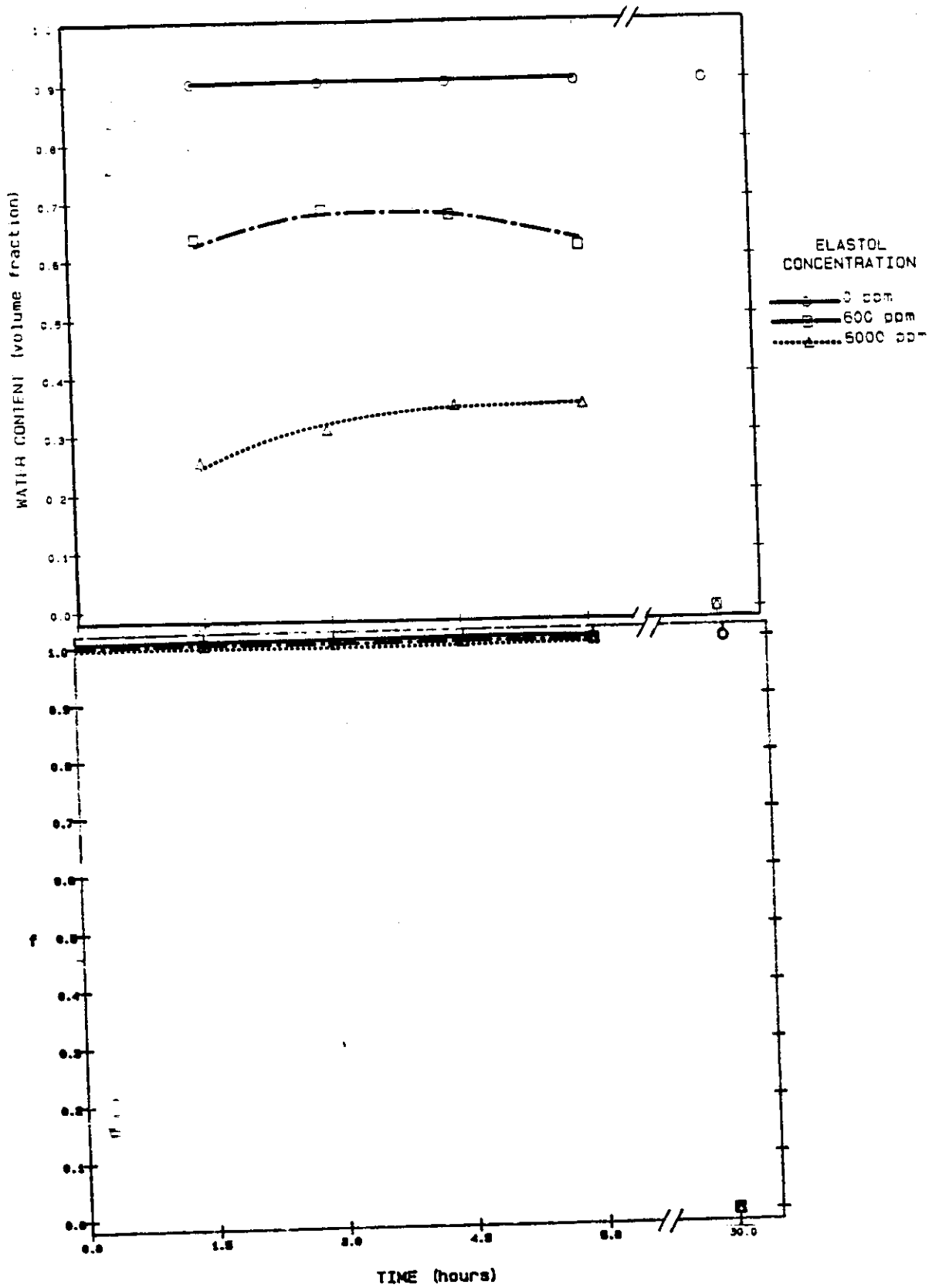


Figure 2-24. Plots of f and water content versus time for Hybernia at 15 deg. C.

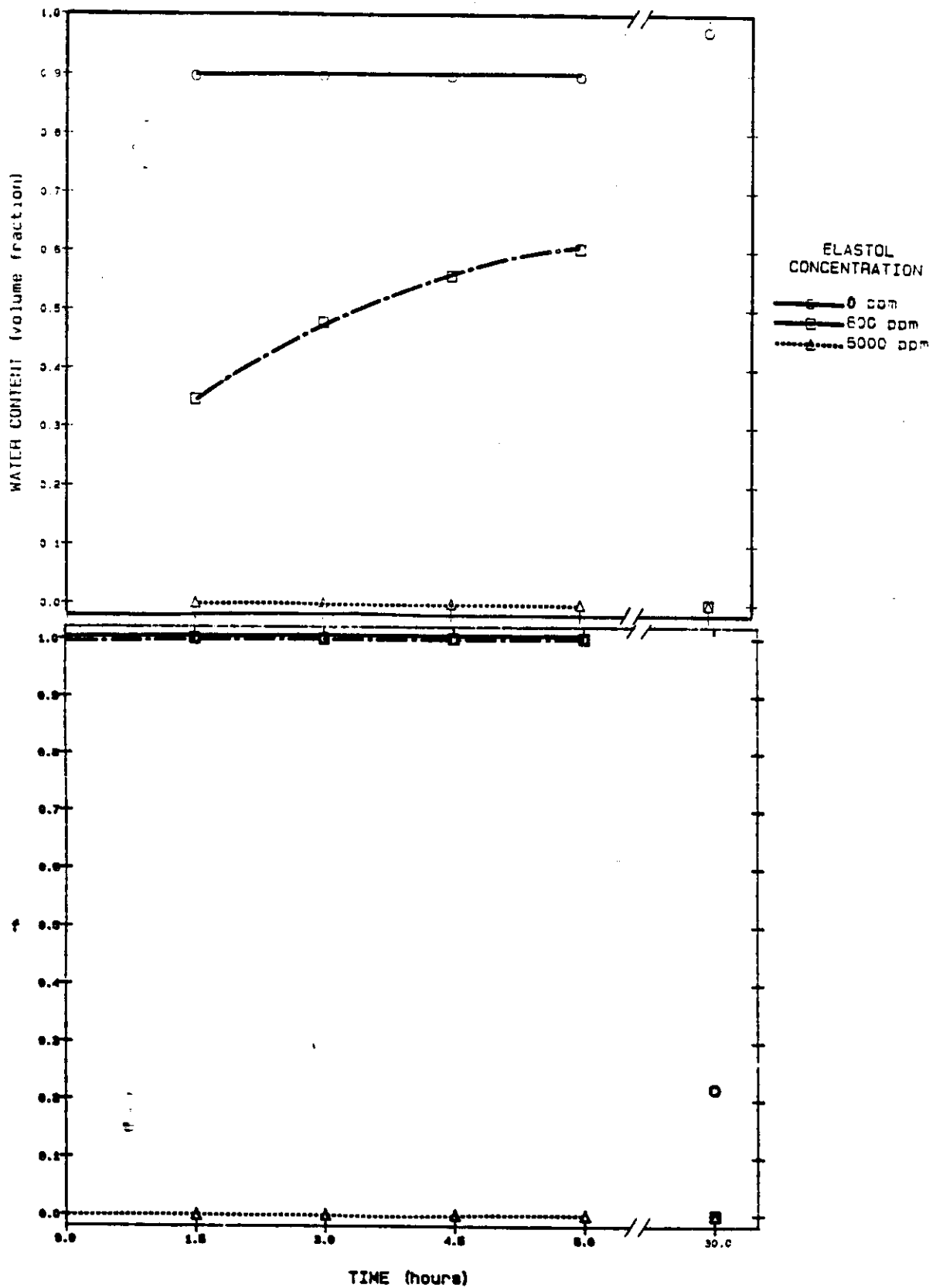


Figure 2-25. Plots of f and water content versus time for Prudhoe Bay at 15 deg. C.

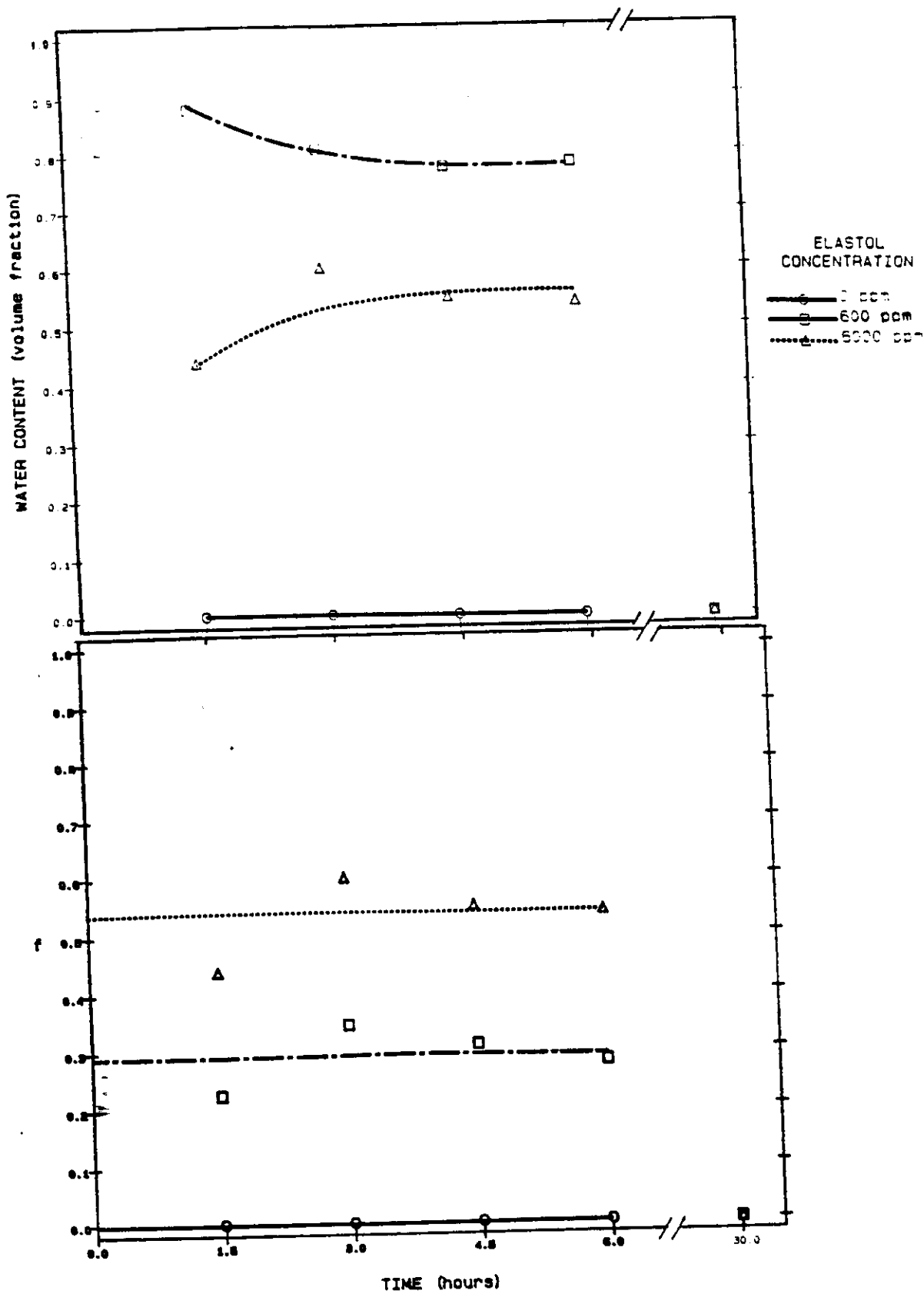


Figure 2-26. Plots of f and water content versus time for Amalgak at 15 deg. C.

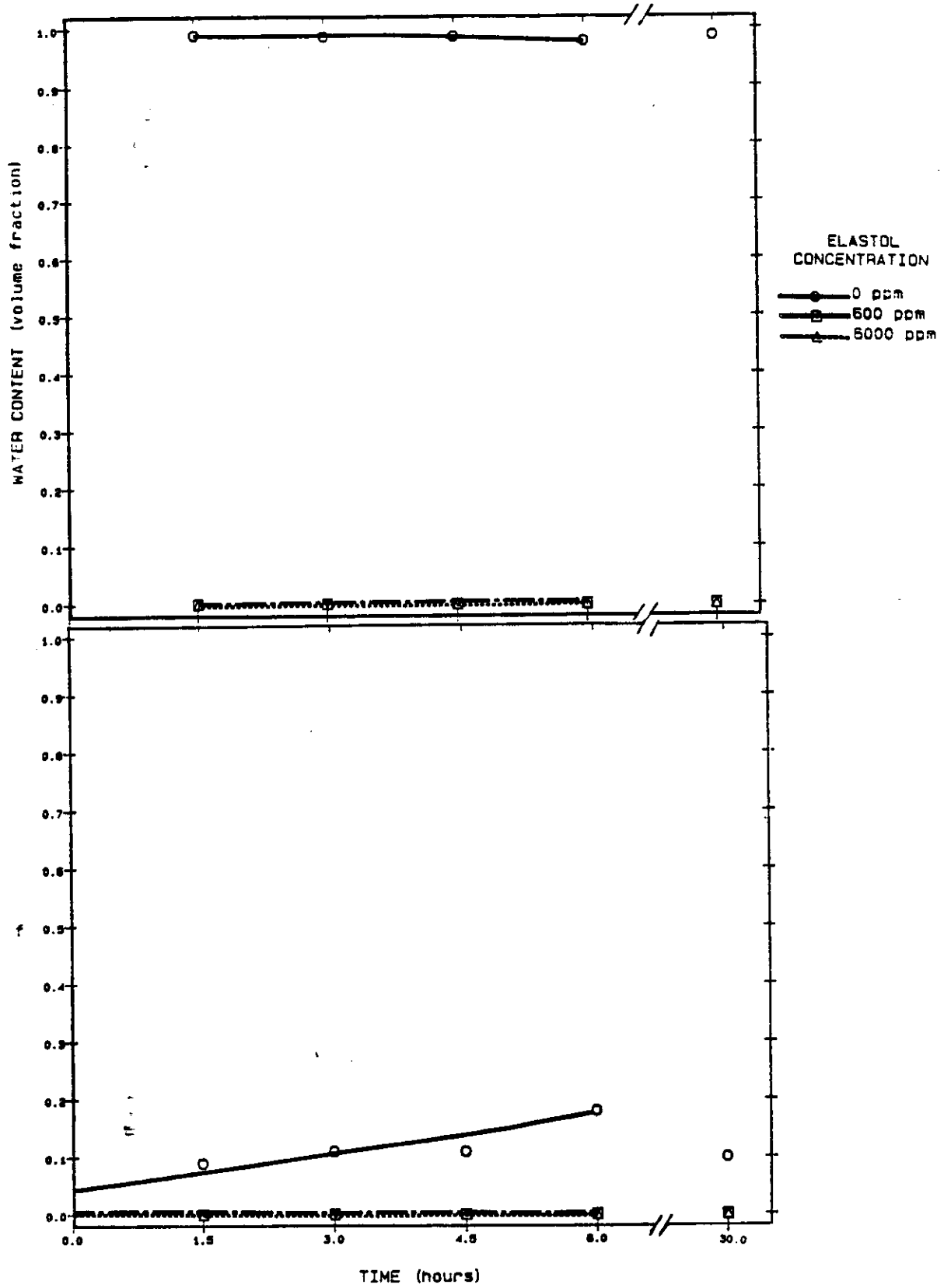


Figure 2-27. Plots of f and water content versus time for Norman Wells at 15 deg. C.

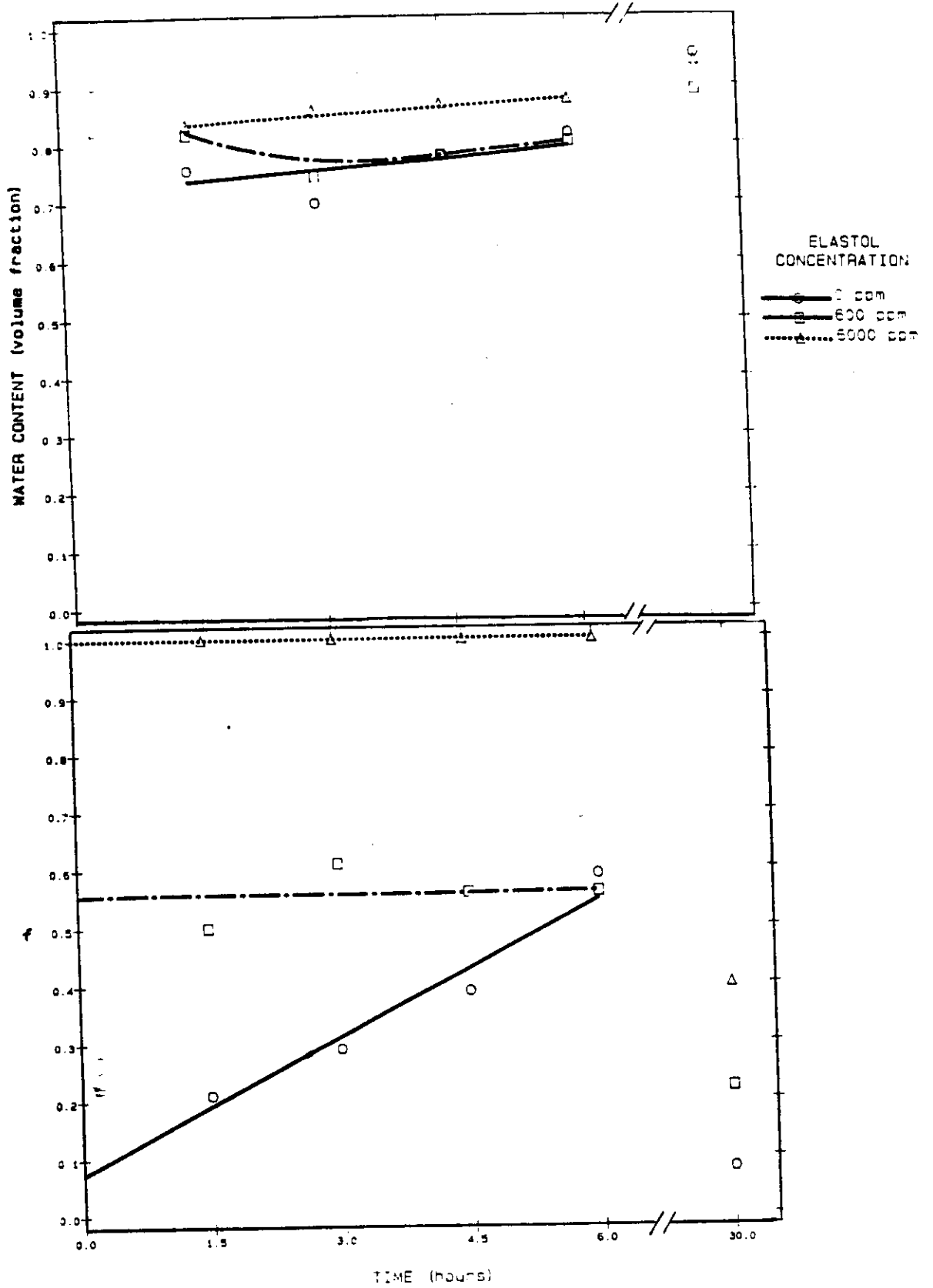


Figure 2-28. Plots of f and water content versus time for Tarsiut at 15 deg. C.

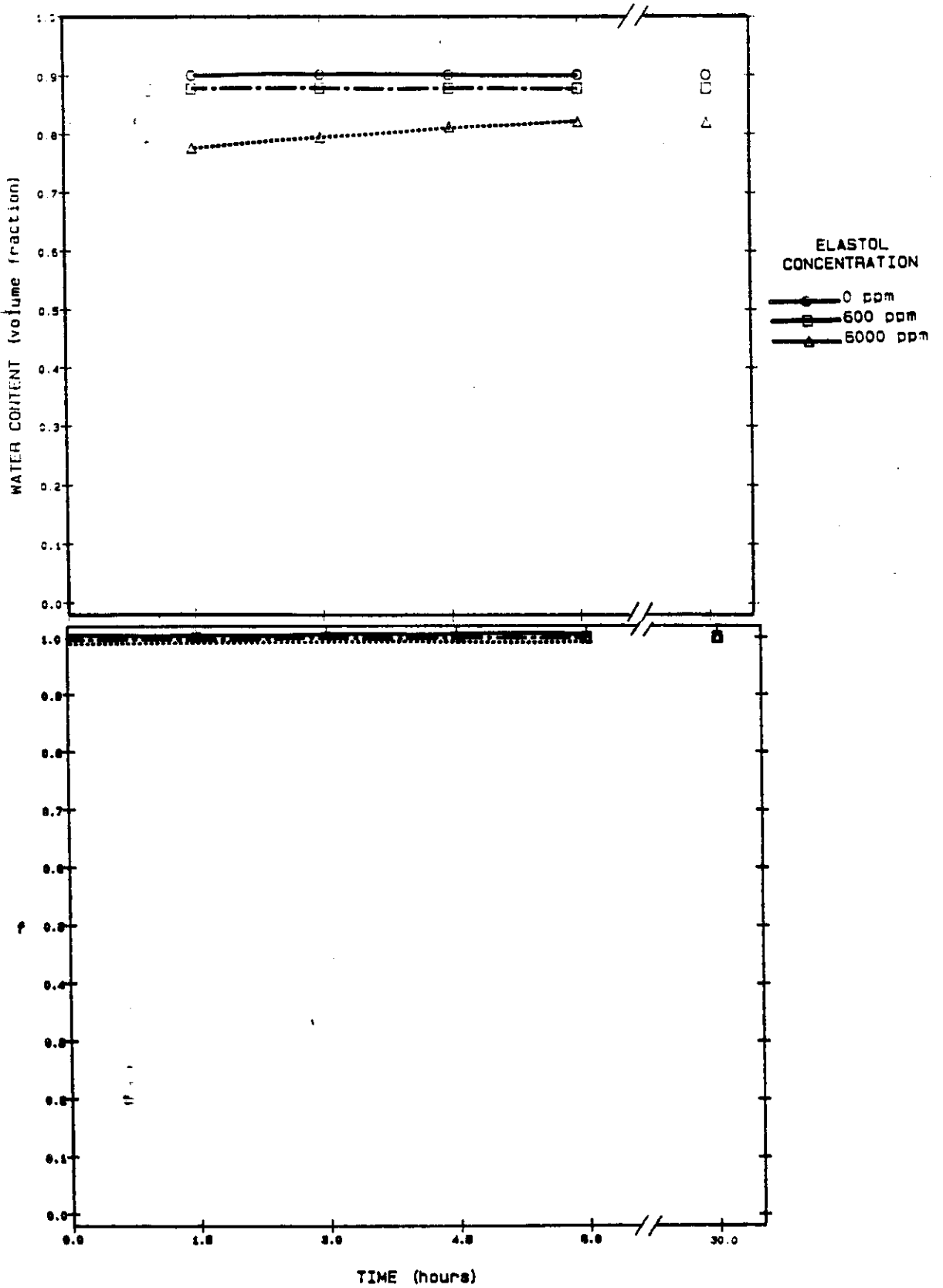


Figure 2-29. Plots of f and water content versus time for ASMB at 0 deg. C.

