
THE EFFECTIVENESS OF SOLIDIFIERS FOR COMBATTING OIL SPILLS

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The Effectiveness of Solidifiers for Combatting Oil Spills

Abstract

An extensive laboratory investigation was conducted to develop methods for screening commercial solidifier products for their effectiveness in an oil spill scenario. A total of five laboratory procedures were developed. The accumulation of data obtained from these testing methods resulted in the development of factors that can be used to compare various solidifier products in different oil spill conditions. In this study, 23 solidifiers were procured and tested, six solidifier products were identified but not tested due to the unavailability of the products, and three crude oil samples were used as the medium for solidification. There are currently no criteria for selection of solidifiers, and there is no standard procedure to test solidifiers. The laboratory methods chosen and developed for this purpose were: static test, dynamic test, byproduct rheometry, calorimetry, spill characterization, and solidification phase viscometry. Additional tests are necessary in order to refine and further optimize the screening and selection of commercially available solidifiers. The results of this study show that solidification is a viable method for controlling and remediating oil spills. The testing methods developed in this study can evaluate the rate and extent of solidifiers' application for oil spill cleanup. Feasibility and toxicity studies have yet to be carried out.

1.0 Introduction

Every year oil spills occur, often causing economical, social and environmental problems. In order to minimize the impacts of oil spills, we propose the use of "solidifiers" as a method of preventing spill propagation and dispersion. By solidifying the oil, the resulting differential or viscosity contrast between the oil and the adjacent body of water slows the spill's spread. This slow-down of spill velocity could potentially lessen the environmental and economic impact of the oil spill. The objective of this project was to evaluate the effectiveness of available solidifiers and to propose methods for overcoming any problems found.

Oil spills vary in magnitude, location and the degree of soil, water, and debris contamination. In addition to accidental spills, oily waters are found in petroleum production (produced water), numerous waste pits, and manufacturing operations involving lubricating oils. Although each situation calls for a special set of operations, it is useful to develop a generalized approach that can be adopted to specific conditions.

The basic methods used for oil spill collection and cleanup are:

- use of dispersant;
- use of booms, slick lickers, skimmers and absorbent pads;
- biodegradation;
- *in situ* burning.

1.1 Statement of the Problem

Environmental regulations in the last ten years have raised the cost of hazardous waste disposal. Costs associated with disposal include:

- application of labor time to the liquid control problem during containment, deployment, pick-up, and disposal;
- reduction of industrial injury;
- improved quality control;
- reclamation of valuable liquids;
- future risks due to improper disposal.

Efficiency, cost and convenience are of major importance. The industrial race is on to find spill removal techniques that can: (1) minimize waste disposal volume and permit liquid reclamation, (2) remove more liquid per unit to minimize disposal and handling costs, and (3) remove the spilled liquid from the environment totally and completely.

1.2 Spill Remediation Technologies and Solidifiers

The U.S. Coast Guard, A.S.T.M. and the Canadian General Standards Board have actively engaged in developing standards for initial and long-term oil spill remediation technologies. All hydrocarbon

spills are different. An integrated cleanup system that works reasonably well for several different types of spills (e.g., for viscous oil and low viscosity oil) is preferable to one that works well in one situation but poorly in another. The behavior of spilled hydrocarbons changes under varying physical, chemical and biological processes. These processes are collectively called "weathering" and include:

- natural dispersion into the water column evaporation
- biodegradation and photolysis spreading
- emulsification sinking
- dissolution.

The significance of these processes on the fate and behavior of spilled oil is determined by a number of factors, such as the type of oil spilled and oceanographic and meteorological conditions.

Solidifiers can be used to render the spill's oil phase viscous and suspended, thus immobilizing the spill's mass. The desirable characteristics of solidifiers are: buoyancy, low water pick up, high oil pick up, low rate of release, and re-use potential.

2.0 Literature Review

2.1 State of Technology

Tennyson (1991) confirmed the fact that more research has to be done in the field of oil spill response. A number of factors must be considered to evaluate the adequacy of oil spill response. These include sea state, weather conditions, type of oil, size of spill, elapsed time from spill to response, presence of ice and level of response effectiveness. The important factors in oil spill response are detection, containment, recovery, chemical treating agents, *in situ* burning, oil characterization and shoreline cleanup.

Reducing the adverse environmental effects of oil spills has always been the goal of the response efforts in United States. Traditional mechanical techniques, such as booms and skimmers, are unable to serve as instant solutions. Encounter rates, weather, and other conditions limit the operation and effectiveness of mechanical countermeasures. Additional techniques are needed to enhance the capabilities of mechanical countermeasures for controlling the effects of large waterborne oil spills.

In his comprehensive review of oil spill treating technology, Fingas (1992) describes four basic approaches to the problem:

1. Surface washing agents: These are products that remove the sticky oil from solid surfaces. An example of a product developed after the *Exxon Valdez* spill is Corexit 9580. This product has been tested by Environment Canada by immersing rock baskets in oil, treating them with Corexit 9580, and finally rinsing the baskets with water. Even though the product removed only 47% of the oil, Corexit 9580 has been accepted among industrial users as more effective than comparable products. The added advantage of Corexit 9580 is its non-toxic nature (LC₅₀ greater than 5000, mg/L) (Fingas *et al.* 1991).

2. Recovery agents: These agents are designed to improve the efficiency of closed vessels like skimmers. Recovery agents are most suited to light oils and fuel spills, and do not work well in open seas. These products function as viscosifiers and make the spill's texture similar to honey or ketchup. An example of this product is Elastol (Fingas *et al.* 1991).