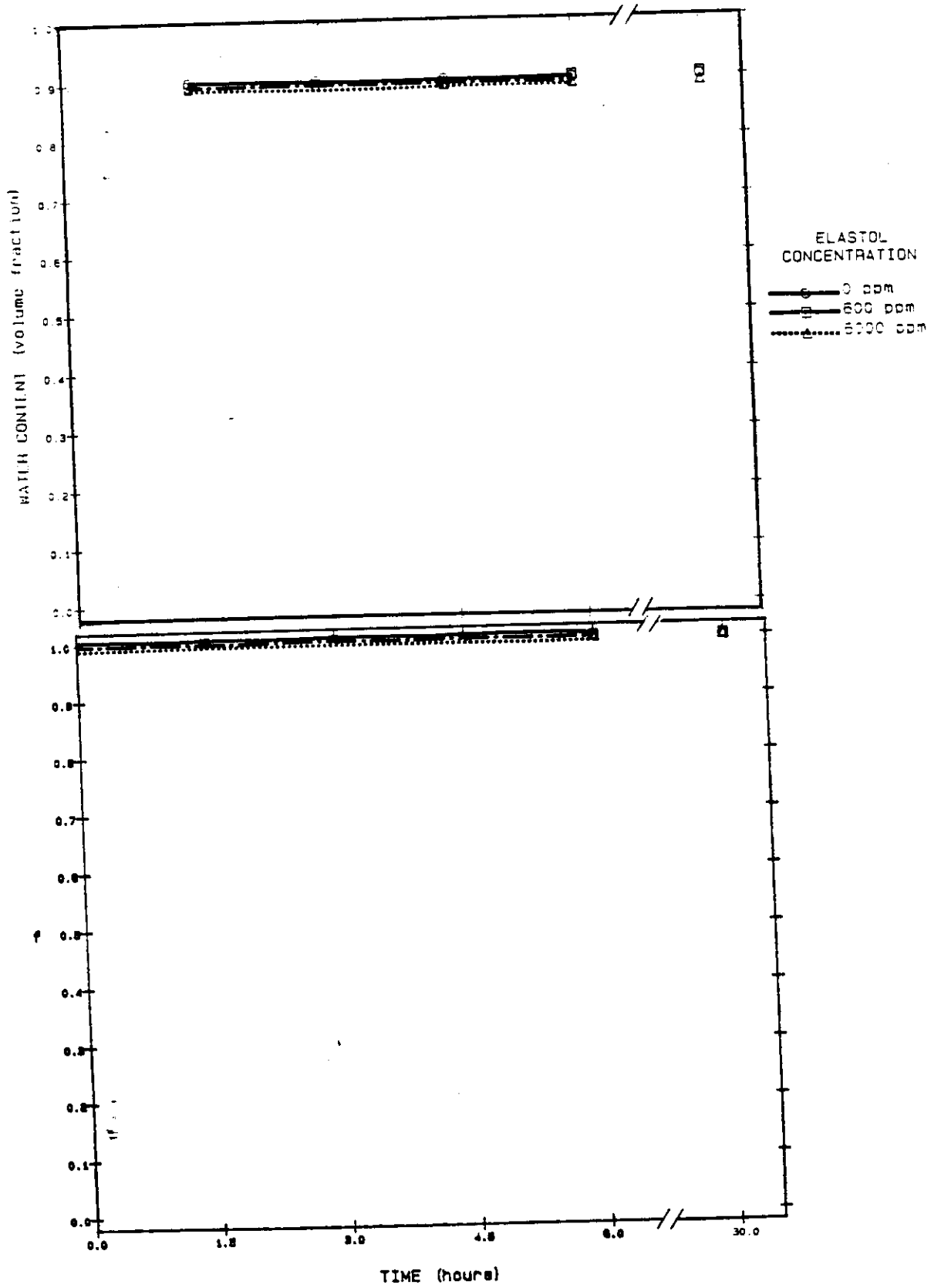


Figure 2-30. Plots of f and water content versus time for ASMB 15% weathered at 0 deg. C.

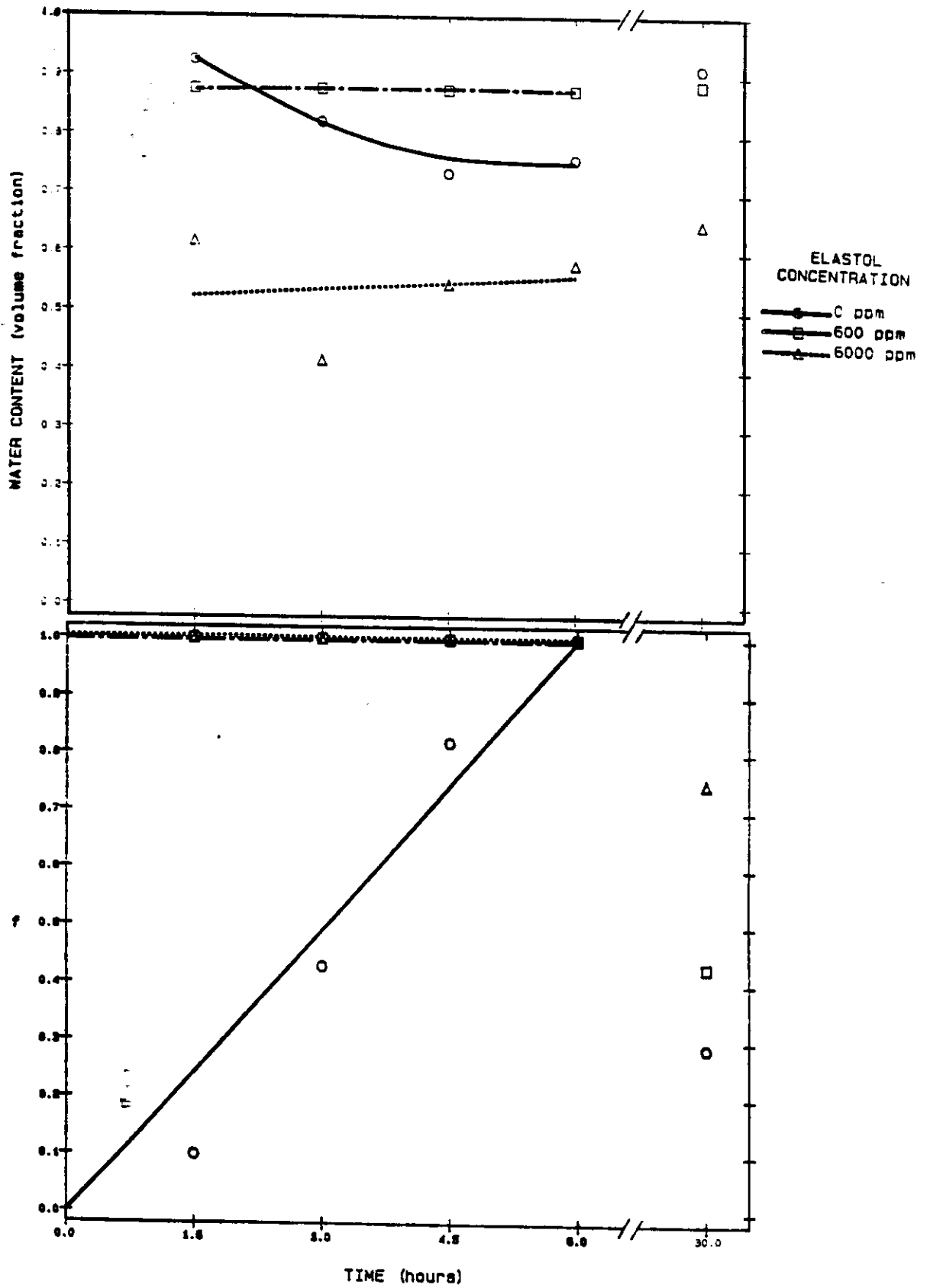


Figure 2-31. Plots of f and water content versus time for Amaligak at 0 deg. C.

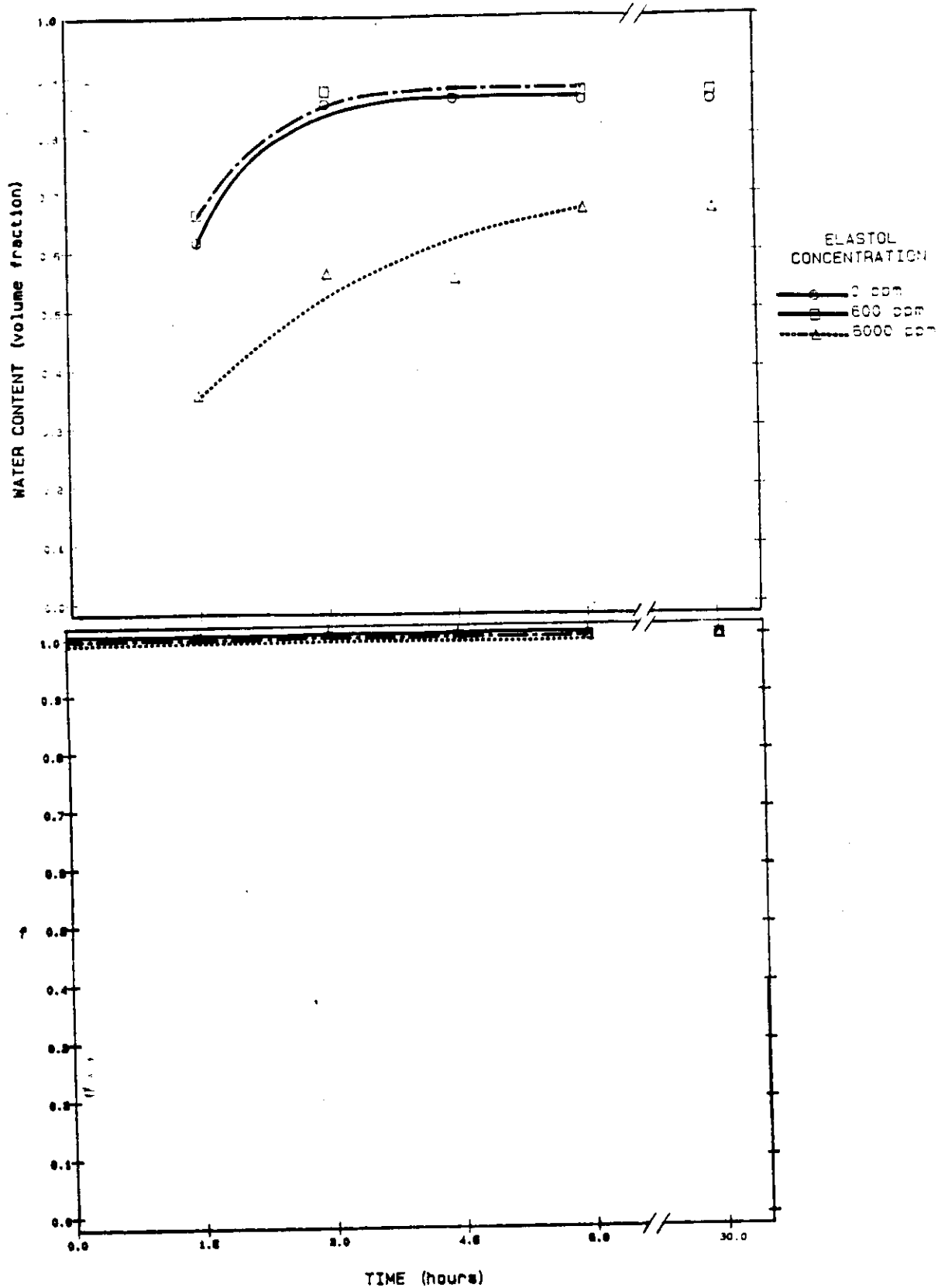


Figure 2-32. Plots of f and water content versus time for the Emulsifying Mix at 0 deg. C.

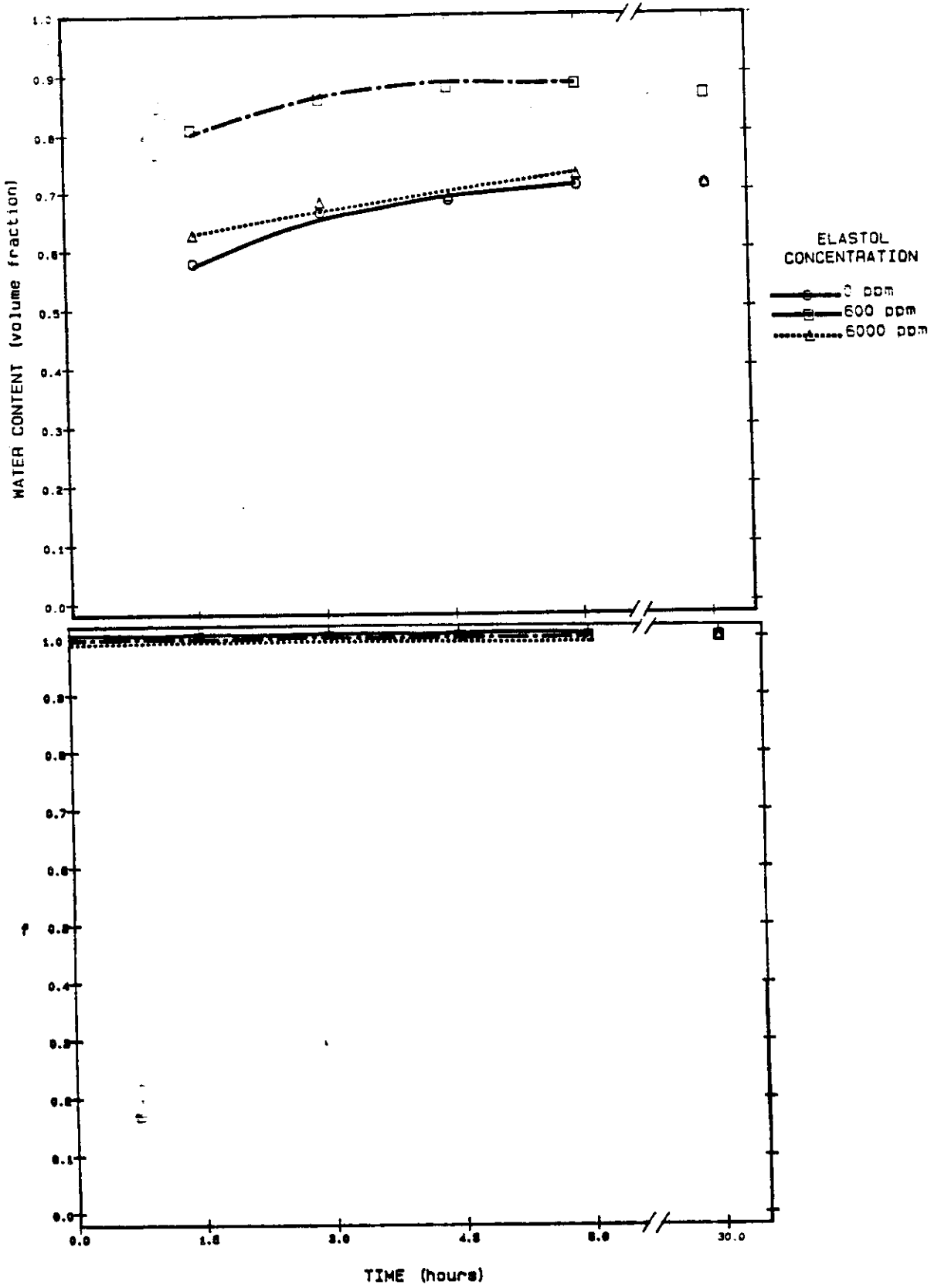


Figure 2-33. Plots of f and water content versus time for Hybernia at 0 deg. C.

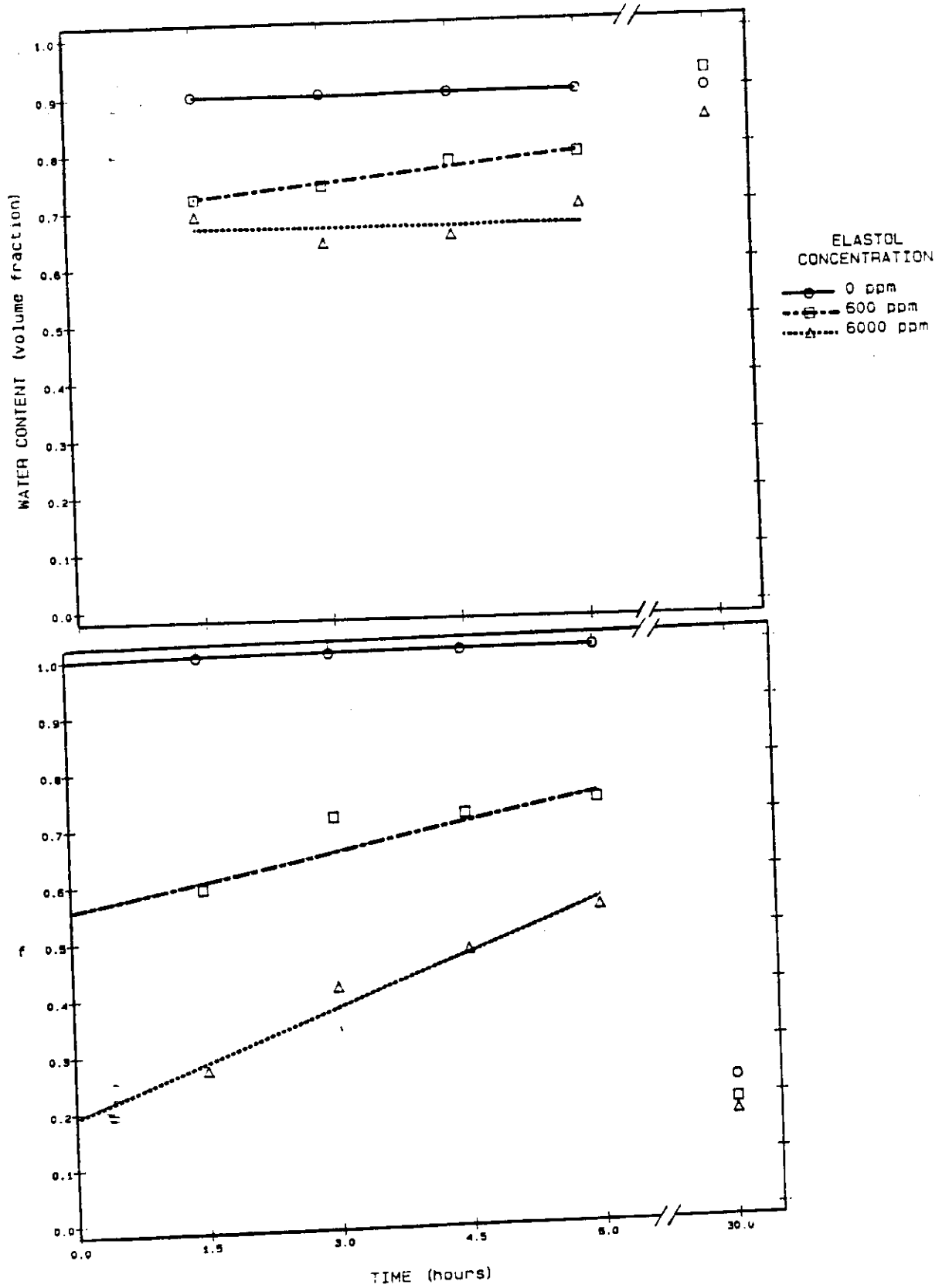


Figure 2-34. Plots of f and water content versus time for Norman Wells at 0 deg. C.

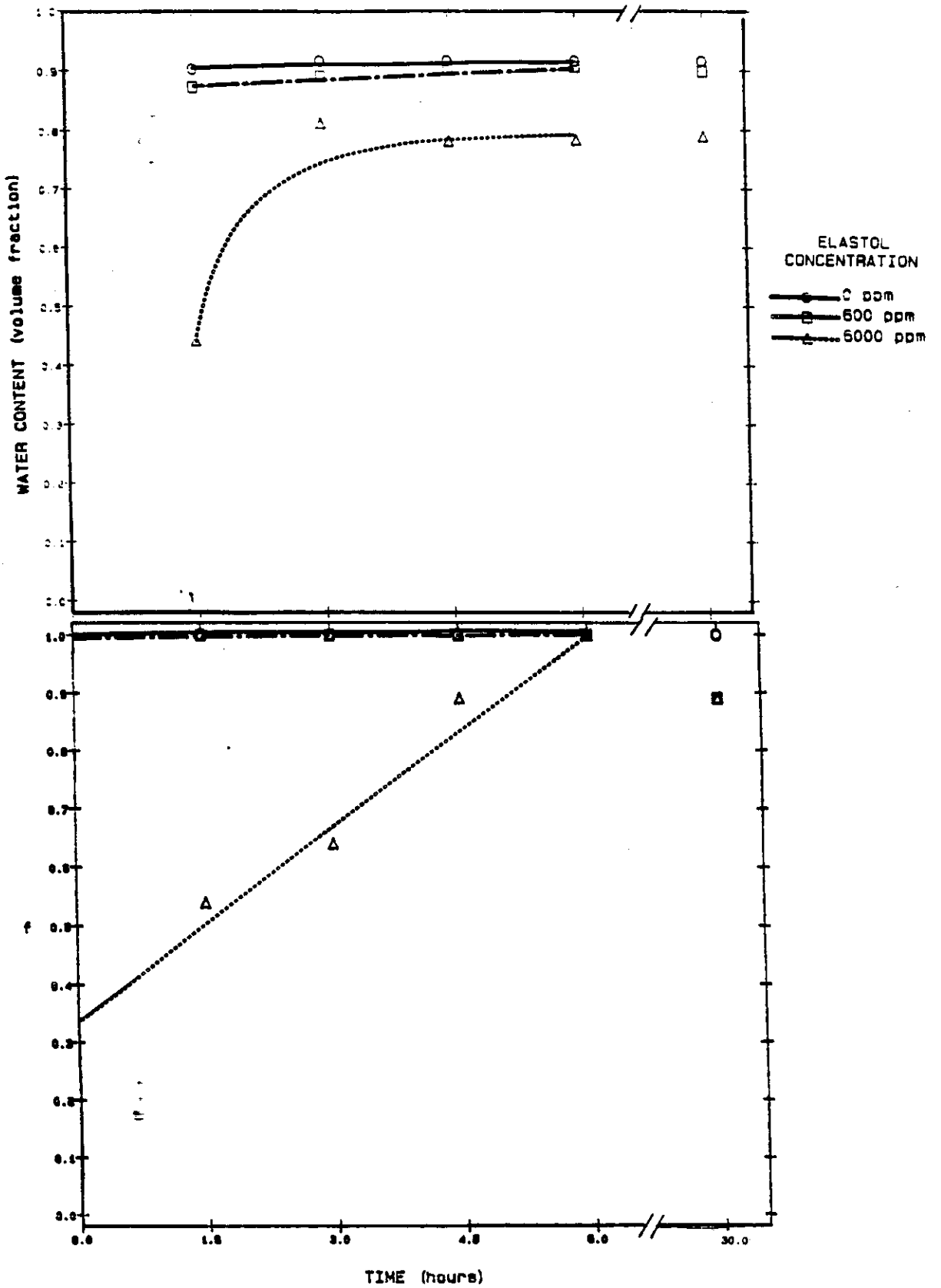


Figure 2-35. Plots of f and water content versus time for Prudhoe Bay at 0 deg. C.

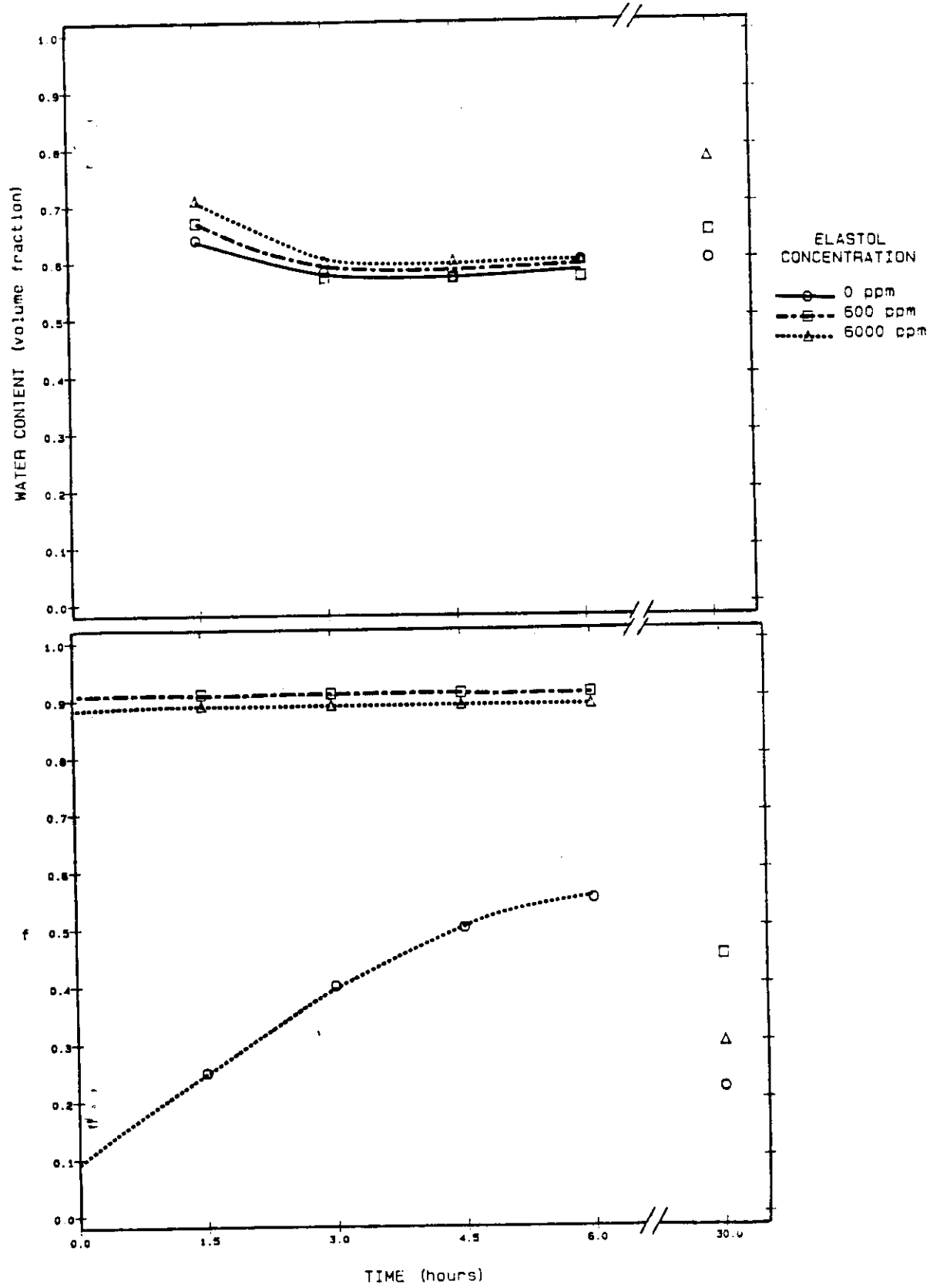


Figure 2-36. Plots of f and water content versus time for Tarsiut at 0 deg. C.

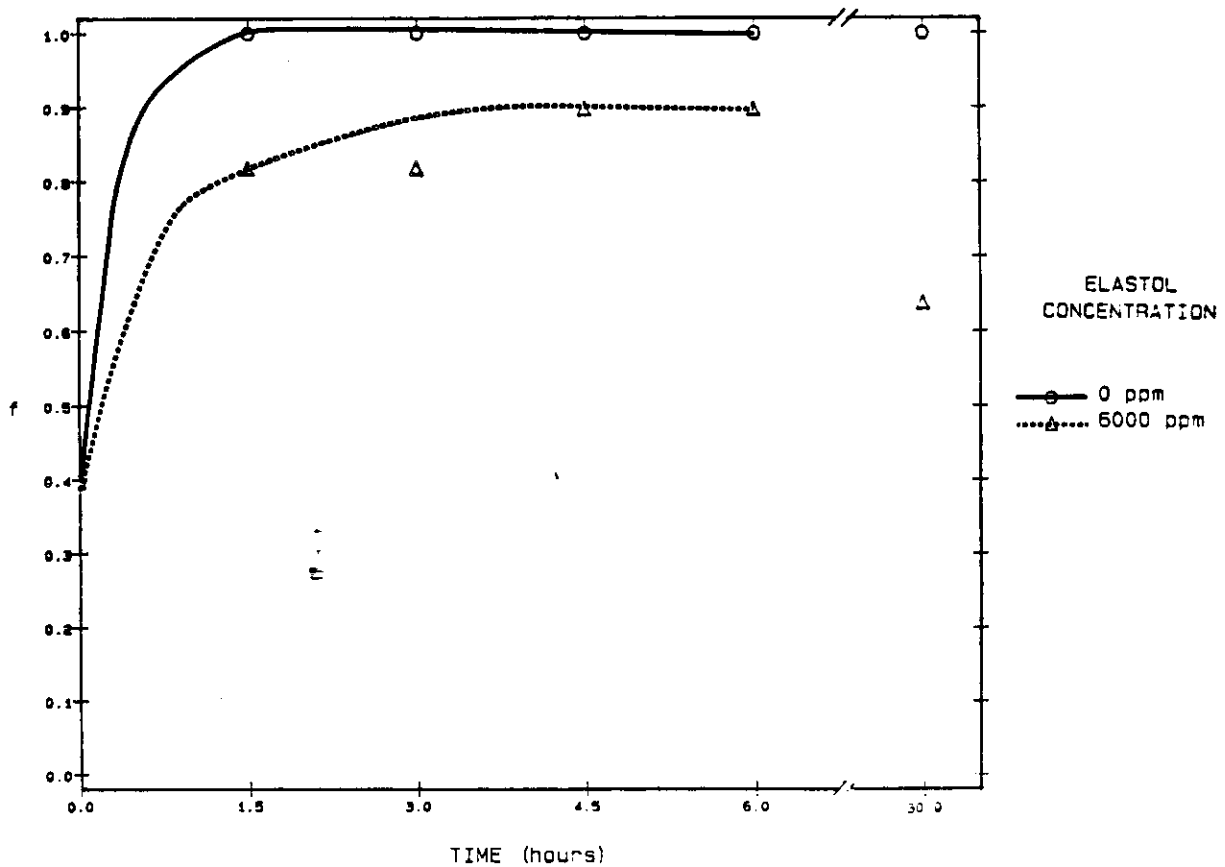
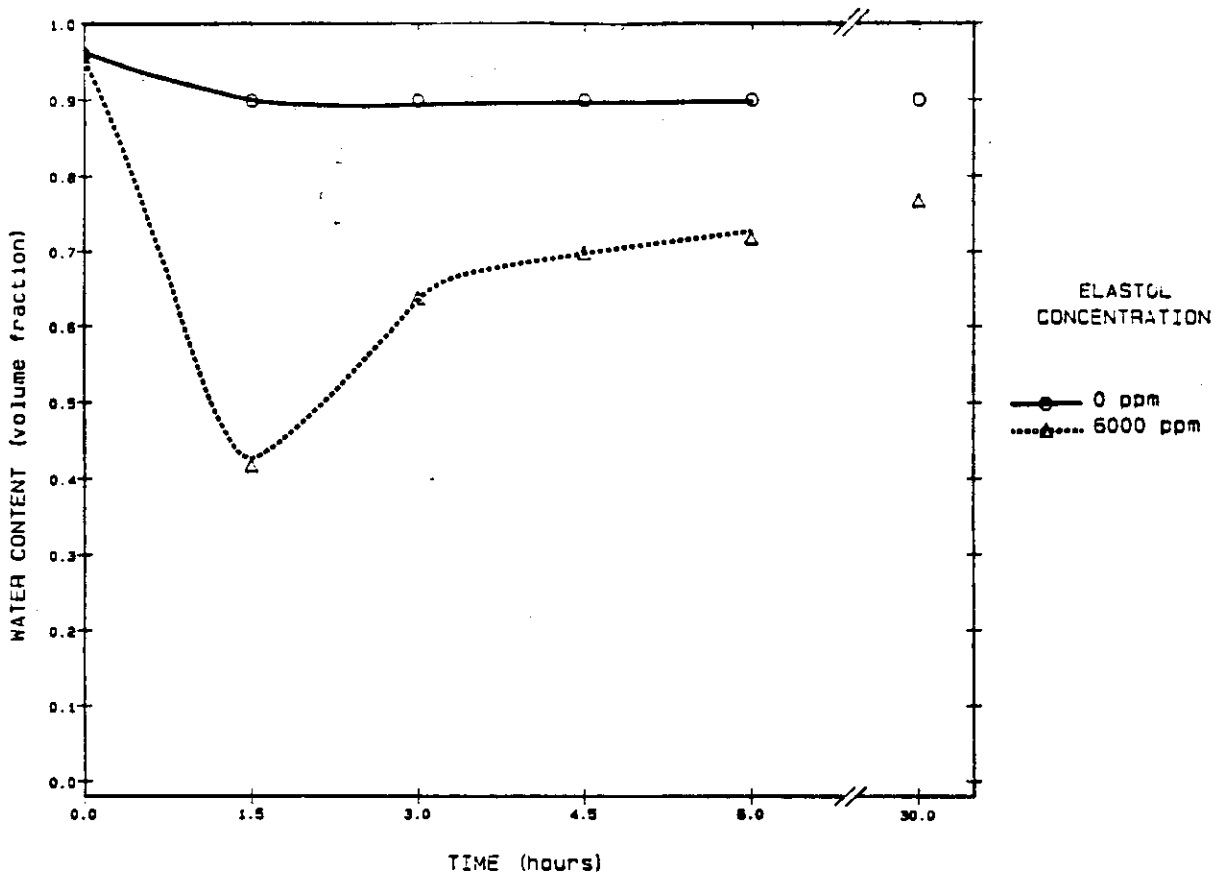


Figure 2-37. Plots of f and water content versus time for emulsified ASMB at 15 deg. C.

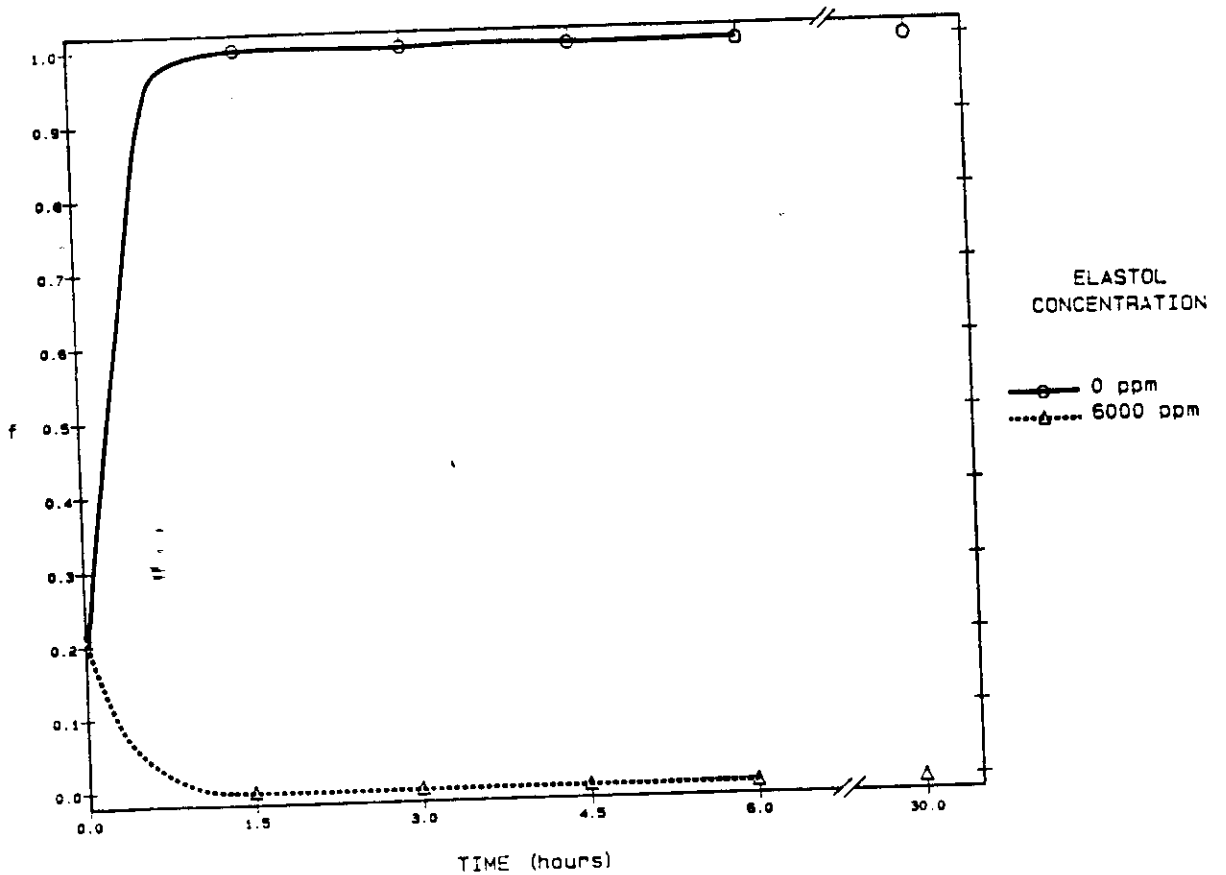
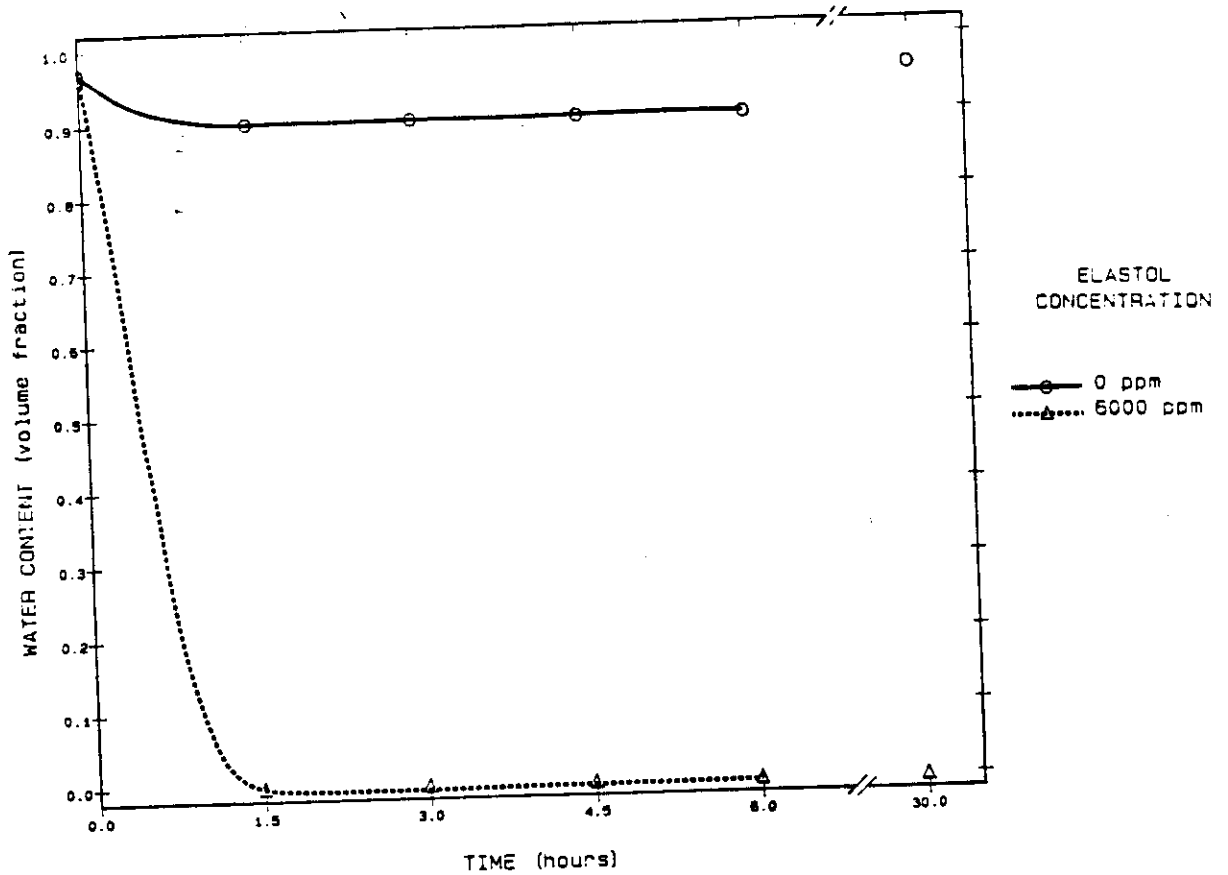


Figure 2-38. Plots of f and water content versus time for emulsified Prudhoe Bay at 15 deg. C.

Table 2.4: Emulsion Formation Tendency, Stability and Water Content of Test Oils

Temperature: 15 deg C.

Elastol Conc.	0 ppm			600 ppm			6000 ppm			Effect of Increasing Elastol Conc. on:		
	Oil	fo	f	w	fo	f	w	fo	f	w	fo	f
ASMB Crude	0.9	0.4	0.96	0.9	0.31	0.96	0.9	0.34	0.78	o	-	-
ASMB, 15% Weathered	1	1	0.9	1	1	0.9	1	0.86	0.78	o	-	-
Amauligak Crude	0	0	0	0.29	0	0	0.53	0	0	+	o	o
Bent Horn Crude	0	0	0	0	0	0	0	0	0	o	o	o
Diesel	0	0	0	0	0	0	0	0	0	o	o	o
Emulsifying Mix*	1	1	0.9	1	1	0.88	1	1	0.77	o	o	-
Hybernia Crude	1	1	0.9	1	0	0	1	0	0	o	-	-
Norman Wells Crude	0.04	0.1	0.98	0	0	0	0	0	0	-	-	-
Prudhoe Bay Crude	1	0.22	0.97	1	0	0	0	0	0	-	-	-
Tarsiut Crude	0.08	0.08	0.96	0.55	0.22	0.88	1	0.4	0.94	+	+	o

fo: f initial

f : f final

w: volume fraction of water in emulsion 24 hrs after last mixing

+: increase

-: decrease

o: no change

* 50% Alberta Sweet Mix Blend; 50% Bunker C.

Table 2.5: Emulsion Formation Tendency, Stability and Water Content of Test Oils

Temperature: 0 deg C

Elastol Conc.	0 ppm			600 ppm			6000 ppm			Effect of Increasing Elastol Conc. on:		
	fo	f	w	fo	f	w	fo	f	w	fo	f	w
ASMB	1	1	0.9	1	1	0.88	1	1	0.82	o	o	-
ASMB, 15% Weathered	1	1	0.9	1	1	0.9	1	1	0.89	o	o	o
Amauligak Crude	0	0.29	0.91	1	0.43	0.89	1	0.75	0.65	+	+	-
Bent Horn Crude	0	0	0	0	0	0	0	0	0	o	o	o
Diesel	0	0	0	0	0	0	0	0	0	o	o	o
Emulsifying Mix*	1	1	0.86	1	1	0.88	1	1	0.68	o	o	-
Hybernia Crude	1	1	0.71	1	1	0.87	1	1	0.71	o	o	o
Norman Wells Crude	1	0.23	0.9	0.68	0.19	0.93	0.22	0.17	0.85	-	-	-
Prudhoe Bay Crude	1	1	0.9	1	0.89	0.9	0.34	0.89	0.79	-	-	-
Tarsiut Crude	0.15	0.22	0.6	0.91	0.45	0.65	0.89	0.3	0.77	+	+	+

fo: f initial
 f : f final
 w: volume fraction of water in emulsion 24 hrs after last mixing

+: increase
 -: decrease
 o: no change

* 50% Alberta Sweet Mix Blend; 50% Bunker C.

3. PERFORMANCE OF ELASTOL IN A SMALL-SCALE WAVE GENERATING TANK

3.1 Purpose

The purpose of this study was to determine the behaviour and properties of Elastol-treated oil slicks when subjected to wave action in a small-scale test apparatus. In particular, the study focused on the effect of Elastol on the combined, simultaneous processes of dispersion, emulsion formation, weathering, and increase in viscoelasticity.

3.2 Experimental

The experiments were conducted in a water-filled tank equipped with a wave generator. The apparatus consisted of a 42 x 42 x 42 cm tank in which radial waves were produced by a vertical motion 30.5 cm ID oscillating hoop with variable speed control. The tank was filled with approximately 34 L of water and the waves were reflected by a plastic 41 cm diameter open ended tube, as seen in Plate 4.

The selected experimental parameters are listed below:

- Oil Type: Alberta Sweet Mixed Blend (ASMB); Emulsifying Mix (50-50 mix of ASMB and Bunker C); 15% weathered ASMB.
- Elastol Concentration: 0, 600, 2000, 4000, 6000 ppm (0, 0.12, 0.41, 0.82, 1.21 mg/cm²).
- Mixing Energy (Hoop Oscillation): 150 and 220 RPM.
- Temperature: 0 and 15 deg C.
- Water Salinity: fresh water and salt water (33 ppt).

Due to time limitations, only selected combinations of the above parameters were chosen.

The experimental procedure is summarized below:

1. Fill the tank with 34 L of either fresh or 33 ppt salt water.
2. Start the oscillating hoop wave generator and set the speed at either 150 or 220 RPM.
3. Add 150 mL of oil, which would produce an initial oil slick thickness



Plate 4: Oscillating Hoop Tank Apparatus

of approximately 2 mm, into the centre of the oscillating hoop and sprinkle Elastol evenly on top of the oil slick using the Elastol dispenser.

4. At time intervals of 1/4, 1/2, 1, 2, and 3 hours, collect a 250 mL water and a 15-20 mL oil sample.

5. Analyze the water sample spectrophotometrically to determine the amount of oil in water.

6. Conduct the following measurements/analysis on the oil sample:

- i. measure the viscosity using the Brookfield viscometer
- ii. measure the elasticity using the die-swell apparatus
- iii. determine the amount of water in the oil by spectrophotometry
- iv. determine the extent of oil weathering by gas chromatography

7. Repeat steps 5 and 6 for each sample.

8. Clean and drain the tank.

3.3 Results and Discussion

The results of this study are presented in graphical form, as seen in Figures 3.1 to 3.12. These figures show the change in the following oil properties of the slick with time: water content; dispersed oil; evaporative losses; dynamic viscosity; and elasticity.

3.3.1 Effect of Elastol on Weathering

At 15 deg C the results indicate that the addition of Elastol slightly decreases the loss due to evaporation during the first two hours for both ASMB and Emulsifying Mix, as indicated in Figures 3.11 and 3.12. This result is similar to the trend observed in an earlier evaporation study (Section 2.3). After this two hour time interval, there was little difference in the total evaporative loss for both Elastol-treated and untreated oils. This pattern was observed at both levels of mixing energy (Figures 3.11 and 3.12).

At 0 deg C, the effect of Elastol on weathering was negligible.

3.3.2 Effect of Elastol on Dispersion

The results from the analysis of water samples for oil dispersion are presented in Figures 3.1 to 3.10. In interpreting the concentration of oil-in-water results, it should be noted that the samples were taken from the bottom of the tank, well below the region in which larger oil droplets were present. These measured concentrations thus represent oil in finely dispersed droplets, probably 0.1 mm in diameter and less, which have a very low rising velocity. A homogeneously mixed oil concentration of about 4000 ppm would represent complete dispersion of the oil.

As seen in the oil dispersion graphs, Elastol-treated oils were found to have a lower amount of oil dispersed in the water phase than untreated oils. This suppression of oil dispersion increased with increasing Elastol concentration. The greatest decrease occurred for ASMB oil at 15 deg C when subjected to mixing at 150 RPM (Figure 3.1), in which a 25 and 95% decrease in oil dispersion was observed at an Elastol concentration of 600 and 6000 ppm, respectively. The respective oil concentrations for the Emulsifying Mix under the same conditions (Figure 3.2) were 2 and 3 times smaller at 600 and 6000 ppm.