3. De-emulsifying agents: These agents are surfactants with a hydrophilic-lithophilic balance that prevents or breaks up emulsification of water in oil. The most effective of these agents are more soluble in oil and water. Examples of de-emulsifying agents are Demoussifier (trade name of Environment Canada), LA 1834 (Shell), Breaxit (Exxon), and sodium dioctyl sulfosuccinate. Among these, Demoussifier at a dosage level of 500 PPM has been found effective. To assess the effectiveness of de-emulsifiers, at least seven tests have been proposed and efforts are still continuing to improve the test methods (Fingas *et al.* 1993).

4. Solidifiers: Solidifiers change oil from liquid to solid. They often consist of polymerization catalysts and cross-linking agents, and are available in dry granular form. The solidifiers vary from sorbents in that they bond the liquid into a solid carpet-like mass with minimal volume increase, and retain the liquid for easy removal. The bonded material also eliminates a dripping-sponge effect by not allowing the material to be squeezed out, thereby minimizing residue or contamination (PERF 1992). The oil can actually turn into a rubber-like substance if enough high molecular weight polymer is added.

Certain solidifiers (encapsulating agents) typically immobilize the oil within the product. The reaction of some solidifiers with the oil is not reversible and the oil can be recovered from some of these agents after solidification. These solidifiers are two or more compounds applied as separate entities that react and form a gel-like structure. The components are composed of polymerization catalysts and cross linking agents and must be mixed uniformly for gelling to occur (Fingas *et al.* 1991). The mechanical strength of gels is weak; thus they can be broken down and the oil returned to its original liquid state.

Solidifiers have only been used on very small oil spills on land or on restricted waterways (Schluze, 1993). There has been little documented use of solidifiers on large spills or on open water. Examples of solidifiers are Rigid Oil (British Petroleum) and Amines with cross-linkers proposed by Japanese. The problems associated with the solidifiers, according to test results conducted in France, appear to be: (1) the reaction of cross-linkers with portions of oil that are in direct contact resulting in non-uniform solidification, (2) the non-selective nature of cross-linkers that will solidify anything that contains hydrocarbons including weeds and other organic matters, (3) mechanical difficulty in removing the solidified spill since it cannot be pumped, and (4) the large amount of solidifier that is required to cross-link and solidify the oil spill.

In light of the above review of oil spill treatment technology, we believe that solidifiers may reduce the spread of waterborne oil and increase removal rates.

There are a number of issues involved in the utilization of solidifiers to combat oil spills. Their impact on habitat should be investigated as should applicable application rates, development of application techniques for oil spills on water, and guidance on pick-up and disposal of treated oil. In fact, the solidifiers' LC₅₀ must be determined before the effectiveness and economics of the solidifying agents can be tested.

The effectiveness of a solidifier is based on the amount of product and time it takes to "fix" a given volume of oil. Preliminary limited tests of a few products found that generally between 13 to 44 % by weight of the product to oil was required to solidify a sweet crude oil over a 30 minute period (Walker *et al.* 1993). However, the question of environmental safety (toxicity) of solidifiers has not been fully addressed.

Good oil-bonding solidifiers are available with average pick up ratios of 10 % by weight (PERF, 1992). There are several applications where foamed, gel-assisted solidifiers could fill a special niche. Because solidifiers react with the first oil they contact, one innovative application would be as a self

creating barrier; e.g., around drains or as a solidified oil "boom" around slicks. It is possible that solidifiers could make treated oil lighter, which could be beneficial to recovery operations in some cases, such as improving the recovery efficiency of certain types of skimmers (Fingas *et al.* 1993). Where deep oil penetration into gravel beaches is of great concern, foamed, gel-assisted solidifiers may be applied to the shoreline just prior to stranding, to keep the oil on the surface. Using solidifiers may make it easier to recover oil because solidified oil can be easier to harvest than oil that is pumped through skimmers.

In a recent study conducted for the Petroleum Environmental Research Forum (PERF), several commercially available solidifiers were examined in laboratory and field conditions (Dahl *et al.* 1996). The study concluded that solidifiers have potential applications for marine spills in calm waters, and for protecting shorelines.

2.2 Oil Solubility and Viscosity

Even though oil is considered to be insoluble in water, a small fraction of oil does dissolve in water. Because this fraction has intimate contact with aquatic organisms, it is an important factor in determining oil toxicity. Bobra (1989) has done extensive studies on the water solubility behavior of petroleum mixtures. Oil is a complex mixture of compounds, and each compound will partition differently between the oil and aqueous phases.

Components with relatively high aqueous solubilities tend to transfer to the aqueous phase while the insoluble components stay in the oil. The term "Water Soluble Fraction" (WSF) is commonly used to describe the aqueous solution that is formed when oil and water are brought into contact. This study showed that crude oils yielded WSFs that are very similar in terms of composition and concentration, with slight differences in the relative abundance of some compounds. One of the most recent findings is that the composition and concentration of WSFs can be extremely sensitive to the oil water volume ratio used during WSF preparation (Smith and Harper, 1982; Lockhart *et al.* 1984; Maijanen *et al.* 1984).