Experiments conducted at 0 deg C showed similar trends but the magnitude of the reductions and the actual oil-in-water concentrations were found to be smaller at the lower temperature. This is in agreement with the fact dispersion is generally suppressed at lower temperatures.

3.3.3 Effect of Elastol on Emulsification

Measured water-in-oil concentrations, which are an indication of the degree of emulsification, show that at the lower mixing energy level, 150 RPM, the addition of Elastol delays the onset of emulsion formation, as seen in Figures 3.1 and 3.2. Elastol-treated slicks had significantly lower water content (average of 28% and 65% less at 600 and 6000 ppm) than untreated slicks.

Figures 3.5 and 3.6 show that at the 220 RPM mixing level, the rate of water entrainment in oil for both treated and untreated oils were approximately the same for the first 15 minutes. After this period, the

treated Emulsifying Mix emulsified at a slower rate and reached a constant but lower level of water content than the untreated oil. ASMB treated with Elastol, on the other hand, exhibited a different behaviour. The water content of the surface slick rose sharply during the initial stages and reached a maximum value at the time of first sampling. This concentration then decreased for the next 15 minutes after which it remained constant.

From this, it appears that Elastol has the ability to reverse the emulsification process and "squeeze out" water from the oil. One possible explanation for this phenomenon lies in the time required for Elastol to "react" with the oil. It was observed that the Elastol-treated ASMB did not reach its potential in terms of elasticity increase until about 1 hour into the experiment (See Sections 3.3.4 and 3.3.5). Therefore, it is thought that during the initial stages (first 15 minutes), water enters the oil freely in the form of large droplets. (For untreated oil, these large water droplets break down to smaller drops (less than 1 mm) which eventually form the smooth brown emulsion colloquially named "chocolate mousse" (S.L. Ross 1986)). As Elastol dissolves in the oil, the oil becomes progressively more cohesive, thereby impeding the introduction of additional water, and at the same time, promoting the emigration of water globules from the oil slick. This may explain the observed decrease in water content during the second 15 minute interval. From about 1 hour to the end of the experiment, a constant value of water-in-oil concentration was recorded. This is thought to indicate one or more of the following: that Elastol has "reacted" with the oil to the maximum elasticity; or it has reached a point where any increase in elasticity has no effect on the net migration of remaining water droplets in the slick; and that there is no deterioration of the elastic properties of the oil with time.

Although this up and down trend did not occur for the treated Emulsifying Mix at 15 deg C, the same reasoning could be used to explain the lower water content observed for this oil.

The appearance of the emulsions formed by Elastol-free oils was that of a stable, brown "chocolate mousse". The underside of the emulsion was distinctly "bumpy". These emulsion pancakes were generally about 1.5 to 3 cm

thick and close examination revealed that the water droplets were finely (< 1 mm) and evenly dispersed throughout the oil phase.

Of the Elastol-treated oils which formed a distinct emulsion at 15 deg C, none had the true appearance of "chocolate mousse". They were darker in colour and were observed to have smoother surfaces. At 0 deg C, only the Elastol-treated Emulsifying Mix approached the "chocolate mousse" appearance. These emulsions differed from the stable Elastol-free emulsions by the presence of many large water droplets (> 1 mm). In addition, several small (< 1 mm) rigid "nodules", which were thought to be tightly bound clumps of Elastol polymer, were observed.

3.3.4 Viscosity of Surface Slick

Under spill conditions, the viscosity of the slick increases with time. This increase is due to the combined effect of weathering, and to a greater extent, emulsification. If Elastol is added to an oil slick, part of the increase will be due to the increase in viscoelasticity imparted by the polymer.

Plots of dynamic viscosity versus time for the ASMB experiments (Figures 3.1 and 3.5) show that the viscosity of the untreated oil increased by a factor of 600 to 900 after 3 hours. This dramatic increase is attributed mainly to emulsification. In comparison, the viscosities of oils treated with Elastol had a 100 to 150 fold increase. This smaller increase is the result of the ability of Elastol to inhibit the extent of emulsification, as discussed in Section 3.3.3. This also shows that the viscosity increase as a result of an increase in elasticity is small compared to the increase due to emulsification.

The measured viscosities for 15% weathered ASMB showed a similar trend (Figure 3.10). The difference in the viscosity increase, however, was much smaller, with an 80 fold increase for Elastol-free oil and a 60 fold increase for the oil treated with 6000 ppm of Elastol.

The viscosities of the Emulsifying Mix at 15 deg C and 150 RPM are shown in Figure 3.2. It is interesting to note that although the emulsion formed

by the oil treated with 600 ppm of Elastol had a 15% lower water content compared to the Elastol-free emulsion, the viscosities of these oils were similar in magnitude. A 55% lower viscosity was measured for the oil treated at a dose of 6000 ppm.

The viscosity measurements for the Emulsifying Mix at 0 deg C showed an opposite trend. In these experiments, the slick viscosity increased with increasing dose of Elastol. The addition of Elastol did not significantly lower the water content of the emulsion. It should be noted that there was significant emulsion formation before the effects of Elastol were realized, since undissolved Elastol was still found floating on top of the oil slick 30 minutes after application.

3.3.5 Evaluation of the Performance of the Die Swell Apparatus

There were concerns that the presence of water droplets in oil would adversely affect the die swell measurements and thus necessitate the separation of water from the oil phase prior to the die swell measurement. This approach was viewed as being highly undesirable for several reasons. Many water-in-oil emulsions are very stable and suffice to say that demulsification is difficult and usually not completely thorough. It was also felt that the methods currently employed for demulsification (thermal, chemical and mechanical or combinations of these) would alter the viscoelasticity of the Elastol-treated oil. Another concern was that removing the water would lead to results that were not representative of the elastic properties exhibited by the in-situ surface slick.

Some of these concerns were laid to rest, since the die swell phenomenon was observed and measured for emulsified oil samples. But as seen from the die swell ratio versus time curves, the overall results showed greater scattering than those of Section 2.2. Part of this variability is attributed to the inconsistent nature of the oil samples. This lack of homogeneity was most evident as the sample exited from the end of the capillary tube of the die swell apparatus. Three distinct phases were observed: small pockets of free water and free oil; emulsified oil containing water droplets of various sizes; and small rigid nodules of Elastol polymer. In addition, some sampling variability probably occurred since it is reasonable to assume that the degree

the degree of elasticity, emulsification and weathering were not completely uniform over the area of the oil slick.

In general, the plots of die swell versus time for oils treated with 6000 ppm Elastol indicate that the maximum elasticity was reached within 15 minutes since equal or smaller die swell ratios were observed after 15 minutes. This appears to imply that the Elastol had dissolved and imparted its full elastic potential to the oils within 15 minutes. This was not supported by recorded observations. Although the oil exhibited some degree of elasticity at 15 minutes, it was felt that a high degree of elasticity was not realized until some time later. For ASMB, it was agreed that this time was about 1 to 1.5 hours at 15 deg C and 2 to 3 hours at 0 deg C, depending on the concentration and mixing energy. For the Emulsifying Mix, and 15% weathered ASMB, a time of 2 hours was required to produce an oil slick exhibiting a high degree of elasticity at 15 deg C. (It should be noted that very little elasticity was observed for the Emulsifying Mix at 0 deg C and at an Elastol dose of 600 ppm at 15 deg C due to significant emulsion formation. This is discussed further in the next section.) These observations may imply that the die swell measurements taken after 15 minutes may be underestimating the true elasticity.

The most probable reason for this lack of agreement between the die swell measurements and observed elasticity is associated with the presence of water droplets in the oil phase. The reason for this is two-fold: first is that the water droplets (as well as the small nodules of polymer that were observed) may act as fillers in the oil phase. The addition of fillers to elastic material reduces the amount of die swell (Samara, 1985). The second effect is that emulsification causes a marked increase in viscosity and may lead the oil to display a pseudoplastic flow behaviour (Mao and Marsten, 1977). This change in viscosity and rheological behaviour significantly reduces the flowrate and alters the characteristics of the oil flow through the capillary tube of the die swell apparatus. This reduced flow rate is also partly attributed to the decrease in the die swell, since Samara (1985) states that lowering the shear rate (flowrate) decreases the die swell. It should be noted that this discrepancy between the measured die swell ratios and elasticity was not observed for the experiments conducted in the absence of

water (Section 2.2). At 15 deg C, the greatest increase in viscosity encountered for Elastol-treated oils in the initial water-free experiments was 34 times, compared to 600 times for the small-scale tank experiments. Increases in viscosity of this magnitude undoubtedly affected the die swell measurements by decreasing the rate of oil flow through the needle of the die swell apparatus. A possible solution to this problem is discussed in Section 7.

3.3.6 Elasticity of Surface Oil

Despite the possible underestimation of the degree of elasticity as discussed in the previous section, the die swell measurements do illustrate some trends in the elastic behaviour of the oils tested.

Figures 3.1 to 3.9 show die swell ratio as a function of time for various combinations of oil, Elastol dose, and test conditions. Untreated oils exhibited no positive elastic behaviour. Treated oils exhibited elastic behaviour within 15 minutes of Elastol application. As expected, increasing the concentration of Elastol resulted in a higher degree of elasticity.

It is worthy to mention the differences in the range of calculated die swell ratios for three oils tested at 15 deg C (Figures 3.1, 3.2, and 3.10), and at the lower mixing speed. At an Elastol dose of 6000 ppm, the "average" die swell ratio for three oils; ASMB, Emulsifying Mix and 15% weathered ASMB were found to be similar in magnitude, with the ratios for the Emulsifying Mix being slightly smaller than those of the other two oils. This difference was found to be more significant at 600 ppm. Slick elasticity observations recorded during these experiments supported this trend. Since the Emulsifying Mix was found to have the greatest emulsion formation at both concentrations, it can be concluded that the emulsification process competes against, and discourages or masks the increase in measurable elasticity of the oil.

(i) Effect of Mixing Energy

Figure 3.3 shows the effect of mixing energy on ASMB at 15 deg C at the two concentrations of Elastol. Die swell measurements indicate that greater elasticity was imparted to the oil when mixed at the higher rate for both concentrations.

The effect of mixing energy on Elastol-treated Emulsifying Mix is presented in Figure 3.4. There was no significant difference in the measured die swell ratios when treated at an Elastol concentration of 600 ppm for the two mixing levels. At 6000 ppm, the die swell ratios were generally slightly lower for the experiment performed at the higher mixing speed. This decrease can most likely be attributed to the higher rate of emulsion formation observed at the higher mixing energy.

(ii) Effect of Temperature

The effect of temperature on the die swell ratios for ASMB at two concentrations of Elastol is presented in Figures 3.1 and 3.7. It can be seen that temperature had little overall effect on the measured die swell ratios. Although these figures do not explicitly show the dependence of effective reaction time (the time required for Elastol to dissolve and impart its elastic behaviour) on temperature, the observations indicated a longer reaction time at the lower temperature.

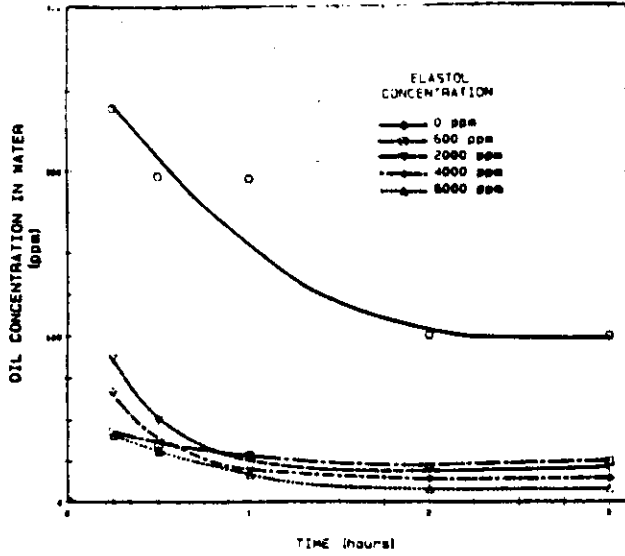
Figures 3.2 and 3.8 illustrates the effect of temperature on the Elastol-treated Emulsifying Mix. At a concentration of 600 ppm, the oil formed thick emulsions, which suppressed the action of Elastol at both temperatures. This is supported, in part, by the relatively small die swell ratios indicated by Figures 3.2 and 3.8. At a dose of 6000 ppm, higher die swell ratios were calculated for the experiment at 15 deg C. This is explained from the fact that the tendency for oils to emulsify increases with decreasing temperature. In the experiment conducted at 0 deg C, significant emulsion formation was observed even before the complete dissolution of Elastol into the oil phase.

(iii) Effect of Water Salinity

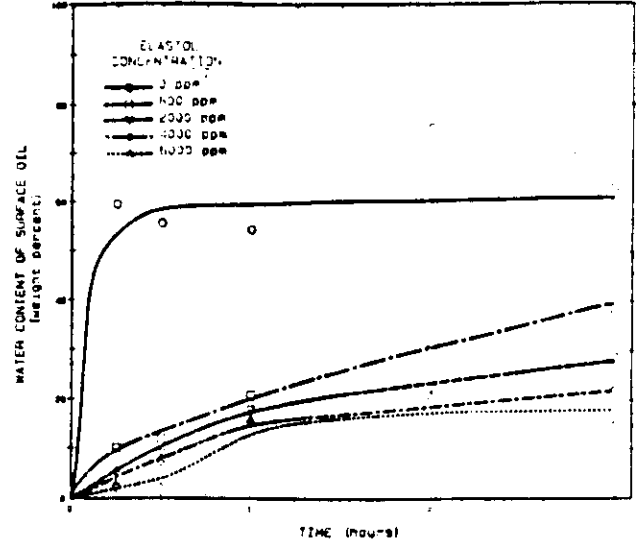
The experiments conducted to determine the effect of salinity on Elastol-treated ASMB showed that a slightly higher degree of elasticity was observed for the tests using fresh water than salt water. This was probably due to the lower degree of emulsification in the fresh water experiments.

(iv) Effect of Weathered Oil

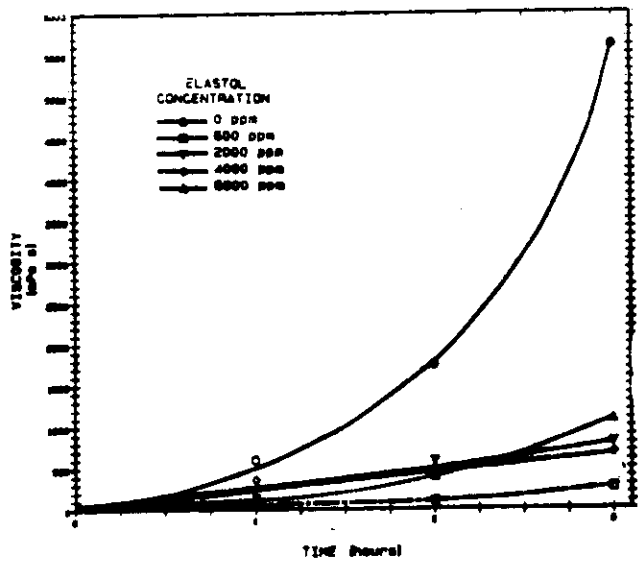
Comparison of Figures 3.1 and 3.10 for the fresh ASMB and 15% weathered ASMB fails to clearly show what effect the degree of weathering has on Elastol's performance. But both oils exhibited considerable elasticity within one to two hours after Elastol application.



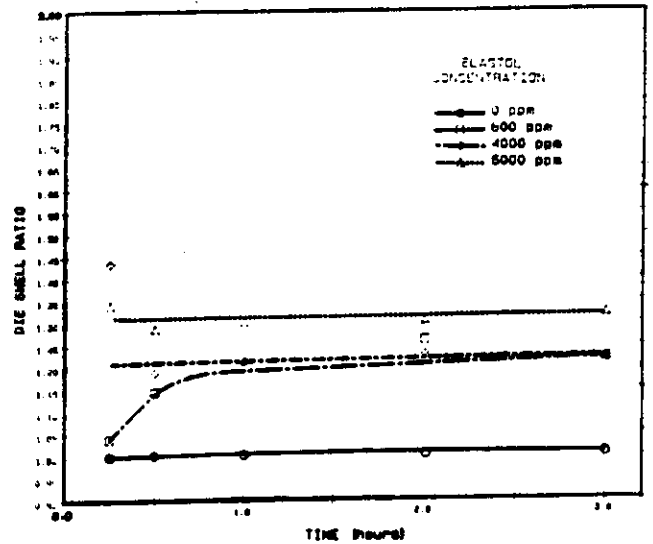
a) Dispersion versus time.



b) Emulsification versus time.

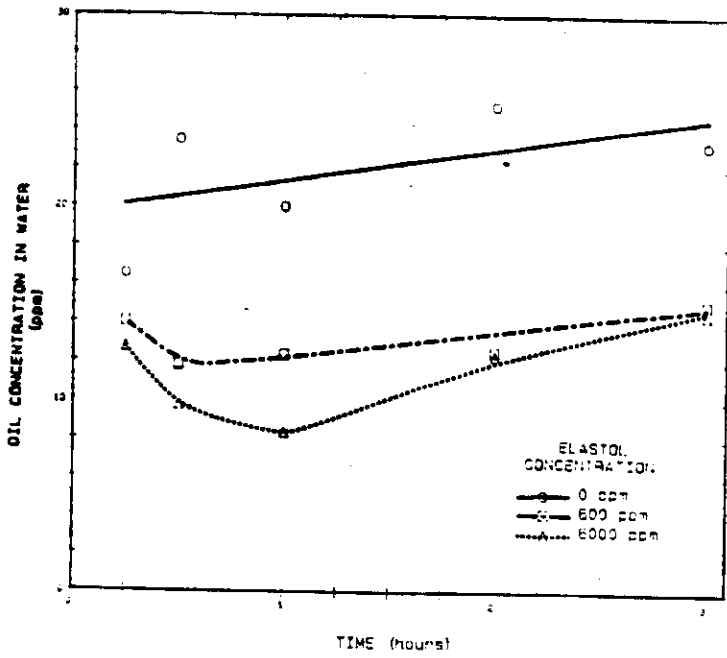


c) Viscosity versus time.

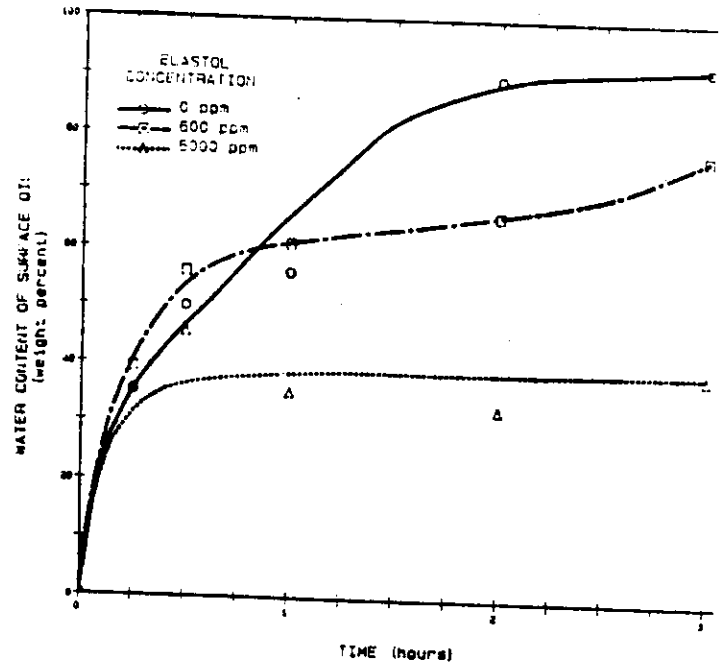


d) Die swell versus time.

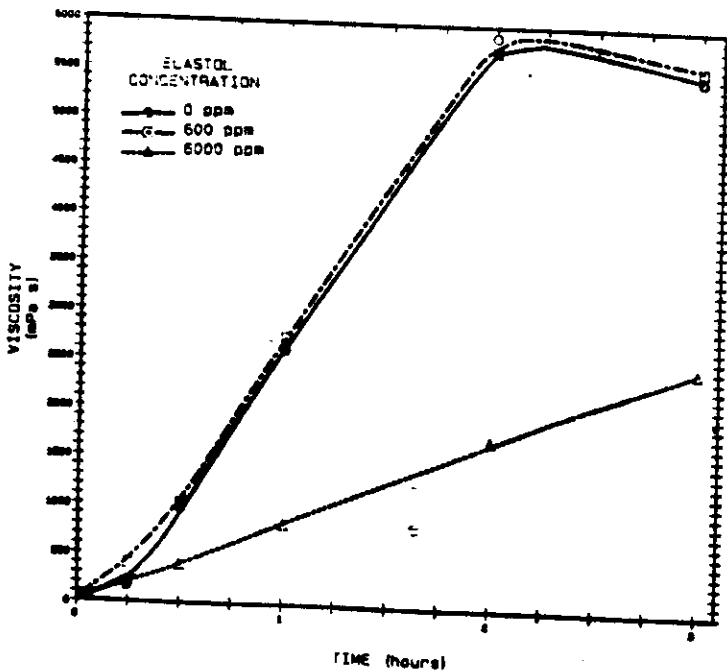
Figure 3-1. Small-scale tank tests for ASMB at 15 deg. C. and 150 r.p.m.



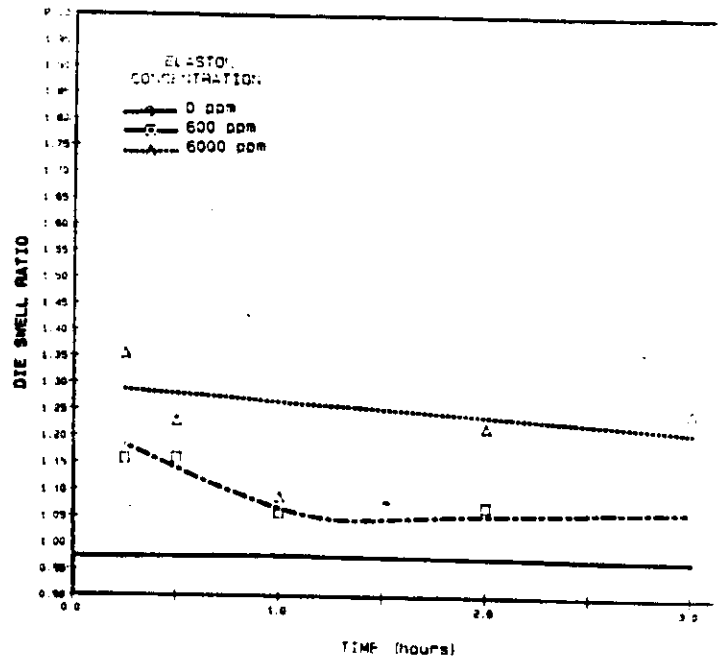
a) Dispersion versus time.



b) Emulsification versus time.

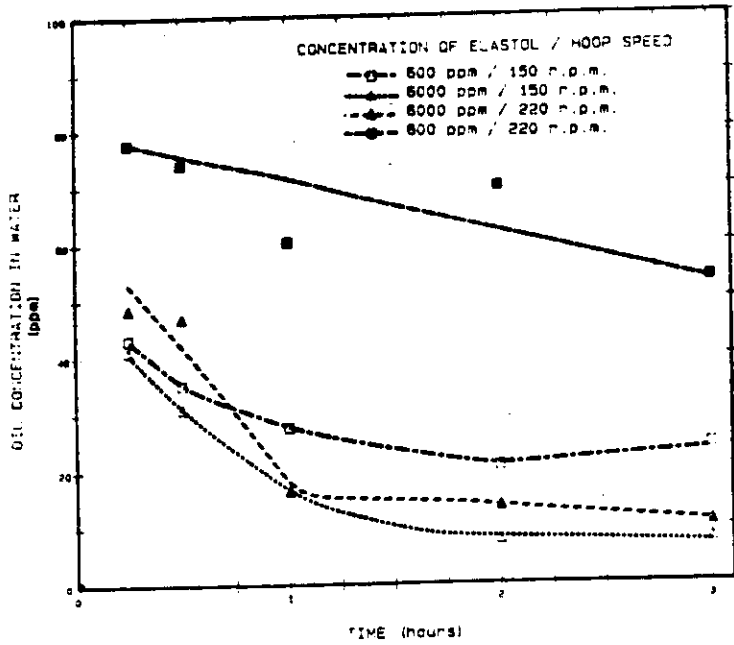


c) Viscosity versus time.

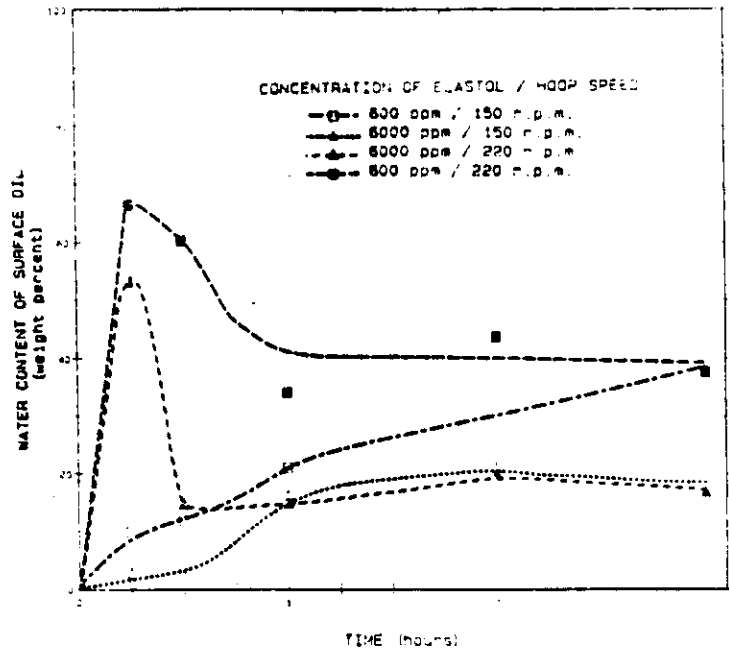


d) Die swell versus time.

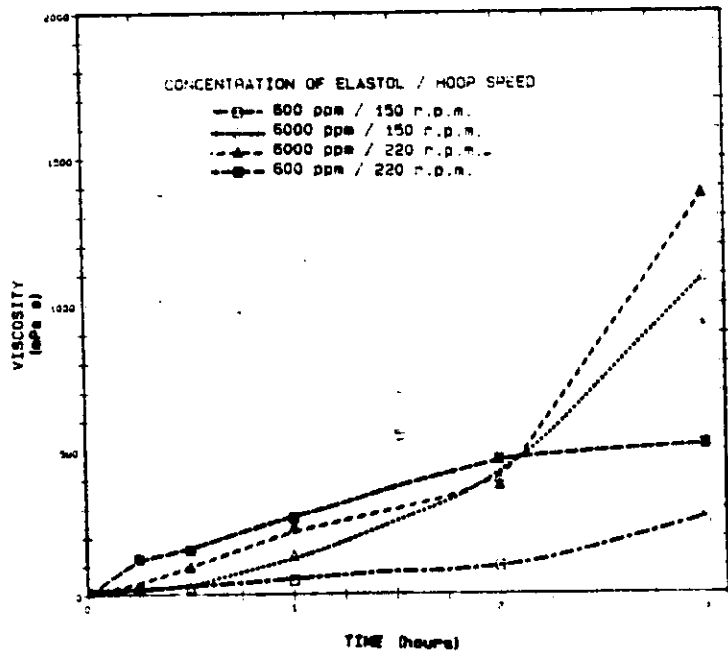
Figure 3-2. Small-scale tank tests for Emulsifying Mix at 15 deg. C and 150 r.p.m.



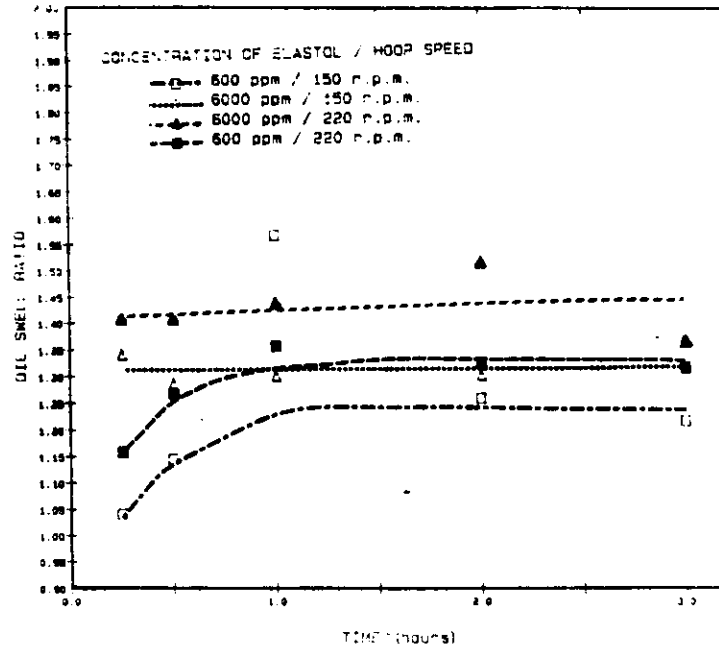
a) Dispersion versus time.



b) Emulsification versus time.

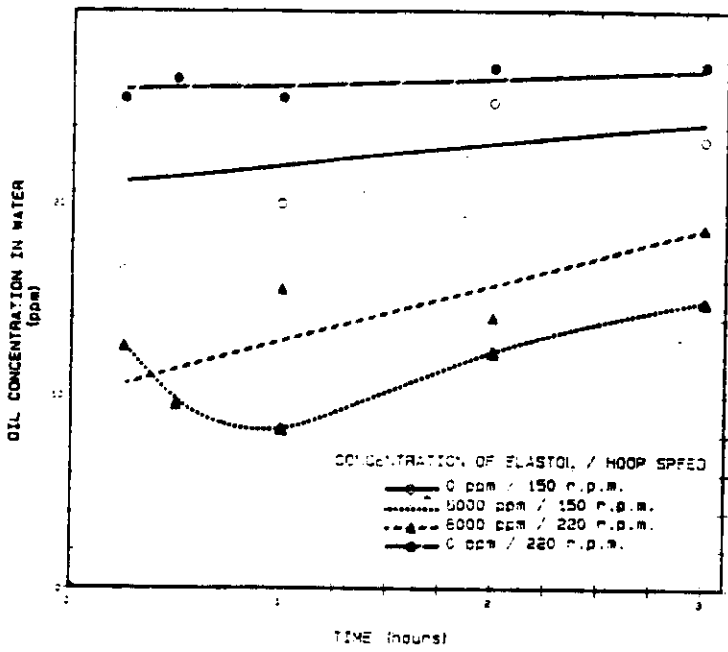


c) Viscosity versus time.

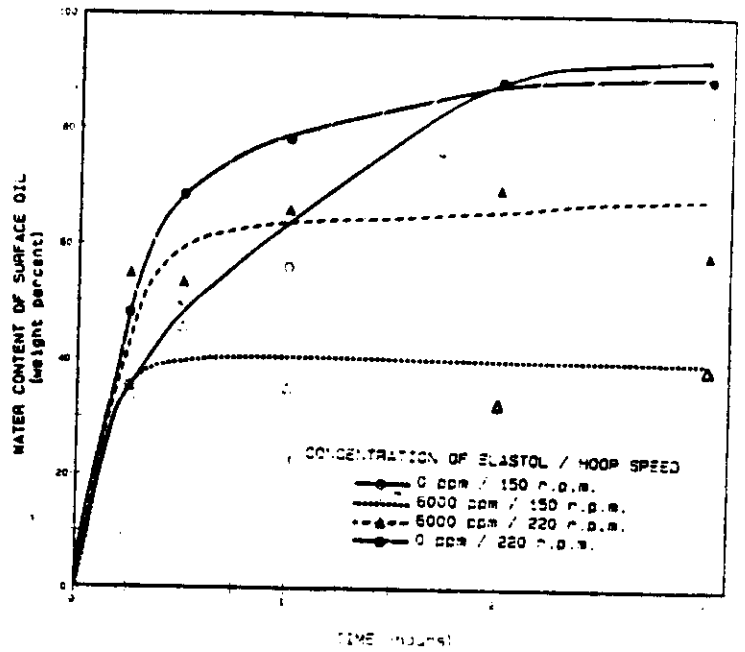


d) Die swell versus time.

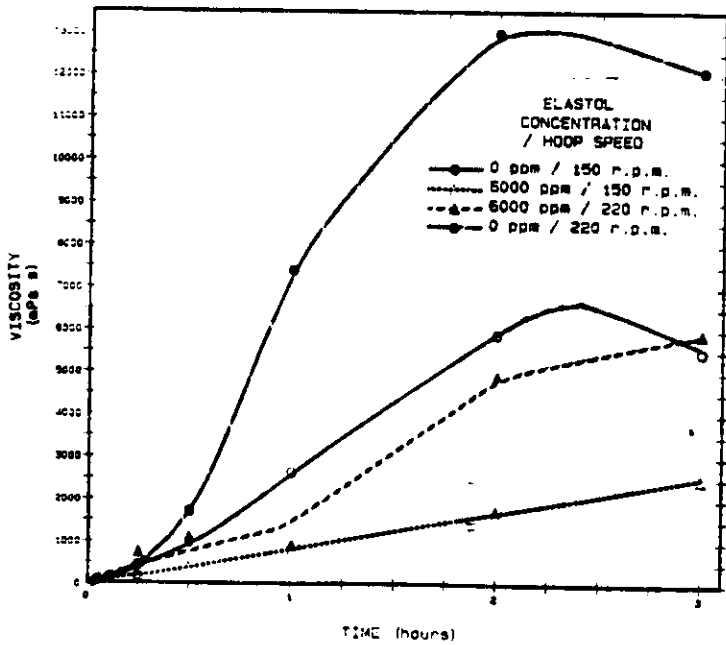
Figure 3-3. Effect of mixing energy on small-scale tank tests for ASMB at 15 deg. C.



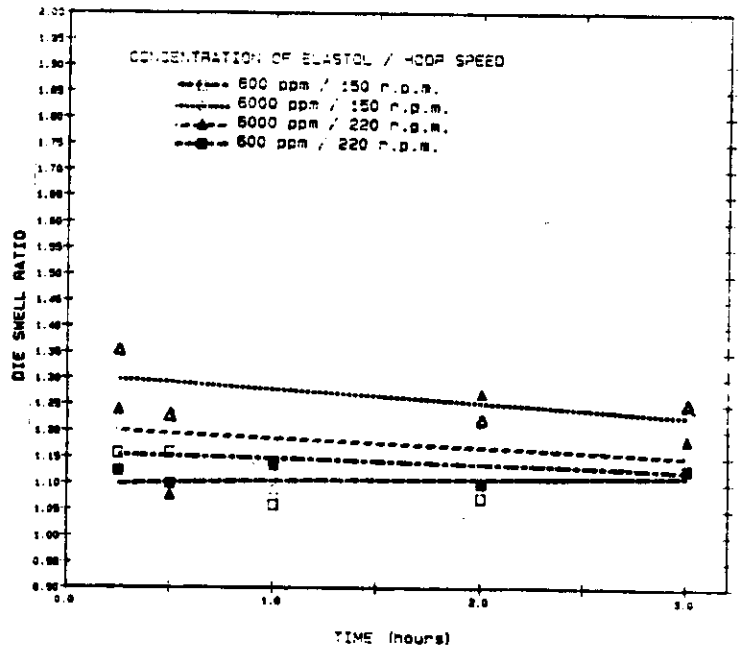
a) Dispersion versus time.



b) Emulsification versus time.

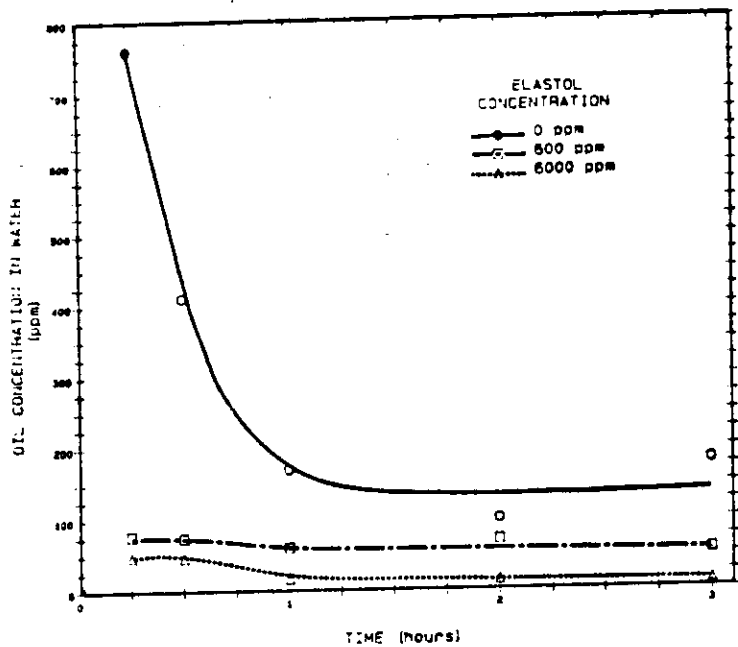


c) Viscosity versus time.

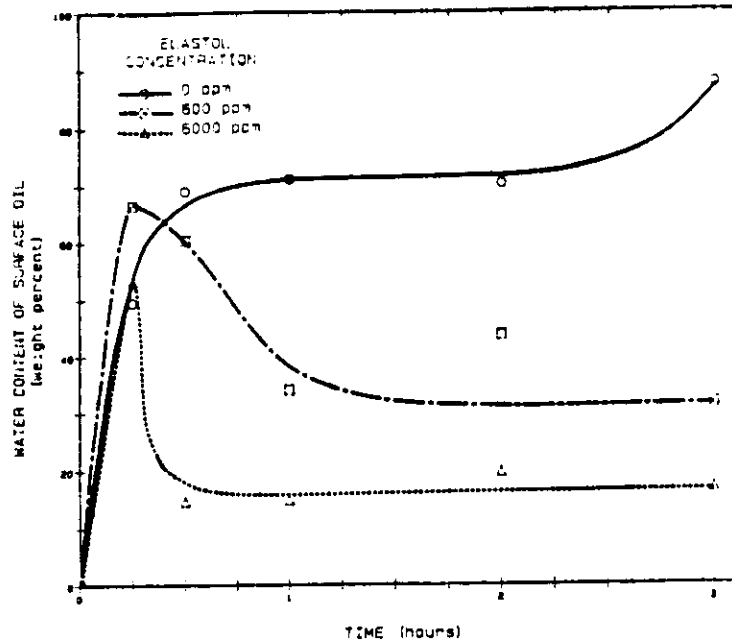


d) Die swell versus time.

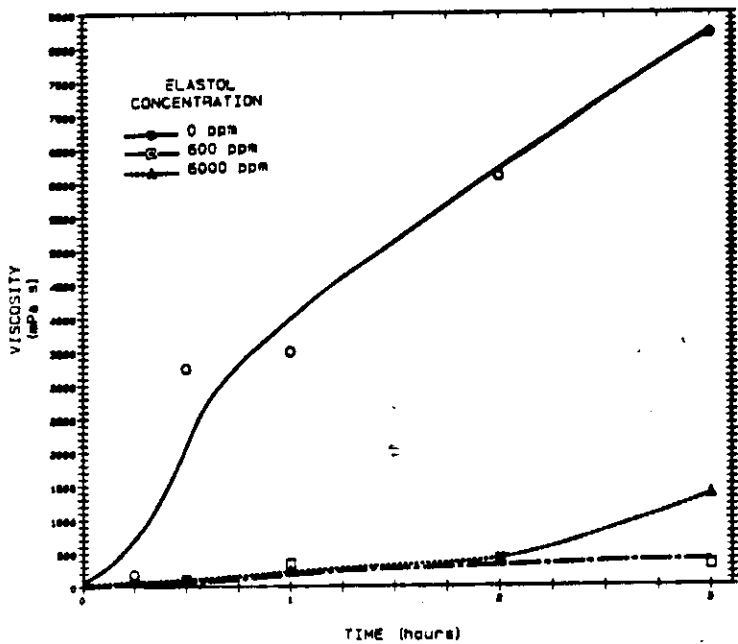
Figure 3-4. Effect of mixing energy on small-scale tank tests for Emulsifying Mix at 15 deg. C.



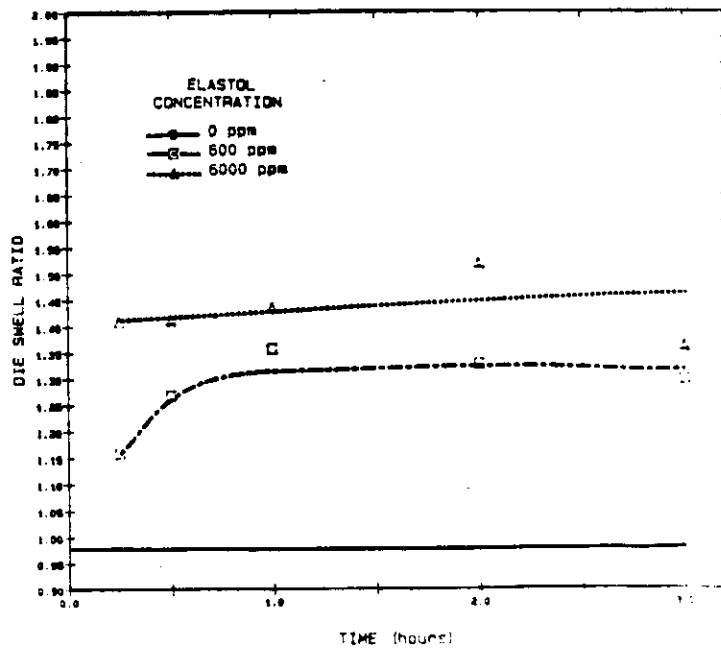
a) Dispersion versus time.



b) Emulsification versus time.

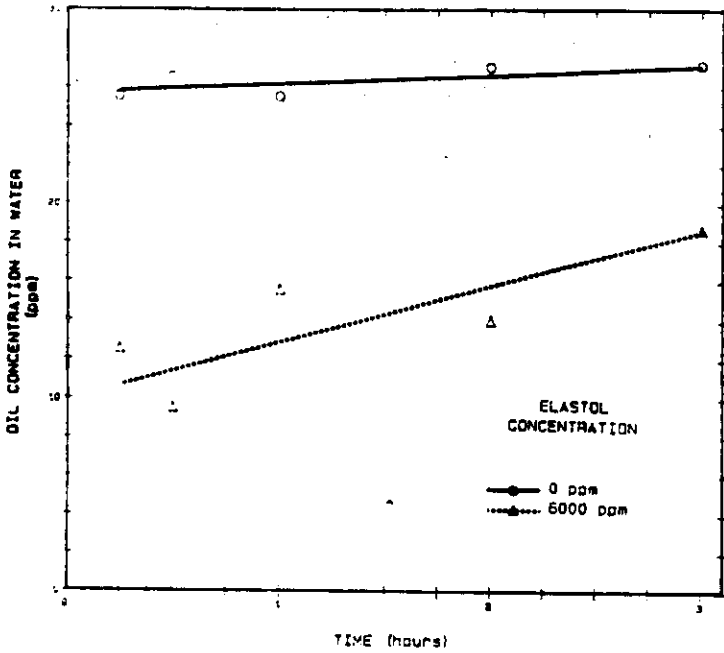


c) Viscosity versus time.

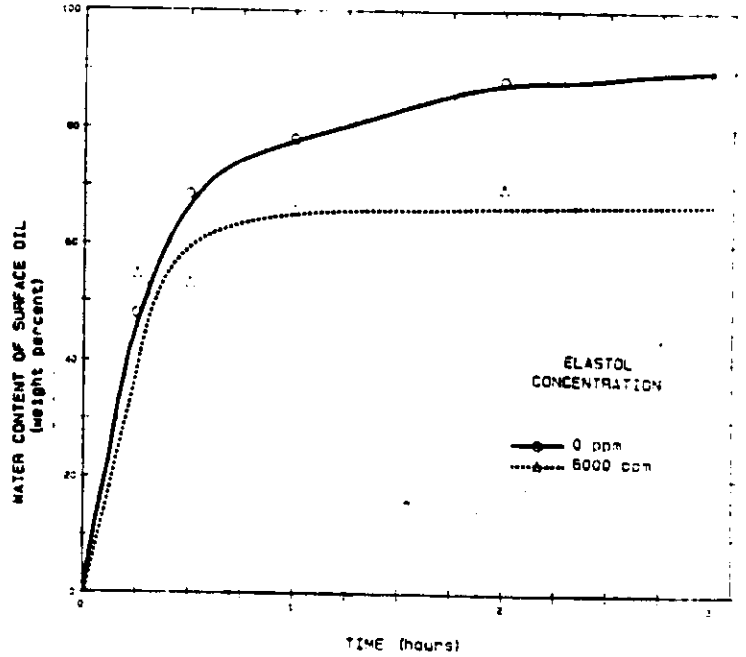


d) Die swell versus time.

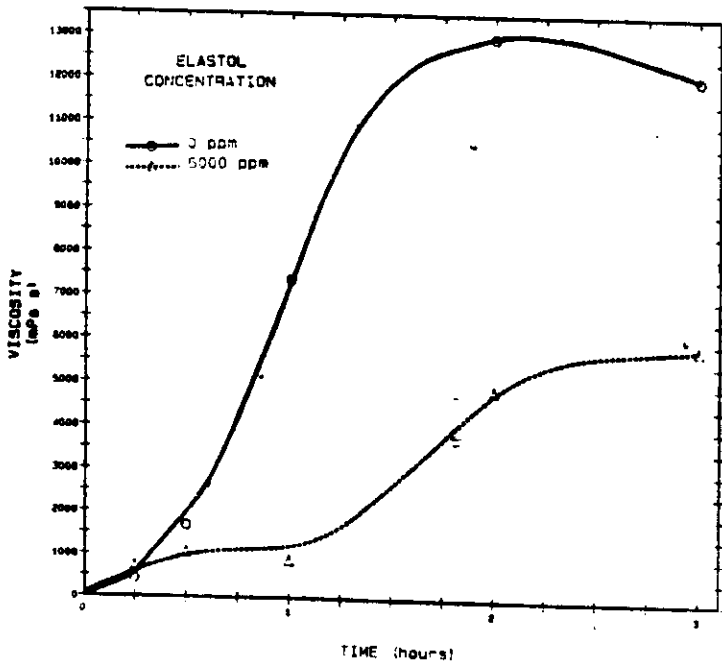
Figure 3-5. Small-scale tank tests for ASMB at 15 deg. C. and 220 r.p.m.