Several factors affect spilled oil, particularly the type of oil spilled. The API gravity of the oil reflects the various chemical and physical variations of crude oils. Usually, the lower the API gravity, the higher the viscosity of the oil. The change in viscosity depends on the environmental conditions. Viscosity will decrease in a warm climate resulting in faster spreading and increased sinking of oil. Observing the Fingas and Sydor (1980) model, it appears that all spills would grow in diameter equally, regardless of the environment. According to tests done at the Millsaps Sorbent Laboratory, this is true for temperatures held at 25C. But when the temperature rose to 30C, the spreading rate doubled; when the temperature was decreased to 10C, the spreading rate decreased by half.

According to Owens, there are nearly 2000 spills occurring in the inland waters of the continental of United States each year (Owens *et al.* 1993). Oil spills into inland waters are different from coastal and marine (salt or brackish water) spills in many ways:

- They are nearly always in fresh water habitats.
- They involve lesser amount of oil but are more common than marine spills.
- Refined product spills are common in fresh water while crude oil spills are common in marine spills.
- The risk of contaminating fresh water supplies is much greater in inland spills.
- Inland spills affect a concentrated population.

- The effect of waves and tidal motion are a lesser factor in cleaning inland spills.

2.3 Other Remediation Methods

1. *In situ* Burning: Allen (1990) studied controlled burning of oil in the Valdez spill. Some oil was removed from the main spill by fire resistant booms towed by vessels. This technique eliminated the need for *in situ* combustion techniques. Flame height was controlled by the speed of the vessels. This controlled elimination resulted in 98% burning efficiency. Allen (1988) also studied mechanical cleanup systems, chemical dispersants and *in situ* burning. These systems are associated with a specific set of operational, environmental and oil slick conditions. The disadvantages of *in situ* burning include:

- oil condition restraints;
- special design booms have to be used to contain the oil;
- since weathering and emulsions affect the oil in sea, burning has to be done as soon as possible (within the first 12 to 24 hours);
- the appearance of black smoke can interfere with the cleanup crew's ability to breathe, see or function properly;
- reduction of air quality.

In situ burning also has advantages over other methods. It offers the potential to rapidly convert large quantities of oil to carbon dioxide and water with a percentage of other unburned and residue byproducts. Because the oil is converted to gaseous products, there is no need for physical collection, storage and transport.

2. Biodegradation: Another major area of interest in oil spill removal is the controlled use of biodegradation for removal of toxic chemicals from soil and water. McCreary (1989) shows that land farming has been used for the disposal of oily wastes and spilled oil in the oil industry. The oil is plowed into the soil and a natural population of bacteria enhanced by nitrogen and phosphorus fertilizers degrades the oil. This method is limited by the low rate of biodegradation and the narrow range of oil components readily biodegraded. Biodegradation of oil is not widely used because it will work only in certain climatic zones and on certain types of shores.

The Canadian Coast Guard (1989) report outlines the responsibilities in dealing with an oil spill. In this report the behavior of oil at sea is discussed, including its movement on the surface, weathering effects on oil, and evaporation of its "light ends" (components with a low boiling point), emulsification and oxidation of hydrocarbons.

3.0 Experimental Materials and Procedures

3.1 Experimental Equipment and Materials

The equipment and the materials utilized for the proposed work are listed below:

- environmentally safe disposable tank

- plastic cups
- thermistor
- graduate cylinder, flasks, beakers, spatula, wax paper, weighing dish titrators, pH meter, vapor pressure apparatus, and various other lab accessories
- rheometer
- viscometer
- solution calorimeter
- analytical balance
- agitator/stirrer with controls (torque indicator, amp meter, etc.,)
- GC/MS
- assorted solidifiers (see Table 1)
- ASTM methods for crude oil characterization (see Table 3)
- computer and process control software.

We identified thirty solidifiers and procured 23 commercially available solidifiers (see Tables 1 & 2). Several products are only known by name, and test samples were not available. Others are no longer available.

Several petroleum companies were contacted to obtain typical oil and condensate samples from various locations in Louisiana (e.g., South Louisiana, North Louisiana, offshore, and inland). An imported crude oil (Arab Medium) was also used. This crude oil is one of the most common crude oils transported in Louisiana waters.

Table 1 List of solidifier products procured.

ELASTOL 1	PETROCAPTURE
ELASTOL 2	PETRO-LOCK
ENVIRO-BOND # 403	RUBBERIZER
NORCHARS A 610	SEAMATE - 3 MM
NORCHARS A 650	SEAMATE - 4 MM
OARS	SEAMATE - FINE
OSSA	SPI PARTICULATE 1
OMNI-ZORB # 2000	SPI PARTICULATE 2
OMNI-ZORB # 4000	SPILL GEL (FRACTECH)
OMNI-ZORB # AZ-1N	WASTE-SET PS # 3200
OMNI-ZORB # BZ 1	WASTE-SET PS # 3400

OMNI-ZORB # PZ 1	
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Table 2 List of solidifier products identified ⁽¹⁾

GRABBER	RAWFLEX
INIPOL	OILBOND 100
NORSOREX	OILSPONGE

⁽¹⁾Samples of these products are no longer available for testing.

3.2 Experimental Procedure Design

The solidifiers and test fluids were subjected to several tests for conditioning, determination of their physical characteristics, and determination of their expected performance. These procedures are partially described in the following sections and may require future modifications. Five procedures were tried and modified.

3.2.1 Static Testing

A procedure was developed to test each solidifier under static conditions using a known volume of oil on a known volume of water. This screening test determined the optimum dosage of each product. The results of this test was used in other phases of the study.