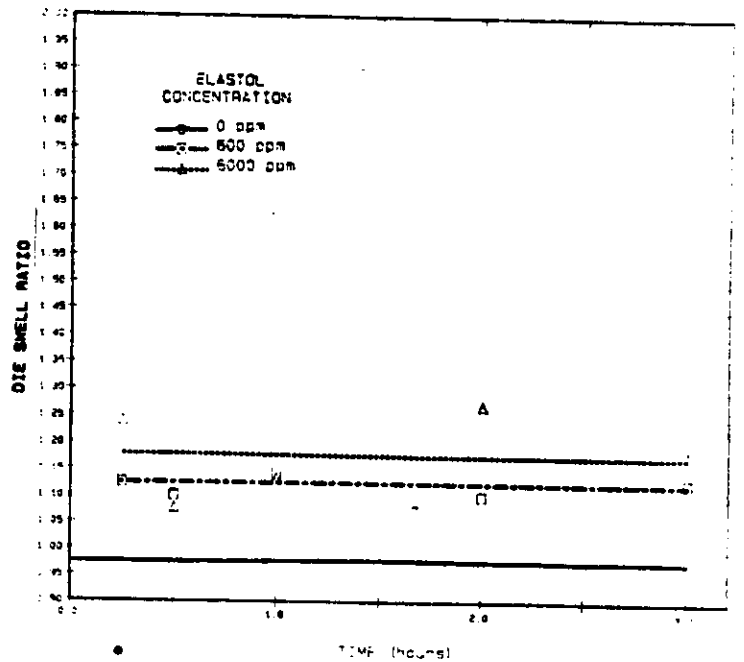
a) Dispersion versus time.



b) Emulsification versus time.

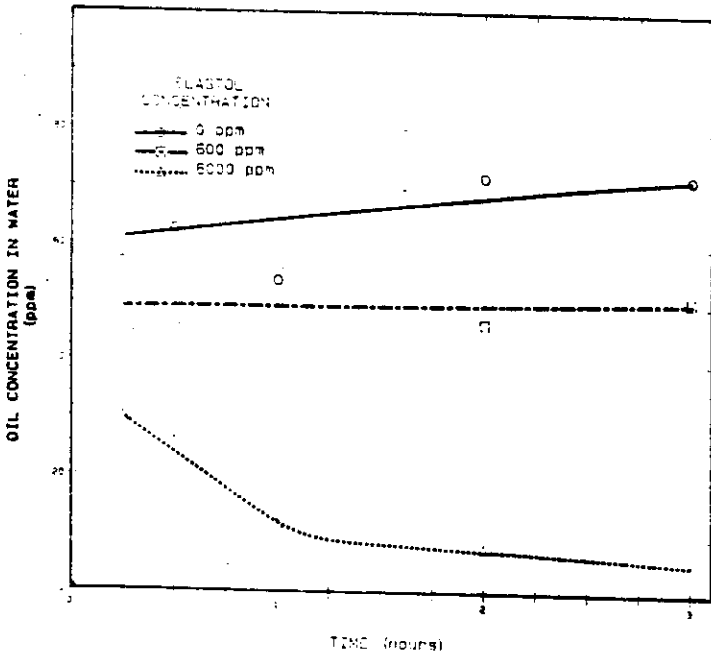


c) Viscosity versus time.

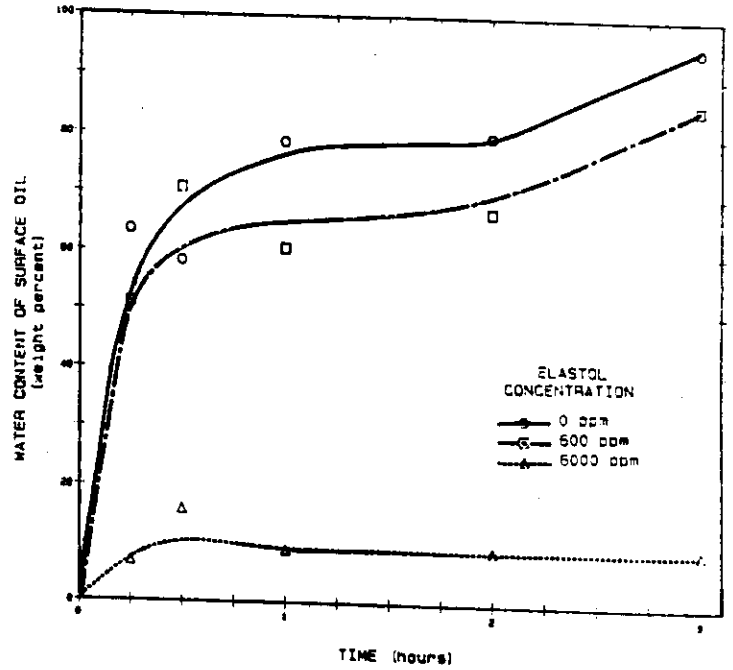


d) Die swell versus time.

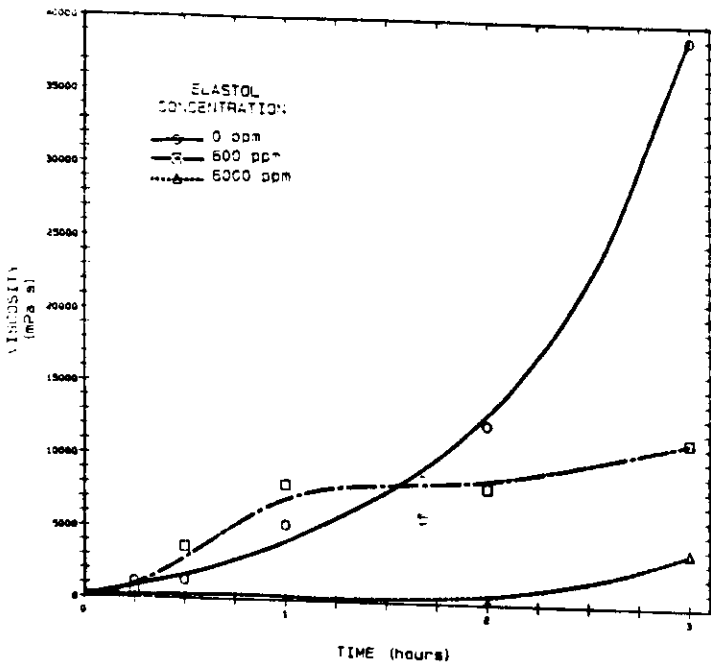
Figure 3-6. Small-scale tank tests for Emulsifying Mix at 15 deg. C. and 220 r.p.m.



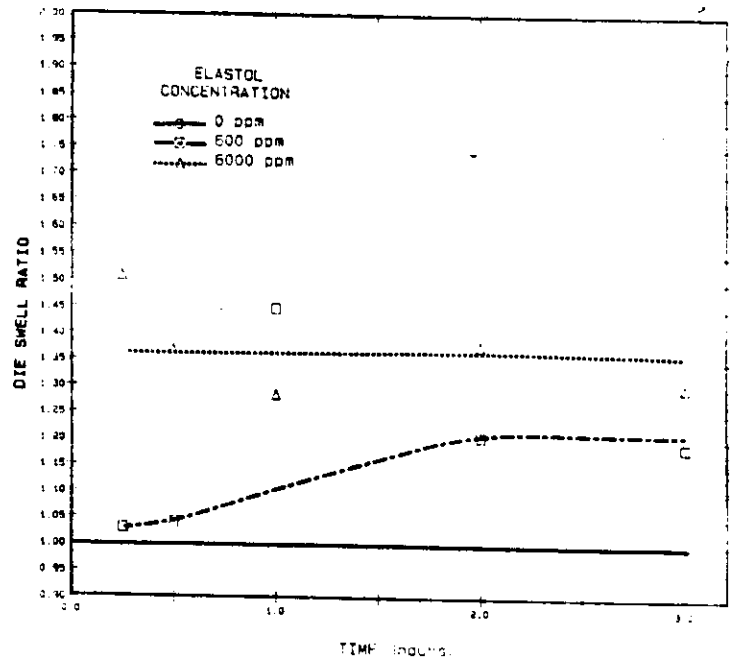
a) Dispersion versus time.



b) Emulsification versus time.

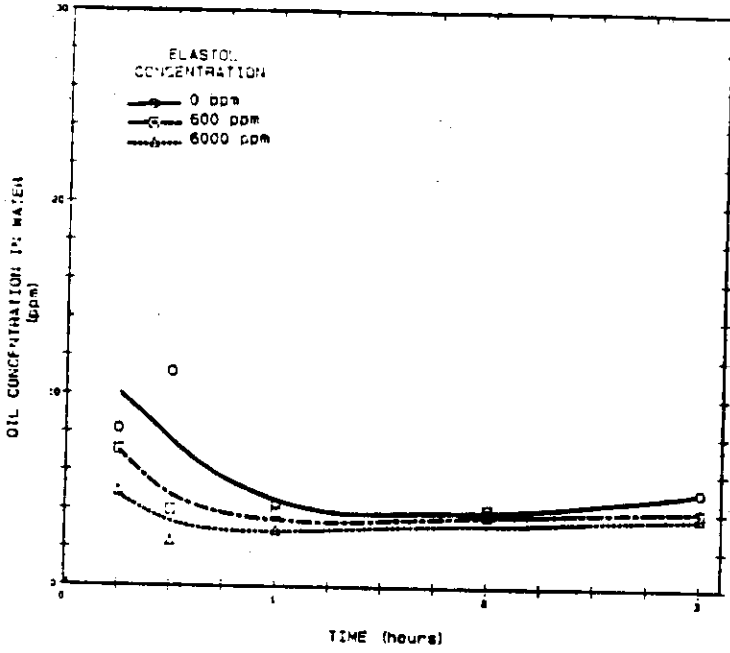


c) Viscosity versus time.

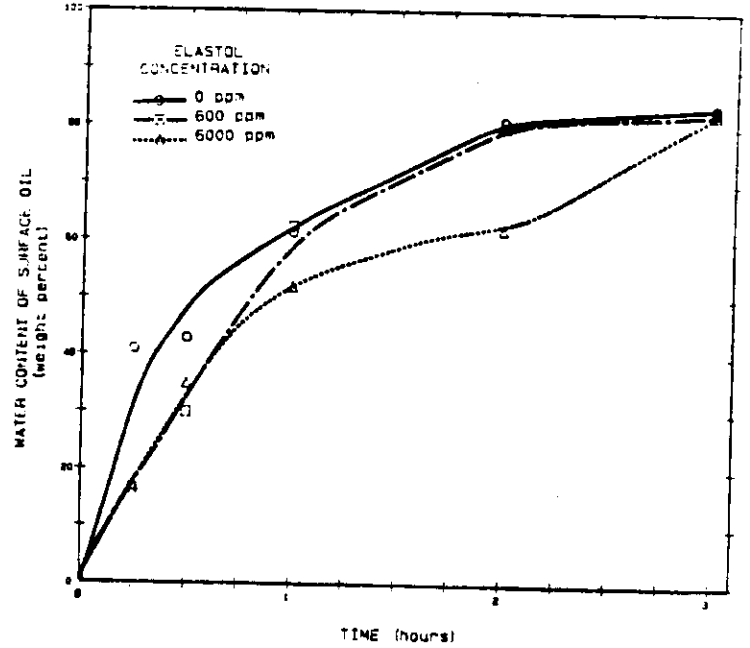


d) Die swell versus time.

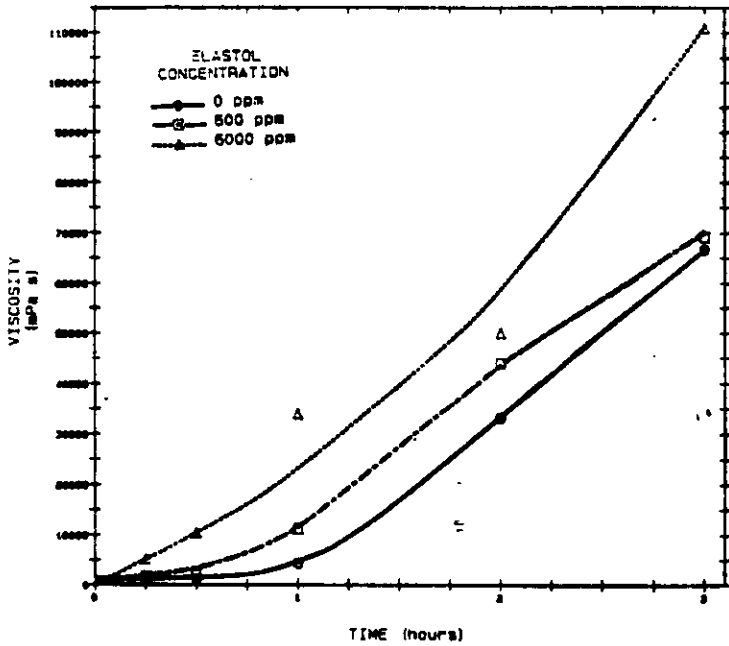
Figure 3-7. Small-scale tank tests for ASMB at 0 deg. C. and 150 r.p.m.



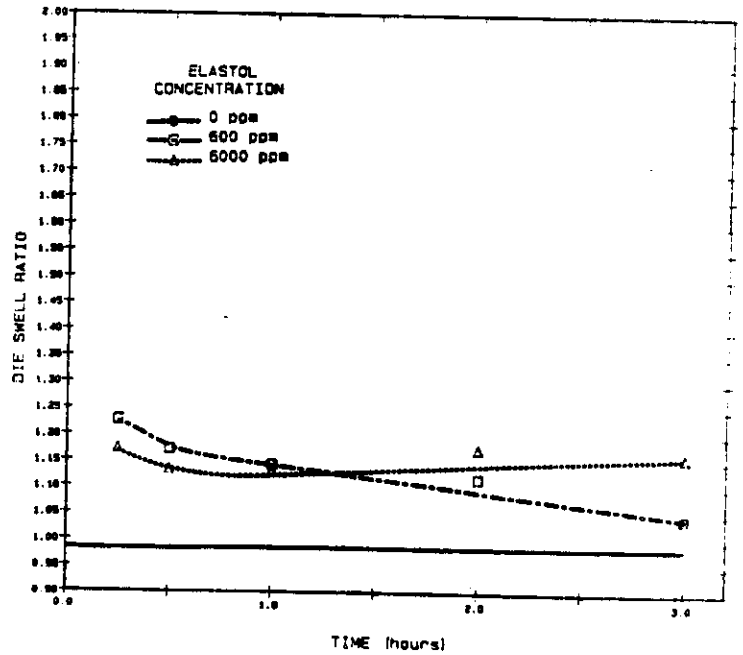
a) Dispersion versus time.



b) Emulsification versus time.

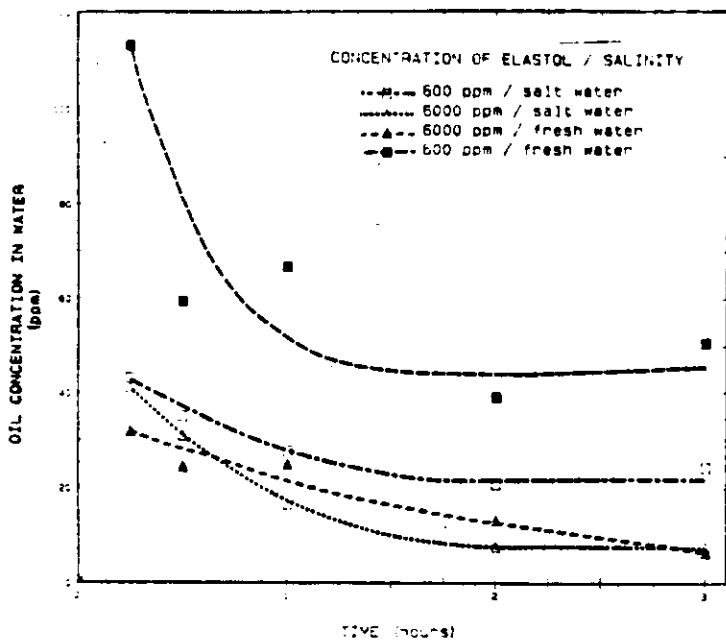


c) Viscosity versus time.

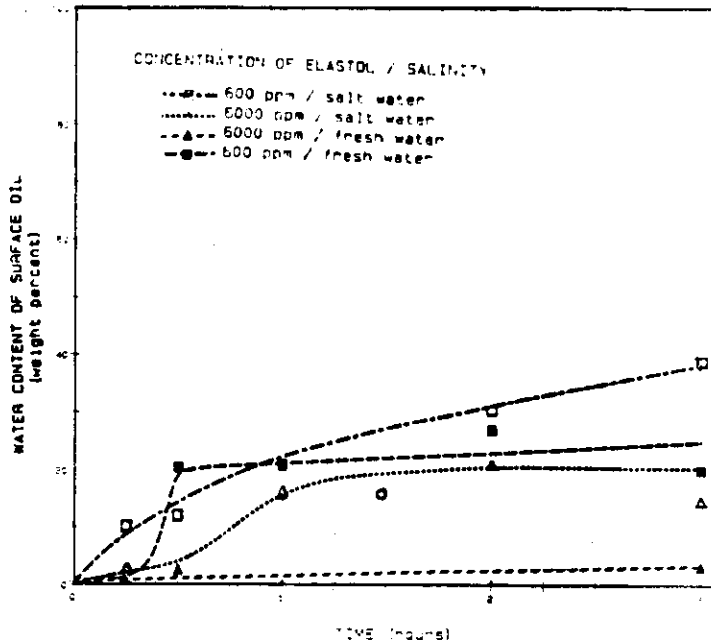


d) Die swell versus time.

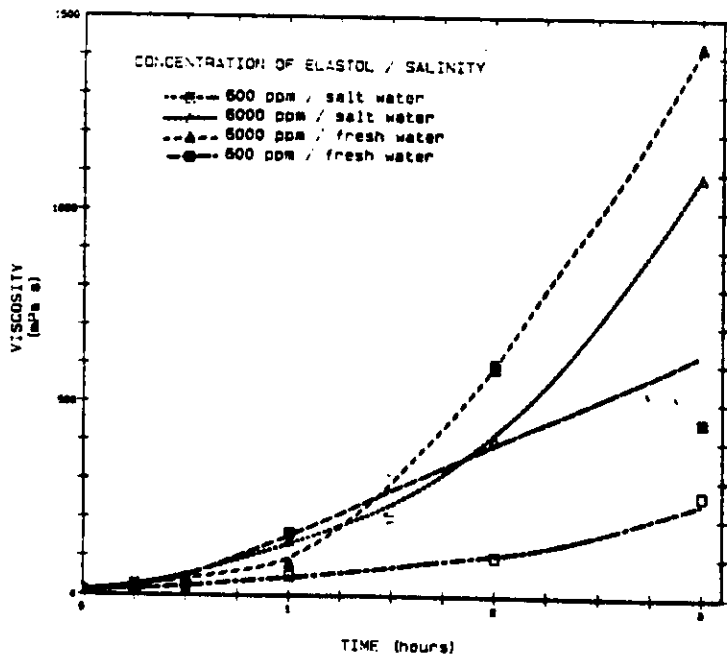
Figure 3-8. Small-scale tank tests for Emulsifying Mix at 0 deg. C and 150 r.p.m.



a) Dispersion versus time.

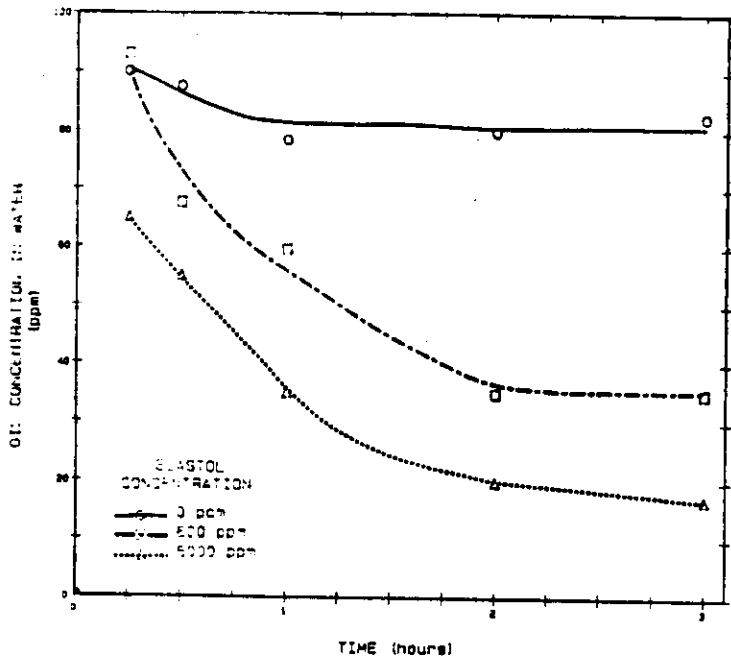


b) Emulsification versus time.

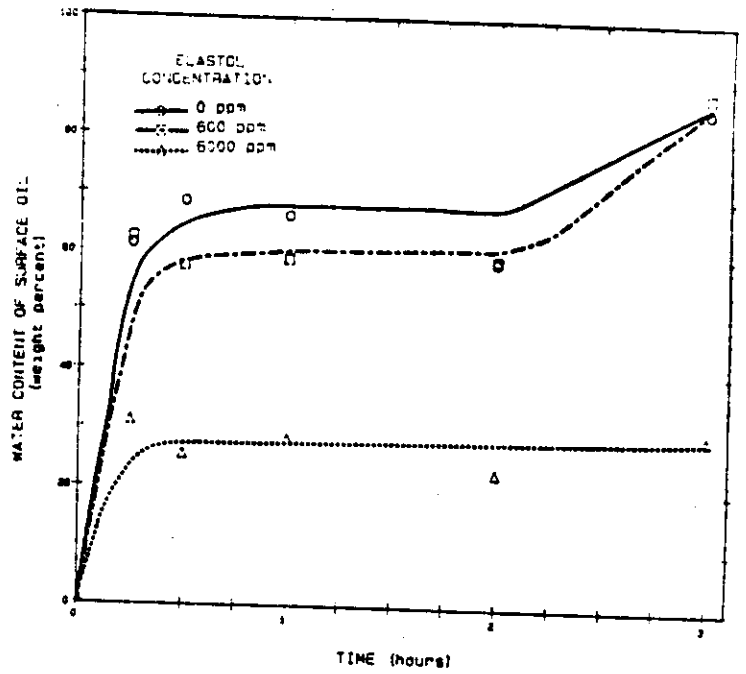


c) Viscosity versus time.

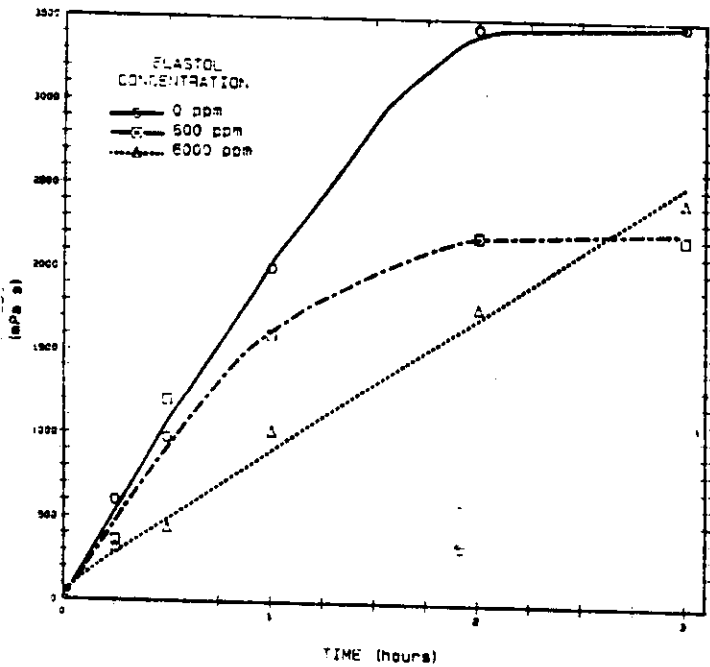
Figure 3-9 Effect of salinity on small-scale tank tests for ASMB at 150 r.p.m.



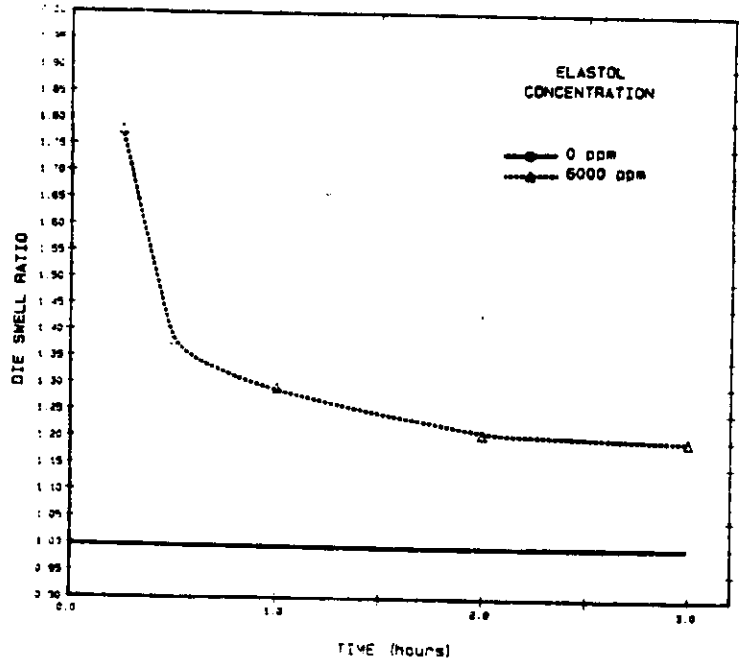
a) Dispersion versus time.



b) Emulsification versus time.

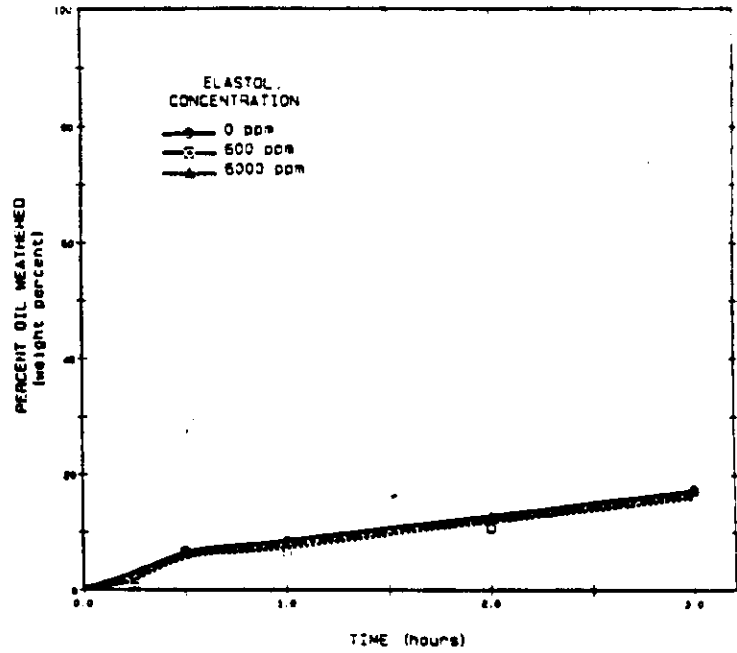
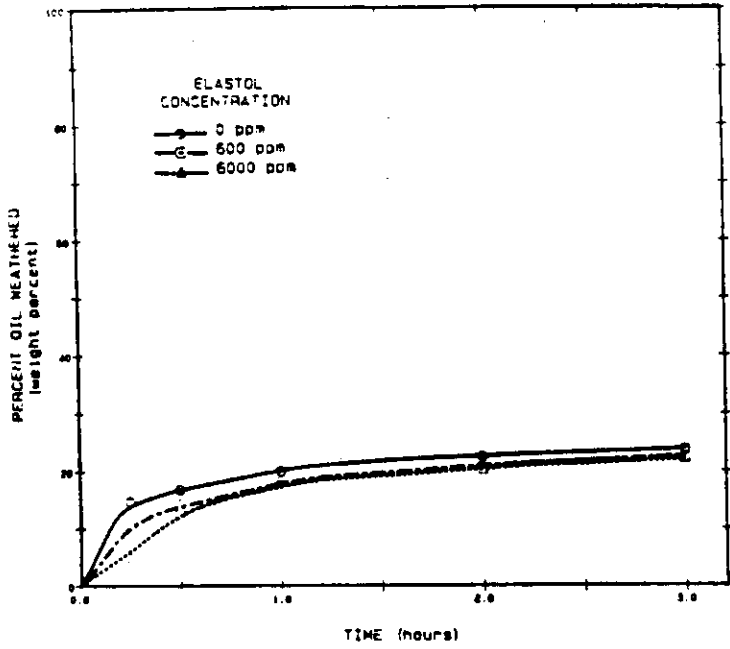


c) Viscosity versus time.



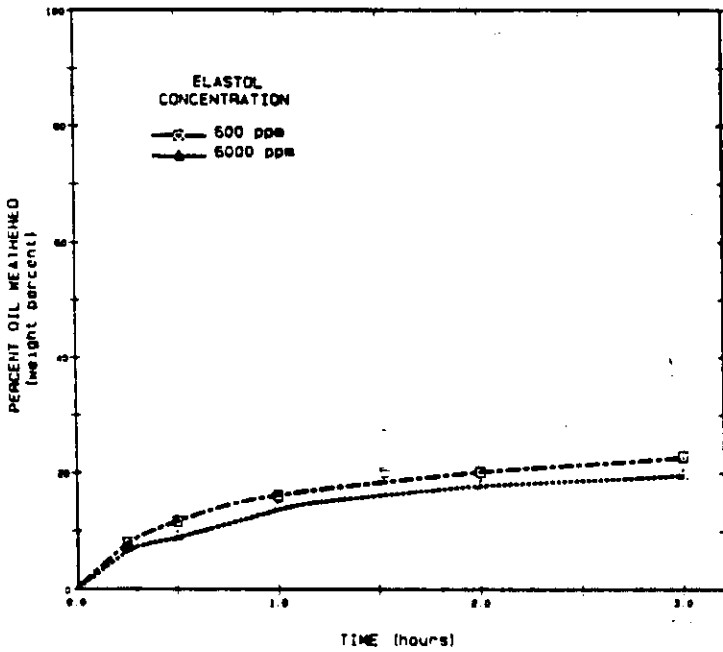
d) Die swell versus time.

Figure 3-10. Small-scale tank tests for ASMB 15% weathered at 15 deg. C and 150 r.p.m.

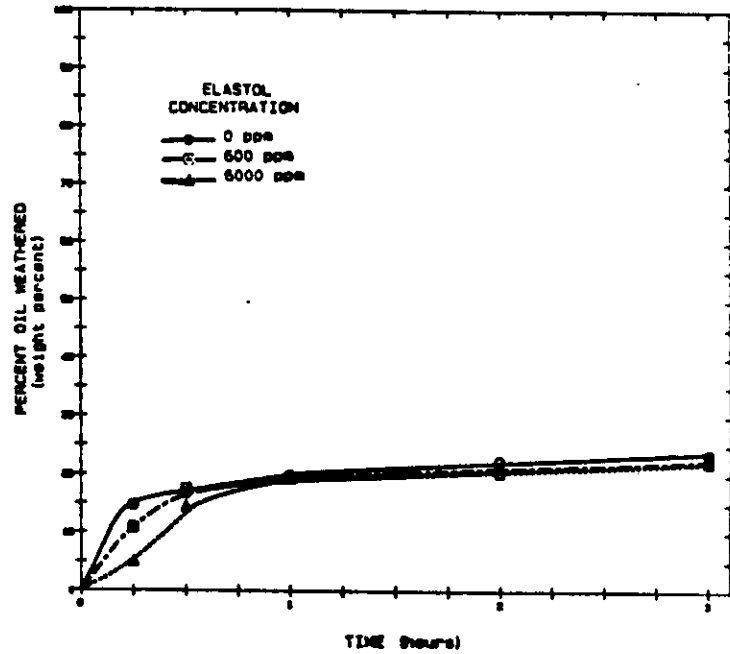


a) ASMB: 15 Deg. C, 150 r.p.m., Salt water.

b) ASMB: 0 Deg. C, 150 r.p.m., Salt water.

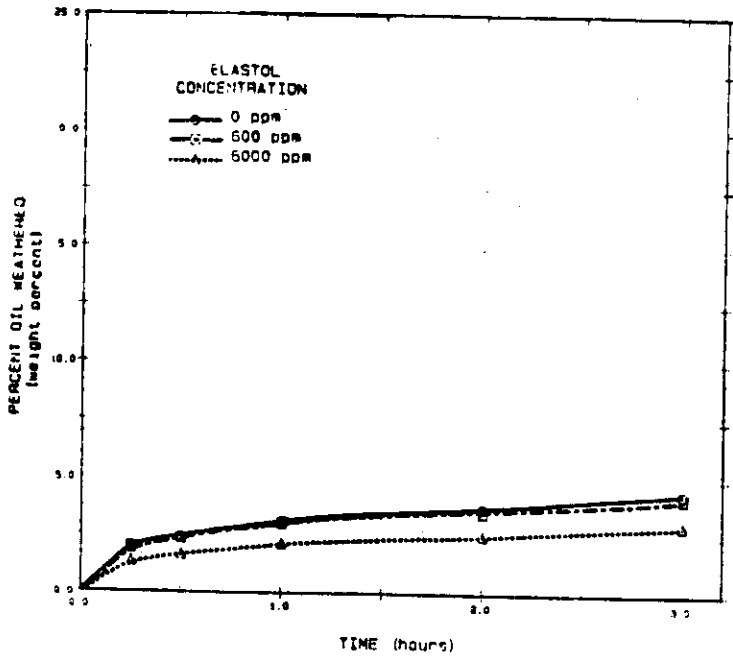


c) ASMB: 15 Deg. C, 150 r.p.m., Fresh water.

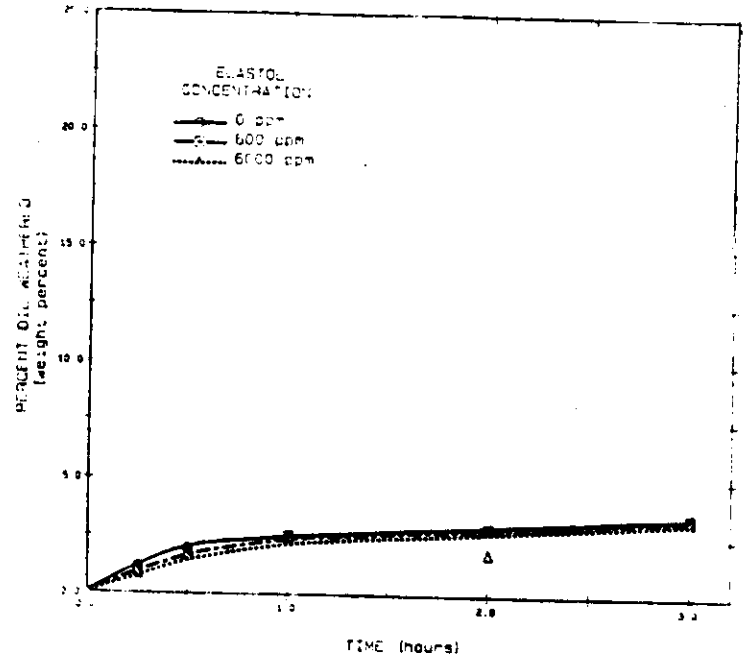


d) ASMB: 15 Deg. C, 220 r.p.m., Salt water.

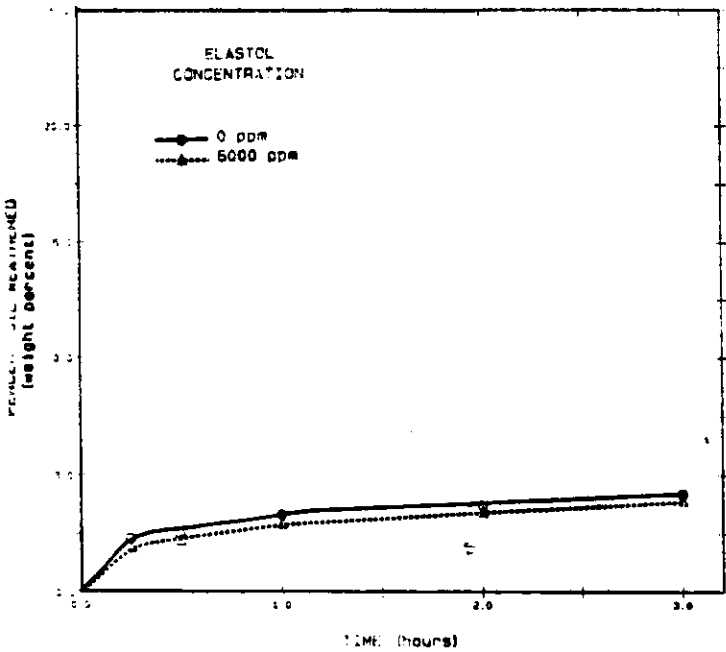
Figure 3-11. Weathering versus time.



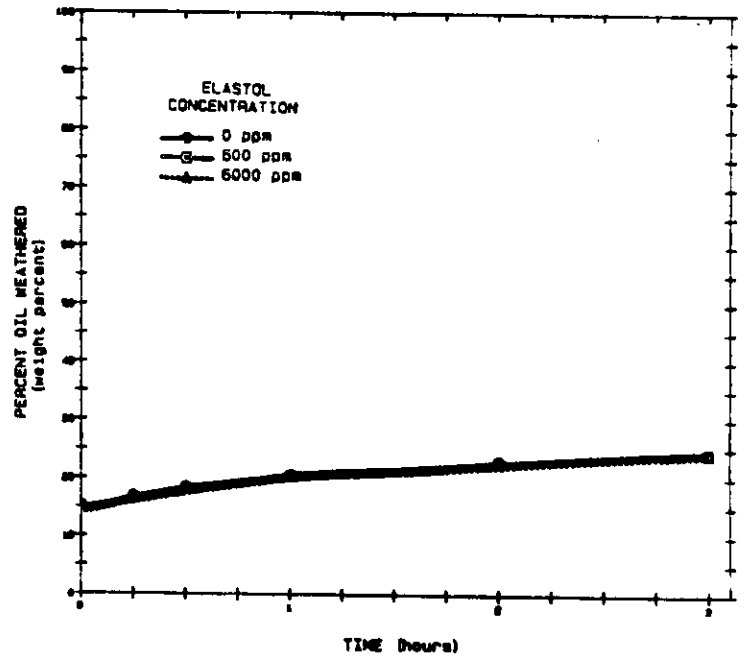
a) Emulsifying Mix: 15 Deg C, 150 r.p.m., Salt water.



b) Emulsifying Mix: 0 Deg C, 150 r.p.m., Salt water.



c) Emulsifying Mix: 15 Deg. C, 220 r.p.m., Salt water.



d) ASMB weathered 15%: 15 Deg. C, 150 r.p.m., Salt water.

Figure 3-12. Weathering versus time.

3.4 Conclusions

The following conclusions were drawn from the small-scale wave generating tank experiments:

- * The addition of Elastol did not significantly affect the rate of weathering.

- * The amount of oil dispersed in the water phase decreased with increasing Elastol concentration.

- * With the exception of the Emulsifying Mix at 0 deg C, the extent of emulsification decreased with increasing Elastol addition.

- * Elastol-treated oil slicks generally exhibited a slower rate of increase in viscosity.

- * Elastol applied at a dose of 6000 ppm imparted significant elastic property to all the oils tested (ASMB, Emulsifying Mix, and 15% weathered ASMB). Only a moderate (ASMB) or insignificant (Emulsifying Mix) increase in elasticity was observed at a dose of 600 ppm.

- * Significant emulsion formation decreased the effectiveness of Elastol to impart elasticity.

- * The elasticity of ASMB increased with greater mixing energy. The opposite occurred for Emulsifying Mix, due to increased emulsion formation.

- * Reaction times of 1 to 1.5 hours at 15 deg C and 2 to 3 hours at 0 deg C for ASMB and 2 hours for Emulsifying Mix at 15 deg C were observed.

- * Oil slicks on fresh water exhibited a slightly greater increase in elasticity than on salt water.

4. EFFECT OF ELASTOL ON OTHER SPILL TREATING AGENTS

4.1 Objective

The goal of this study was to determine the effect of Elastol on the performance of two surfactant-based oil spill treating agents: Corexit 9527 oil dispersant and Brand S, an emulsion inhibitor. In a recent study (S.L.Ross, 1986), Brand S showed the most promise among several other emulsion inhibiting surfactants.

4.2 Experimental

To determine the effect of Elastol on the performance of Corexit 9527, experiments were conducted in the small-scale wave generating tank described in Section 3.2. The oil used in this study was ASMB. Two tests were performed: one in which 6000 ppm of Elastol was added to the oil slick 1 hour prior to the application of the dispersant (dispersant-to-oil volume ratio of 1:100), followed by a control experiment in which only the dispersant was introduced 1 hour after the addition of oil in the tank. Only water samples were taken at the sampling times outlined in Section 3.2 (time zero was identified at the point of dispersant addition).

The study to determine the effect of Elastol on the emulsion inhibitor was conducted in the emulsion apparatus described in Section 2.7.1. Four oils were employed: ASMB, Emulsifying Mix, Amauliqak and Tarsiut. For each of these oils, two tests were conducted: one with the additions of Elastol at a concentration of 6000 ppm and Brand S at an oil-to-surfactant volume ratio of 1:1500; and a control test, in which only Brand S was added. The treating agents were introduced to the oil samples prior to the start of the experiment. The procedure outlined in Section 2.7.1 was then followed. Observations were recorded at the end of each settling period to determine the performance of Brand S for the oils treated with Elastol.

4.3 Results and Discussion

i) Dispersant Effectiveness

The results from the analysis of water samples for both Oil-Corexit-Elastol and Oil-Corexit (control) tests are presented in Figure 4.1. It is clear from the figure that the addition of Elastol reduced the effectiveness of the dispersant, as indicated by the lower oil content in the water phase (reduction of approximately 70%).

In both oil tests, the water became distinctly cloudy with dispersed oil within 15 minutes of dispersant application. In the test where no Elastol was added, the surface slick quickly decreased in size and by the end of the run, the slick had almost disappeared. The Elastol-treated slick also showed a marked decrease in size but a surface slick of about half its initial size was still present at the end of the test. The elastic nature of the oil slick did not appear to be affected by the dispersant.

ii) Effect of Emulsion Inhibitor

The addition of Elastol to Brand S treated oils had no effect on the effectiveness of this emulsion inhibitor. No emulsions were formed by oils treated with Brand S.

4.4. Conclusions

Elastol reduced the effectiveness of Corexit 9527 in dispersing the oil slick by 70%.

The application of Elastol had no effect on the performance of Brand S in inhibiting emulsion formation for the four oils tested.

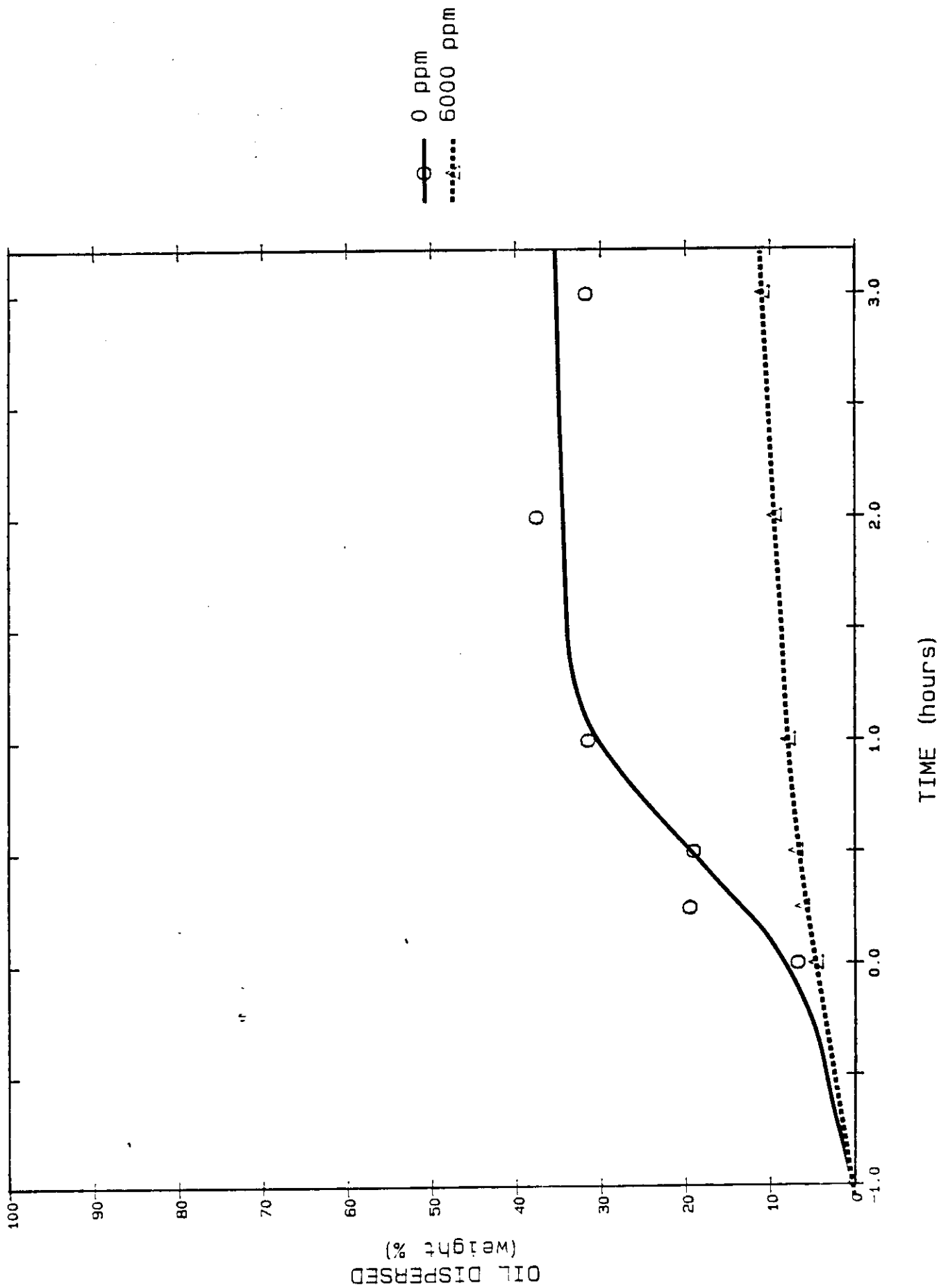


FIGURE 4-1. OIL DISPERSED VERSUS TIME FOR ASMB WITH 1:100 COREXIT AT 15 DEG. C.

5. PRELIMINARY LARGE-SCALE TANK TESTS AT ESSO

5.1 Purpose

The prime purpose was to test Elastol on a larger scale and to see what occurred in a situation involving waves. The questions of what it did in waves - would it break up and was there any potential for burning - had to be answered before proceeding on with many lab tests.

5.2 Procedure

Seventy-five litres of Norman Wells crude oil were placed in a boom, then Elastol (at a concentration of 6700 ppm) was added by casting the powder from jars. This was done in a random and unscientific manner. Samples of the oil were taken and analyzed for viscosity at 0, 20, 80 and 230 minutes after the application of Elastol. Analysis was performed using a FANN viscometer. At least two RPM settings were used and the results averaged.

The wave generators were turned on after the Elastol was applied and were turned off again for sample taking. The wave height was about 1/2 metre on the first day and about 1/4 metre on the second day. The respective temperatures of the tank and air were 3 and 5 degrees C.

5.3 Results and Discussion

(1) Observations Day 1: Numerical results for both days are shown in Figure 5.1.