For the static test we used a test cell container with a known volume of water and oil. For example, we used 20 ml or 10 ml of water with 10 ml or 5 ml of any type of oil respectively (onshore, offshore, imported). A known amount of solidifier was then weighed using an analytical balance. The procedure initially used 1 gram to the maximum extent of absorption of oil for that particular solidifier. The weighed solidifier in increments of 1 g was poured in the test cell containers along with the mixture of oil and water and then stirred. The samples were checked every half hour and the maximum efficiency of the solidifier was noted. This optimum range varied from sample to sample and type of oil. For example, the solidifier OARS, had an optimum value of 7.0 g using offshore oil, and an optimum value of 5.0 g using imported oil.

3.2.2 Dynamic Testing

This test utilized the results of the static test to develop uniform/consistent solidified byproduct. This test involved using a mechanical stirrer to simulate wave conditions and homogeneous mixing (the stirring was done at 200 or 400 rpm depending upon the consistency of the sample). As the oil sample was stirred, the solidifier product was added using the optimum dosage determined in the static test.

3.2.3 Byproduct Viscometry (Rheometry)

Following the solidification process, the byproduct exhibited a higher viscosity and therefore, could not be measured with the same instrument as described in section 3.4.2. To overcome this difficulty we developed a procedure using a capillary rheometer. This technique permits the characterization of materials that exhibit both stable and unstable melt viscosity properties.

The testing was conducted by ASTM D 3835-90: Standard Test Method for Determination of Properties of Polymeric Materials by means of a capillary rheometer. This test method describes measurement of the rheological properties of polymeric materials at various temperatures and shear rates. It covers measurement of melt viscosity, sensitivity, or stability of melt viscosity with respect to temperature and polymer dwell time in the rheometer, die swell ratio (polymer memory), and shear sensitivity when extruding under constant rate or stress. We tested the samples at a constant temperature and shear rate, and calculated the melt viscosity of the samples in that condition. The rheometer was a model Galaxy V manufactured by Kayeness Inc.

According Newton's Law, viscosity is shear stress over shear rate,

$$\eta = \frac{\tau}{\dot{\gamma}}$$

where η is viscosity, τ is shear stress and $\dot{\gamma}$ is the shear rate.

Apparent shear stress is :

$$\tau = \frac{F}{A} = \frac{D_c \Delta P}{4 L_c} = \frac{F_p r_c}{2\pi R_b^2 L_c}$$

where τ is the shear stress, F is the force acting on the surface area A . F_p is the force on the plunger and r_c , D_c are the inner radius and inner diameter of the capillary, respectively. R_b is the inner radius of the barrel, L_c is the length of the capillary, and P is the pressure drop along the capillary.

Apparent shear rate:

$$\dot{\gamma} = \frac{32 Q}{\pi D_c^3} = \frac{4 R_b^2 S}{r_c^3}$$

where $\dot{\gamma}$ is the shear rate, R_b is the inner radius of the barrel, S is the speed of the plunger, r_c is the inner radius, D_c is the diameter of the capillary and Q is the volumetric flow rate.

$$\eta = \frac{F r_c^4}{8 \pi R_b^4 L_c S}$$

Viscosity reduces to the above equation. Physically it is proportional to the force on the plunger divided by the speed of the plunger. That constant is strongly dependent on barrel and die radius.

We used the testing procedure described in the user's manual of the rheometer model Galaxy V manufactured by Kayeness Inc (1992). Preliminary results from these experiments showed that the capillary rheometer will provide these high viscosity readings. Although not yet totally perfected, our experiments show that the results are repeatable within an experimental error of about 10%. The measurements will characterize the solidified byproduct and allow us to arrive at an effective and economical dosage for the solidification treatment of oil spills. This condition (effective and economical) may not exist for certain products. Therefore, this procedure should provide us with a screening method for selecting the type of solidifier to use in a particular condition.

3.2.4 Calorimetry Test

Every chemical reaction proceeds by either releasing or absorbing some form of energy from its surrounding environment. By measuring the heat of reaction, the ease with which the reaction takes place between the reactants can be estimated. This is the principle that we applied for testing the different solidification products.

A solution calorimeter is an instrument used to measure the heat evolved or absorbed by chemical reactions in a liquid media. Measurements are made at room temperature and at atmospheric pressure for systems producing energy changes ranging from 2 to 1000 calories. A Parr Instrument Solution Calorimeter was utilized in this work. The complete procedure is given in the operating manual (Parr Instrument Co., 1975).

The experimental setup consisted of a glass Dewar in which the liquid was held. The other reactant (a liquid or a solid) was placed in a sealed glass rotating cell and immersed in the first liquid. After both reactants came into thermal equilibrium, the reaction was started by dropping the contents of the cell into the surrounding liquid. The rotating cell was then stirred vigorously.

A solution calorimeter is used to measure the heat of reaction between two liquids or between a liquid and a solid. The equipment is perfectly insulated from the surroundings so that a minute change in the energy of the system's contents can be detected with great accuracy. Also, the precision of the equipment is adjusted to fit the heat range of the energy change so as to measure it accurately.

In our tests, the solidifiers were first tested in various combinations with the three kinds of crude oils. A bench scale study was used to calculate the optimum ratio of solidifier to oil. The same ratio was used with the same test conditions in the solution calorimeter to find the reaction heat during the process. Results were obtained from different combinations of solidifiers with oil samples, and the readings were plotted to obtain the reaction heat.

Tests were also conducted to determine the heat generated during the process of mixing with the stirrer. Oil samples without any solidifier were run in the calorimeter, and the heat generated by the stirrer was recorded. The oil viscosity increased following contact between the solidifier and the oil. The increase in viscosity created more heat after addition of the solidifier and stirring than after the crude oil was stirred without the solidifier.

Since the viscosity of oil was different for each set of combinations, similar experiments were conducted to detect the effect of mixing on the reaction speed. The various sets of data obtained were plotted and replicate runs were made to test the reliability of the results.

Trial runs of the solidifiers with the oil samples showed that as the oil in the Dewar was being stirred, heat was generated that interfered with the heat produced from the reaction. As the reaction proceeded, the final product became more viscous than the unreacted crude oil, further raising the heat produced by stirring. Thus, it was difficult to find the exact heat of reaction.

Later, we ran the samples of oil only, without any reaction with the solidifier, in order to find the heat produced by stirring. Blank runs were also conducted with previously prepared samples (final product of the solidifier with oil from bench scale studies) in oil to determine the heat produced by stirring. We tried to incorporate these data into the trial run data and determine the reaction heat from the initial values. The reaction had a complicated chemistry that prevented us from correlating the results and determining the heat produced by stirring.

Because the heat produced by stirring made it difficult to calibrate the exact heat of reaction, we decided that there would be no mixing during the reaction.

Solidifiers often consist of polymerization catalysts and cross-linking agents. Thus, in order for the reaction to take place, cross links between agents must be broken. The reaction of the solidifiers with the oil then proceeds by absorbing energy from the surrounding atmosphere. This process can be envisioned from the drop in oil temperature after the solidifier is introduced. This theory was confirmed when all samples showed the same trend of behavior with the three kinds of crude oils.

From the value of the heat of reaction, the ease with which the solidifier reacts with the oil can be determined. The greater the heat value, the faster the reaction and the better the integrity of the final byproduct. The heat of reaction is calculated from the following relationship:

$$\Delta H_R = \frac{\Delta T}{m}$$

where,

H_R = heat of reaction, Cal/gram

T = temperature difference (i.e., initial temperature - final temperature), °C

m = mass of solidifier used for the reaction, gram

The application of this process determined how and to what extent solidifiers can be applied in oil spill scenarios. The release or absorption of heat during the solidification process thus have implications for how solidifier applications should be conducted.

3.2.5 Crude Oil Characterization

The properties of the three crude oil samples were analyzed. The determination of acid components was the major focus of this phase of the study. This analysis was not routine and required a special experimental setup. Our goal was to relate the solidification process to the acid components of the oil. Asphaltenes, paraffins, pour point, API gravity, TPH distillation, sulfur content, acid number, and base number were also determined (see Table 3).

3.2.6 Solidification Viscometry

We determined that there are at least three phases of viscosity during the solidification process. First, an initial viscosity develops after introduction of the solidifier. This effect depends mainly on the characteristics of the oil and solidifier as well as secondary factors such as atmospheric conditions. An attempt was made to investigate this phenomena using a 39B model Fann Viscometer to develop shear rate-shear stress relationships. This viscometer is normally used in the oil field for rheological determination of oil field drilling fluids. The instrument was modified to perform shear stress-shear rate measurements on low viscosity fluids such as crude oil and fuel products. Trial runs were conducted using the modified instrument. The preliminary results showed that the shear rate-shear stress relationship will likely uncover the mechanisms of the solidification process. The initial viscosity may have critical effects on the effectiveness of the solidifier as an oil spill remediation method. Mathematical methods can be developed using the shear rate-shear stress relationships to arrive at the screening criteria for various products.

The 39B Model Fann Viscometer instrument is designed to provide absolute viscosity measurements (Fann Instrument Co. 1995). Test results are recorded over a wide range as the instrument is adaptable to many viscosity testing problems. It can also be used to characterize shear stress/shear rate data. Unfortunately this instrument is limited to measuring the viscosity of liquids. The viscosity of mediums containing particles (e.g., solidifier particles and crude oil) cannot be accurately measured.

3.2.7 Future Testing

Although we have already devised several systems to assess the effectiveness of the solidifiers, other procedures should be explored to make the evaluation process easier and more efficient.

Table 3 Properties of crude oils used in the experiments

		RESULTS		
Parameter	Method	IMPORTED	OFFSHORE	ONSHORE

Acetic Acid	8270M	<10(P)	<10(P)	<10(P)
Oxalic Acid	8270M	<10(P)	<10(P)	<10(P)
Malonic Acid	8270M	<10(P)	<10(P)	<10(P)
Succinic Acid	8270M	<10(P)	<10(P)	<10(P)
Carbonic Acid	& Isomers	2300(P)	1250(P)	3140(P)
Acid Number	ASTM D-664	0.14 mgKOH/g	0.15 mgKOH/g	0.13 mgKOH/g
Base Number	ASTM D-4739	0.16 mgHOH/g	0.14 mgHOH/g	0.17 mgHOH/g
API Gravity @60F	ASTM D-287	31.1	36.4	42.8
Asphaltenes	UOP	1.34wt%	0.17wt%	0.01wt%
Color	Visual	Dark Amber	Dark Amber	Dark Amber
Paraffin Wax Content	UOP 46	9.03wt%	5.45wt%	3.54wt%
Pour Point	ASTM D-97	Below 32F	Below 32F	39F
Sulfur Content	ASTM D2622	2.21wt%	0.25wt%	0.03wt%
ASTM D-86	Distillation	180	180	180
	Initial Boiling Point	218	250	248
	5 % Recovered @	270	292	314
	10 % Recovered @	372	393	377
	20 % Recovered @	462	478	440
	30 % Recovered @	560	530	483
	40 % Recovered @	648	590	512
	50 % Recovered @	700	650	543
	60 % Recovered @	724	708	572
70 % Recovered @	738	725	616	

	80 % Recovered @			
89.0 % End Pont	@ Max. Temp.	748	-	-
	90 % Recovered @	-	752	681
	95 % Recovered @	-	-	745
93.0 % End Point	@ Max. Temp.	-	760	-
97.0 % End Point	@ Max. Temp.	-	-	751
	Recover	92%	94.90%	98.00%
	Residue	1.00%	0.10%	2.00%
	Loss	7.00%	5.00%	0.00%
Sediment & Water	ASTM D-1796	0.00Vol%	0.025Vol%	0.00Vol%
Total Nickel	SW846-6010A	11.1	5.6mg/Kg	NDmg/Kg
Total Lead	SW846-6010A	NDmg/Kg	NDmg/Kg	NDmg/Kg
Reid Vaport Pressure	@ 100F	2.2 psia	2.7 psia	1.4 psia
Salt in Crude Oil	ASTM D-3230	55 lbs/1000 bbls	90 lbs/1000 bbls	8 lbs/1000 bbls
Viscosity @ 100F	ASTM D-445	73.09 SUS	44.48 SUS	33.50SUS
Total Vanadium	SW846-6010A	19.3 mg/Kg	ND mg/Kg	ND mg/Kg

ND = Not Detected

(P) = Practical Quantitation Limit

NOTE: Unable to perform Cloud Point in all three (3) samples: samples opaque.

4.0 Discussion of Results

As previously discussed, the experiments for this study were performed with different instruments. The results of each set of experiments will be discussed separately.

4.1 Static Tests

These experiments were designed to determine the optimum dosage of solidifier needed to solidify a known volume of oil. The optimum dosage was reached when: (1) no unsolidified oil remained on the water, (2) no excess solidifier remained unreacted with the oil, and (3) the resulting byproduct was a solidified mass after a maximum of 30 minutes. This test showed that the optimum dosage varied for the various products. The results of these observations are shown in Figures 1-3 for the three crude oil samples. As these figures show, the optimum dosage for solidifying an equal amount of crude oil depends upon the type of product and crude oil used. Generally the solidification of onshore crude oil used less of the same solidifier than the imported and offshore crude oils.

4.2 Dynamic Tests

Once the optimum solidifier dosage had been determined from the static test, it was used in the dynamic test. The objective of this test was to produce a solidified byproduct of crude oil and to determine its viscosity by the use of a capillary rheometer.

The solidified crude oil varied in consistency. Most products formed a rubber-like mass. A few products had a firm elastic consistency, and others formed a non-cohesive or paste consistency as shown in Figures 4-7.

4.3 Byproduct Viscometry (Rheometry)

The samples obtained from dynamic tests were subjected to capillary rheometer testing to determine the viscosity of the solidified byproduct. Viscosity affects the integrity of the solidified byproduct-a critical factor in the product's recovery and disposal. Viscometry temperature was conducted at 60F for most of the products. Product numbers 1, 2, 17, 18, 21 & 22 were not tested at this temperature because the extrusion of their byproduct prevented sufficient shear from being achieved. They were tested for viscosity measurements at higher temperatures.

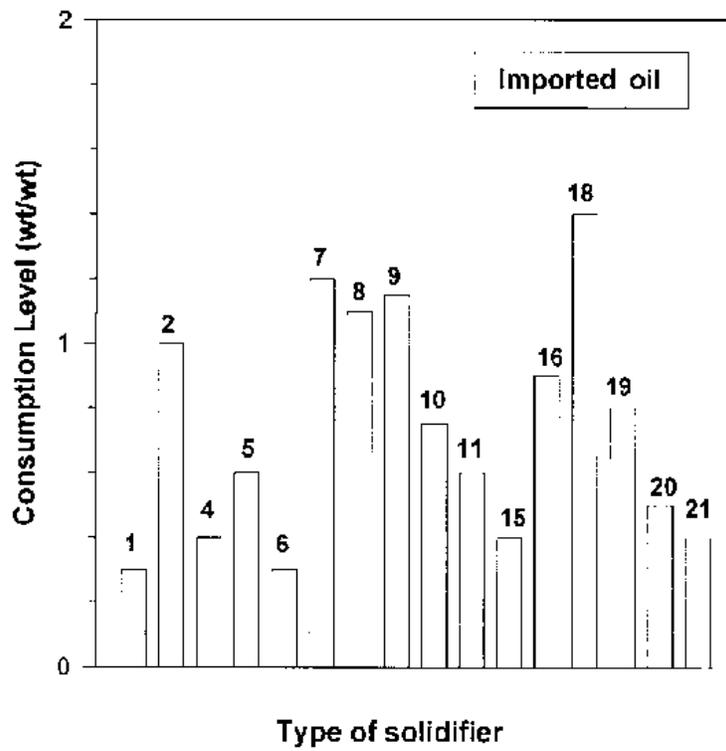


Figure 1 Consumption level for various solidifiers (imported oil).

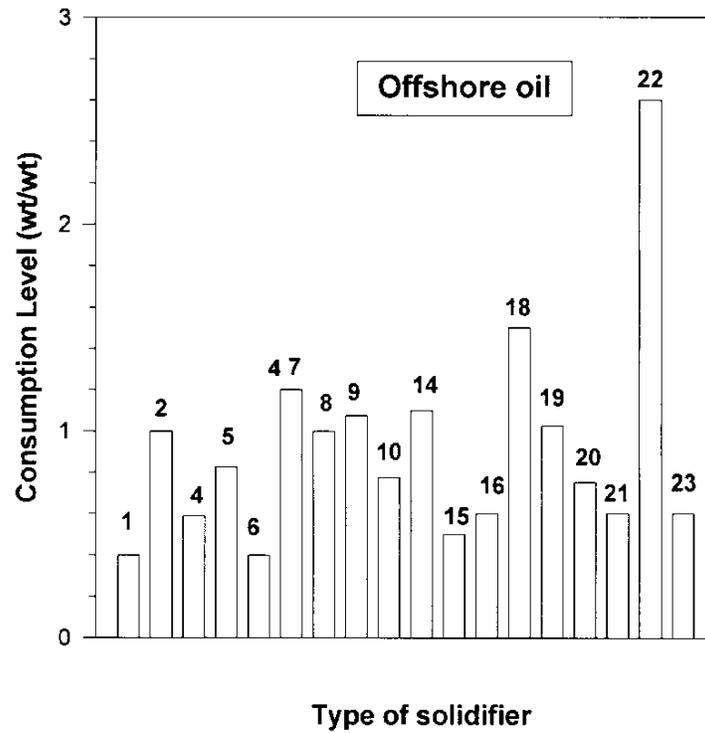


Figure 2 Consumption level for various solidifiers (offshore oil).

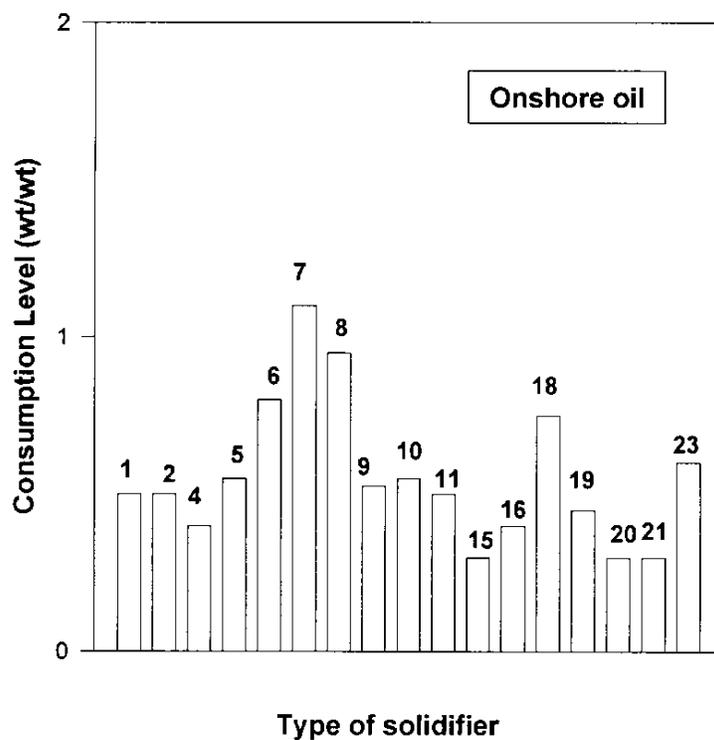


Figure 3 Consumption level for various solidifiers (onshore oil).

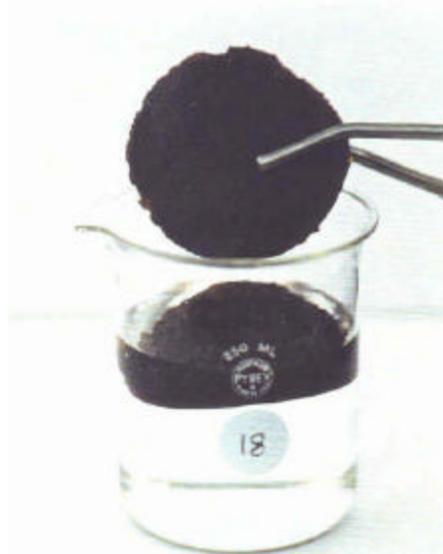


Figure 4 A solidifier that produced a floating rubber-like mass with firm consistency in its solidified byproduct from crude oil.



Figure 5 *A solidifier that produced a floating elastic consistency in its solidified byproduct from crude oil.*



Figure 6 *A solidifier that produced a floating non-cohesive consistency in its solidified byproduct from crude oil.*



Figure 7 *A solidifier that produced a partially floating paste consistency in its solidified byproduct from crude oil.*

The plots in Figures 8-10 show the a wide range of viscosities for various solidified byproducts depending on the type of crude oil tested. A solidifier that effectively solidifies one type of crude oil may not solidify another type. Therefore, a good database should be developed for each solidifier, crude oil, and type of processed fuel.

4.4 Solution Calorimeter

The experiments conducted with the solution calorimeter showed that solidifiers tend to absorb energy from the surrounding atmosphere (endothermic reaction) in their reactions with crude oil.

The experimental runs showed that the crude oil tended to have a higher temperature than the surrounding room temperature. Once the reaction began, the temperature of the oil dropped considerably, and then came to a thermal equilibrium with its surroundings. The drop in temperature is calibrated from the difference in the temperature of the pre-period (left portion of the plot) and post-period (right portion of the plot) reaction as shown in Figures 11-13 (other plots are in Appendix A). The procedure used for the calculation of the reaction heat is described in the calorimeter operation manual (also see Section 3.4.4). From the value of the heat of reaction, the ease with which the solidifier reacts with the oil can be determined. The greater the value of the heat of reaction, the faster the reaction and the higher the integrity of the product. A byproduct with a higher integrity is preferred, because it will be more stable and less likely to break down during pickup and disposal.

The values of the heat of reaction of crude oil samples with various solidifiers are shown in Figures 14-16. Solidifier 9 had the highest reaction heat with offshore and onshore crude oils. The reaction of solidifiers with imported oil is best when compared to other solidifiers at about the same conditions.

We observed that final products composed of larger particles have more integrity than products

composed of small particles (Figure 16). This distinct trend may not hold true for other crude oil samples. For example, when Solidifiers 6, 7, and 8 were combined with imported oil, smaller sized particles had very high heats of reaction, and they produced products with higher integrity.

Comparison of Figures 11, 12 and 13 reveals a distinct pattern in the reaction behavior of crude oil with various solidifier products. The region of thermal equilibrium has a lower temperature for Solidifier 9 (Figure 11), a mid-range temperature for Solidifier 21 (Figure 12), and a high temperature for Solidifier 23 (Figure 13). The inspection of the calculated reaction heat in Figures 14, 15 and 16 with Figures 11, 12 and 13 show that Solidifiers 9, 21 and 23 produced high heats of reaction with the corresponding crude oil sample.

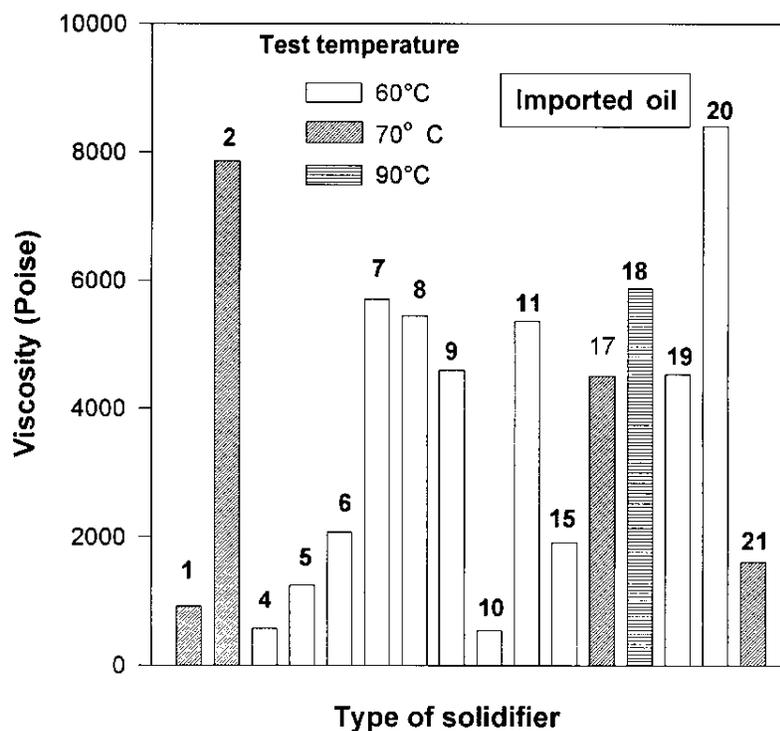


Figure 8 Viscosity of solidified oil for various solidifiers (imported oil).

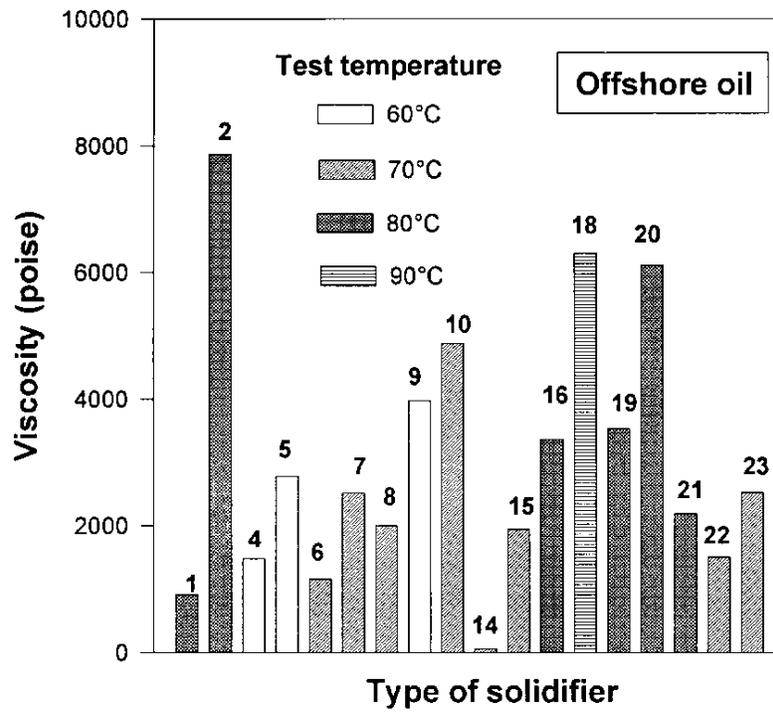


Figure 9 