The wave energy on day 1 was very high and subsequently much of the oil splashed over a cusp of the boom in the first few minutes. Because this occurred very rapidly, it is difficult to say what effect the Elastol had on oil containment dynamics. This loss of oil made sampling difficult as little oil was left in the boom. The oil that escaped stuck to the new steel beach and the walls of the tank. Interestingly, the oil appeared to be uniformly elastic, even though it was spread all over. At the 20 minute sampling time there was still undissolved Elastol in the samples in the boom.

At the end of the experiment, the oil was highly elastic and was very difficult to get into a bottle. The oil certainly did not break down in the waves. Little oil remained in the booms to assess its burnability.

(ii) Observations Day 2: The wave height was much lower than in day 1 and, with adjustments to the boom, no oil splashed over.

The oil remained in the boom and progressively became thicker during the day. Unmixed Elastol particles were still in the oil at the 80 minute sampling time. Mixing and elasticity were much less than the previous day. This can be seen from the graph (Figure 5.1).

At the end of the experiment a Morris skimmer was used to recover the oil. It was too windy to attempt a burn. The skimmer recovered 70 litres (75 were spilled) and water was not evident! Obviously, the oil did not weather much or recovered water made up for the difference. The final area of the slick was estimated to be 6 to 10 square metres and this would give an average slick thickness of 7 to 11 mm whereas 3 is the minimum for burning.

5.3 Conclusions

* Moderate wave energy as employed here does not break down the polymer elasticity, in fact it appears to improve mixing and thus speeds up the elasticity development.

* The recovery rate and extent achieved in the second day experiment was dramatic and is convincing evidence that Elastol is useful for such countermeasures.

* The oil on the second day was sufficiently thickened to allow for burning.

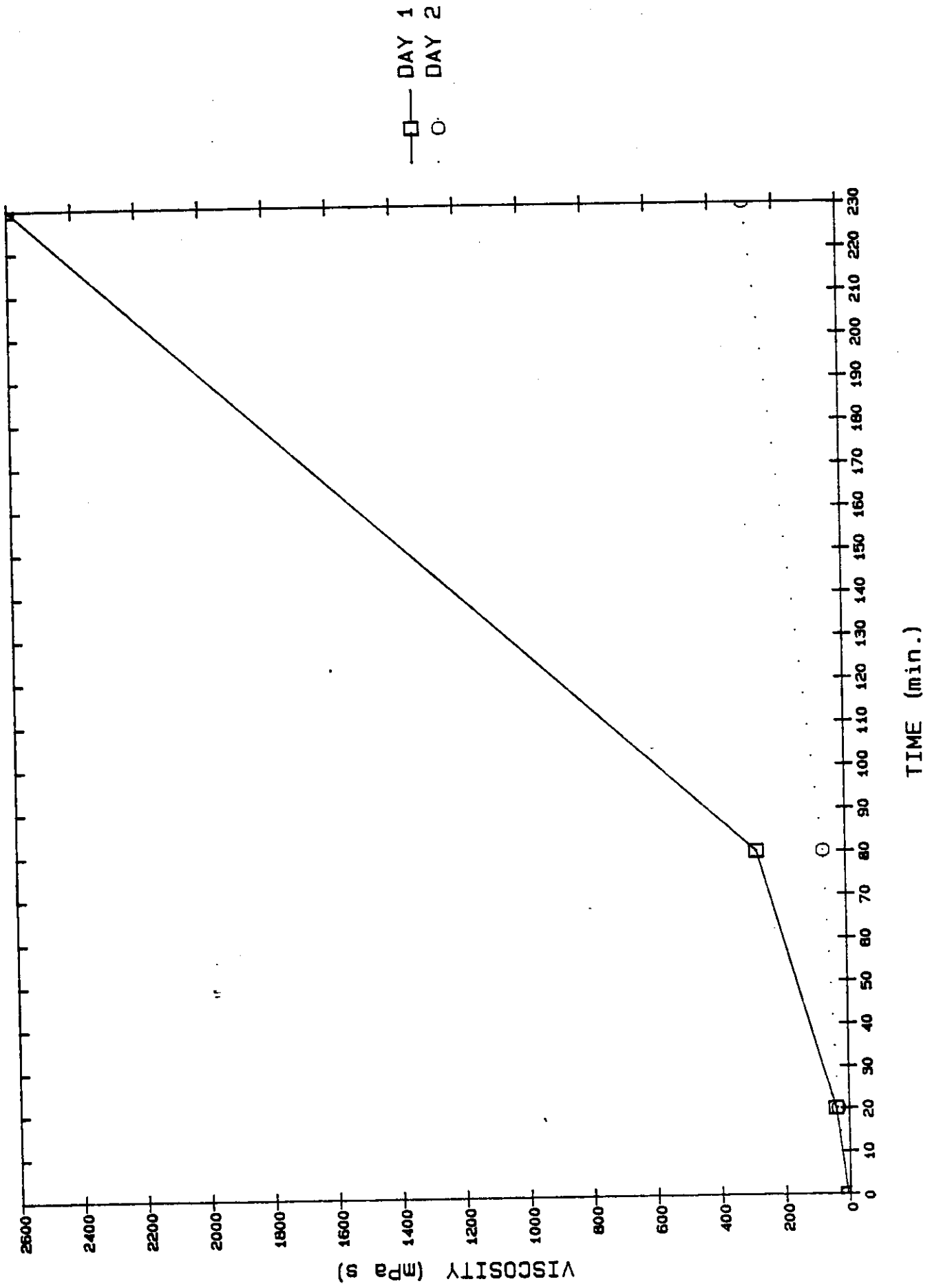


FIGURE 5-1. VISCOSITY VERSUS TIME FOR LARGE-SCALE TANK TESTS;

6. CONCLUSIONS

* All oils tested displayed viscoelastic properties when treated with doses of 600 to 6000 ppm Elastol. The time for Elastol to take effect and the degree of elasticity achieved were different for each oil. No simple correlation between an oil property and Elastol effectiveness was established. In general, more viscous oils attained a relatively higher degree of elasticity than less viscous oils. The more viscous oils tended to take longer to "react". Elastol's effectiveness was enhanced by mixing and higher temperatures.

* In this study, the oils exhibited some degree of elasticity within 15 minutes of Elastol application. But a high degree of elasticity was not observed until after one hour.

* Elastol caused a minor reduction in the rate of oil evaporation and had no effect on flash point.

* Elastol reduces slick spreading, and at sufficiently high doses (>1%) can cause the slick to contract.

* With the exception of Amauligak and Tarsiut crude oils, the addition of Elastol to oil either had no effect or an inhibiting effect on emulsification. There is also some evidence that the application of Elastol to emulsified oil leads to demulsification (water is forced out of the water-in-oil emulsion).

* Elastol did not affect the performance of Brand S emulsion inhibitor.

* The experiments performed in the small-scale tank showed that the application of Elastol to oil slicks suppressed both natural and chemical dispersion and the degree of emulsification. Treated slicks also exhibited significantly lower viscosities than untreated oils.

* Significant emulsion formation decreased the effectiveness of Elastol.

* The results from the large-scale tank tests showed that moderate wave energy enhanced Elastol effectiveness. The thickness of the treated slick was believed to be sufficient to allow for burning. The skimmer recovered 93% of the oil spilled and no water was observed in the oil.

* The die swell apparatus developed for this study to provide real-time measurement of elasticity worked well under ideal laboratory conditions. It displayed good sensitivity to polymer concentration and to the degree of observed elasticity. But the presence of emulsified oil suppressed die swell and thus probably resulted in an underestimation of the degree of elasticity for the small-scale tank tests. Nevertheless, die swell itself is a viscoelastic phenomenon and the apparatus as-is provides an indication of elasticity.

* Elastol reduces 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.

7. RECOMMENDATIONS

As stated in Section 3.3.5, the presence of water droplets in emulsified oil suppressed the die swell. The present design of the die swell apparatus utilizes an air-pressure driven piston to induce the flow of the sample through the needle. This design worked well for non-emulsified oils and resulted in a flow through the needle that is in the desired Reynold's number (>100) regime (Mannheimer, 1986). Emulsions, on the other hand, have extremely high viscosities and can exhibit pseudoplastic rheological behaviour. This results in greater resistance to flow and thus lowers the Reynold's number into an undesirable regime. It is felt that the present design can be improved by replacing the air-pressure driven piston with a motorized constant-speed plunger. This would eliminate the problem of the dependence of flowrate on viscosity.

The problem of the presence of water droplets and small nodules of polymer, which act as fillers that suppress the die swell, may be harder to resolve. Some method of demulsification will be necessary. It was observed that the process of passing the samples through the die swell apparatus resulted in some demulsification. Therefore, repeating this procedure several times may reduce the water content in the oil phase to an acceptable level.

Other recommendations are listed below:

* Further study should be performed to correlate the effectiveness of Elastol and its reaction time with oil properties and composition.

* The role of Elastol in the emulsification process and in the increase in viscoelasticity should be studied.

* Further testing of Elastol on oils not employed in this study should be conducted.

* Further large-scale testing under real or simulated environmental conditions is recommended.

* During the initial stages of this study, several methods of mixing oil and Elastol were examined. It was observed that under static conditions Elastol sank to the bottom of the oil layer, thereby imparting greater elasticity near the bottom of the oil than at the surface. Therefore, studies to determine the effect of slick thickness on Elastol's effectiveness should be undertaken.

* Correlation between the degree of viscoelastic increase and the efficiency of oil spill cleanup procedure and equipment should be established.

8. REFERENCES

Bird R., Armstrong R., Hassager O. Dynamics of Polymeric Liquids John Wiley and Sons, New York, 1977.

Bobra M.A., Chung P.T. A Catalogue of Oil Properties EPS Report EE77, Environment Canada, 1986.

Burwood R., Speers G.C. "Photooxidation as a Factor in the Environmental Dispersal of Crude Oil" Estuarine Coastal Mar. Sci. 2:117-135, (1974).

Chao K.K., Child C.A., Grens E.A.II, Williams M.C. "Antimisting Action of Polymeric Additives in Jet Fuels" AIChE Journal 30 (1), 111-119, (1984).

Hadermann A.F., Trippe J.C., Water P.F. "The Effects of the Molecular Weight of Additive on the Properties of Antimisting Fuels" Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society Washington D.C. Meeting, Aug.28-Sept.2, 1153-1156, (1983).

Hill G.A., Chenier C.L. "Die Swell Experiments for Newtonian Fluids" The Canadian Journal of Chemical Engineering 62, 40-45, (1984).

Mackay D., Zagorski W. Studies of Water-in-Oil Emulsions EPS Report EE34, Environment Canada, 1982.

Mannheimer R.J. "Die Swell of Antimisting Kerosene: Parts 1 and 2" Chem.Eng. Commun. 48, 57-77;79-92, (1986).

Mao M.L., Marsden S.S. J. Can. Petrol Tech. 16 (2), 54-59, (1977).

Middleman S. Fundamentals of Polymer Processing McGraw Hill, New York, 1977.

Samara M.K. Design and Construction of a Computerized Die Swell Apparatus M.Eng Thesis, McGill University, Montreal, 1985.

S.L.Ross Environmental Research Limited. An Experimental Study of Oil Spill Treating Agents That Inhibit Emulsification and Promote Dispersion EPS Report EE87, Environment Canada, 1986.

Vlachopoulos J. Reviews on the Deformation Behaviour of Materials III, 4, 219, 1981.

Water P. Hadermann A.F. "The Efficiency of Elastomers in Oil Spill Cleanup" 1987 Oil Spill Conference Proceedings 231-233, (1987).

APPENDIX I

PHYSICAL-CHEMICAL PROPERTIES

OF TEST OILS

Data taken from Bobra and Chung (1986).

ALBERTA SWEET MIXED BLEND CRUDE OIL

Temperature (deg C)	DENSITY (g/mL)		DYNAMIC VISCOSITY (mPas)	
	Weathering (vol %)		Weathering (vol %)	
	0	15	0	15
0	0.847	0.874	47.3	7500
15	0.839	0.868	9.2	43.5

Temperature (deg C)	AIR/OIL INTERFACIAL TENSION (dynes/cm)		OIL/SEAWATER INTERFACIAL TENSION (dynes/cm)	
	Weathering (vol %)		Weathering (vol %)	
	0	15	0	15
0	32.0	--	17.5	--
15	25.6	28.1	8.4	8.6

POUR POINT

0 % Weathered: -8 deg C
 15% Weathered: 7 deg C.

FLASH POINT: 7 deg C (fresh crude).

DISTILLATION DATA (Temperature in deg C)

Volume %	Modified ASTM D 86 Distillation	ASTM D 86 Distillation
IBP	155	37
5	158	95
10	182	111
15	206	126
20	234	142
25	260	155
30	286	198
35	304	213

AMAULIGAK CRUDE OIL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Air/Oil Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.901	25.0	30.0	31.1
15	0.890	14.0	29.2	29.0

POUR POINT: less than -25 deg C.

FLASH POINT: 0 deg C.

DISTILLATION DATA: (Temperature in deg C)

Volume %	Modified ASTM D 86 Distillation	ASTM D 86 Distillation
IBP	198	66
5	216	134
10	238	156
15	259	172
20	275	187
25	289	194
29	301	246

BENT HORN CRUDE OIL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Air/Oil Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.830	53.8	27.7	53.5
15	0.818	24.0	26.2	38.5

POUR POINT: -18 deg C.

FLASH POINT: -9 deg C.

DISTILLATION DATA (Temperature in deg C)

Volume %	Modified ASTM D 86 Distillation	ASTM D 86 Distillation
IBP	111	33
5	164	89
10	187	110
15	210	130
20	235	147
25	259	174
30	284	188
34	305	203

DIESEL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Air/Oil Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.838	3.9	27.7	28.2
15	0.827	2.7	26.0	28.0

POUR POINT: -20 deg C.

FLASH POINT: 52 deg C.

EMULSIFYING MIX (50% ASMB, 50% BUNKER C)

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)
0	0.920	360
15	0.908	140

HYBERNIA CRUDE OIL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Air/Oil Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.897	10155	--	--
15	0.885	44.2	26.2	13.5

POUR POINT: 15 deg C.

FLASH POINT: -14 deg C.

DISTILLATION DATA (deg C)

Volume %	Modified ASTM D 86 Distillation	ASTM D 86 Distillation
IBP	137	34.5
5	217	85
10	252	115
15	282	139
20	311	160
25	336	185
30	359	210
35	382	234
40	400	253
45	417	267
50	428	284
55	440	325

NORMAN WELLS CRUDE OIL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Air/Oil Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.858	---	24.9	16.5
15	0.832	6.0	23.6	16.4

POUR POINT: -50 deg C.

FLASH POINT: 3 deg C.

ASTM DISTILLATION DATA

Volume %	Temperature (deg C)
IBP	60
10	118
20	145
30	174
40	223
50	280

PRUDHOE BAY CRUDE OIL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Air/Oil Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.915	---	30.4	15.0
15	0.905	38.0	28.3	9.7

POUR POINT: -2 deg C.

FLASH POINT: 30 deg C.

ASTM DISTILLATION DATA

Volume %	Temperature (deg C)
IBP	50
10	168
20	235
30	290
40	328

TARSIUT CRUDE OIL

Temperature (deg C)	Density (g/mL)	Dynamic Viscosity (mPa s)	Oil/Air Interfacial Tension (dynes/cm)	Oil/Seawater Interfacial Tension (dynes/cm)
0	0.884	12.3	28.0	16.6
15	0.875	7.4	26.5	14.1

POUR POINT: less than -60 deg C.

FLASH POINT: 65 deg C.

DISTILLATION DATA (deg C)

Volume %	ASTM	Modified ASTM D 86
IBP	82-138	214
5		227
10	168-198	237
15		248
20		261
25		274
30	227-253	287
35		298
40		305
50	274-306	
70	334-371	
90	431-457	
FINAL	567-610	

APPENDIX II: PRODUCT INFORMATION ON ELASTOL

The Solution...

ELASTOL

A major breakthrough for OIL recovery.

Developed especially for containment and recovery of oil on water, this non toxic, free flowing powder dissolves rapidly when dispensed on hydrocarbon liquids, thereby giving them visco-elastic properties.

VISCOELASTICITY

The NEW FORCE in oil spill response is that property which imparts to hydrocarbons a high resistance to being pulled apart or breaking up while remaining in liquid form. This increases the ability for containment and ease of recovery by causing oil to be pulled to the skimmer.

INCREASE PERFORMANCE

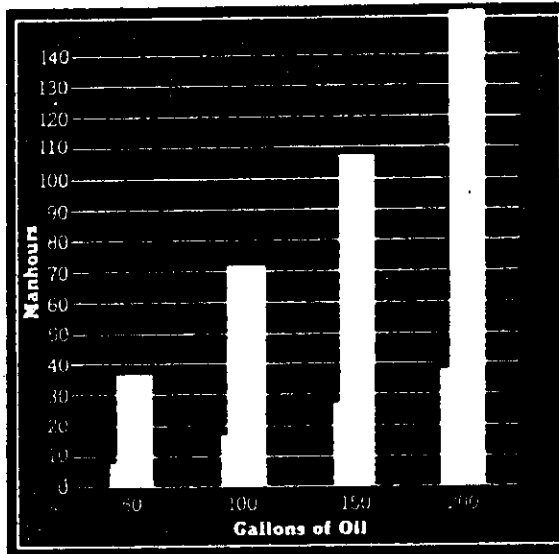
U.S., German, British, and Canadian demonstrations have proven:

- ELASTOL increases performance of your existing mechanical skimming equipment 2 to 5 times over its present rate of recovery.
- ELASTOL used with vacuum systems results in essentially no water pick up.
- ELASTOL used with booms, virtually eliminates entrainment failure and shows successful containment in currents over 1 knot.
- ELASTOL minimizes oil spreading, streaking, and breaking up due to wind and wave conditions of up to 15 knots.
- ELASTOL successfully reduces penetration depth on sandy beaches and shorelines due to washed ashore oil.

DECREASE COST

By reducing both the labor costs at the spill site and the waste disposal factor, these two items alone can save more than 50% of the present cost of recovery. Recovery time using mechanical skimming equipment is reduced to as little as 1/2 to 1/5 the normal recovery rate.

Barring excessive contamination, emulsification, or debris, recovered hydrocarbons are readily reusable, with essentially no other waste to dispose of.



□ with ELASTOL □ without ELASTOL

The "NEW FORCE" at Work

APPLICATION AND DISPENSING

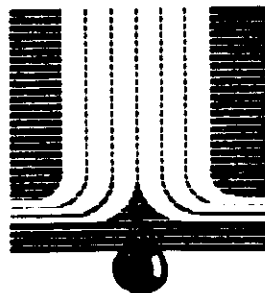
ELASTOL, agglomerated into particles averaging 100 to 1,000 microns, can be dispensed in moderate wind conditions without significant loss. The particles are designed to float and not dissolve until coming in contact with liquid hydrocarbons. ELASTOL is dispensed in a light dusting fashion with most of the conventional shakers, blowers, slingers, sand-blast type educators, and ship or aircraft mounted equipment currently available. Oil is ready for recovery within 5 to 20 minutes after application, depending on its viscosity.

How much ELASTOL to be used depends on viscosity of the hydrocarbon spilled and type of removal device. In most applications, concentrations between 0.1% and 0.5% are required (1,000 ppm = 1:1,000 ratio and 5,000 ppm = 1:200 ratio). Specific requirements can be obtained from your ELASTOL distributor or the GTA factory.

A Product of:

GTA

General Technology Applications, Inc.
7720 Mason King Court
Manassas, Virginia 22110
(703) 631-6655 Telex: 497 4339 GTA UI



Distributed by:

Elastol

A New Approach to Oil Spill Clean Up

Purpose

Elastol, a non-toxic powder, modifies the oil spill so as to speed up its recovery by most current types of skimmer equipments.

Ease of use

Disperse Elastol powder on surface of an oil spill in concentrations of 1,000 to 6,000 parts per million (ppm) powder dissolves upon contact with oil spill giving the oil a viscoelastic property.

Tested and proved

Full-scale tests have demonstrated a five-fold increase in oil recovery rates for vacuum or disc skimmers. Viscoelasticity makes oil recovery possible from a stationary point with virtually total water separation at the point of pick-up.

Applications

Applicable to light and heavy crudes, kerosene, diesel, gasoline, bunker and most other hydrocarbons.

Method of application

This granular powder can be spread on oil spills by commercial air blower systems or airborne powder sprayers.

Background

GTA offers a new approach to oil spill clean up by modifying the behavior of the oil to speed up the clean up process. It increases the capacity of skimmer devices by several times. The Elastol additive is for use with most hydrocarbon spill, under most sea or weather conditions.

Performance features

Elastol imparts a viscoelastic property to the spill which then resists being pulled apart by wind or wave action. With viscoelasticity, a large area of oil spill can be "pulled" to a fixed skimmer operating at many times the capacity it can attain with untreated oil. Viscoelasticity of the oil spill automatically provides water separation at the skimmer.

Elastol is a non-toxic powder, non-agglomerating, and free-flowing. It is easily dispersed over a surface slick.

Elastol requires a nominal ratio of powder to pollution liquid of 6,000 ppm; thus, a 10,000 gallon spill would require less than 500 pounds of Elastol.

Dispersion of the Elastol additive may be easily accomplished because of its basic free-flowing characteristics. Some of the systems that can effectively disperse Elastol are:

- Back pack and manually carried dust blowers
- Ship or airborne powder dispersion systems.

Elastol will significantly improve the performance of most oil spill systems in use today: disc, weir and belt skimmers; paravane towed collectors; suction pick-ups; containment collector booms; barriers; and oil fences.

For oil rig protection or any other stationary polluter (such as a ship at anchor), convenient dispersion methods can be arranged to most effectively provide the requirement pollution control and clean-up.

Elastol specifications

Powder granules

150 to 500 microns in size

Bulk Density

30 #/cu.ft.

Solid Density

Approximately 105 #/cu.ft.

Toxicity

None (basic ingredients currently used in food stuffs)

Shelf Life

At least 3 years at temperatures below 150 °F

Characteristics

Inert, stable, hydrophobic

Color

White

Handling

Maintain dry

For more information, call or write:

General Technology Applications, INC.
Sunrise Technology Park
12343-D Sunrise Valley Drive
Reston, Virginia 22091
Telephone: (703) 476-6280

APPENDIX III: SHEAR RATES FOR VISCOSITY MEASUREMENTS

Shear Rate (sec⁻¹)

SMALL-SCALE WAVE GENERATING TANK TESTS (SECTION 3)

Emulsifying Mix (15 deg C)	1.98
Emulsifying Mix (0 deg C)	0.435
ASMB (15 deg C)	3.96
ASMB (0 deg C)	1.02
15% weathered ASMB (15 deg C)	1.98

INITIAL BENCH-SCALE EXPERIMENTS (SECTION 2.2)

ASMB: (15 deg C) 600 ppm	79.2
6000 ppm	39.6
ASMB: (0 deg C) 600 ppm	3.96
6000 ppm	0.396
Emulsifying Mix: (0 deg C) 600 ppm	0.792
6000 ppm	0.792
Hybernia: (15 deg C) 600 ppm	3.96
6000 ppm	3.96
Diesel: (15 deg C) 600 ppm	79.2
6000 ppm	79.2
Tarsiut: (15 deg C) 600 ppm	79.2
6000 ppm	15.8
Amauligak: (15 deg C) 600 ppm	79.2
6000 ppm	39.6
Bent Horn: (15 deg C) 600 ppm	39.2
6000 ppm	7.92
Norman Wells: (15 deg C) 600 ppm	79.2
6000 ppm	7.92
Prudhoe Bay: (15 deg C) 600 ppm	7.92
6000 ppm	3.96
ASMB: (15 deg C; no mixing) 6000 ppm	39.6
Emulsifying Mix: (15 deg C; no mixing) 6000 ppm	3.96

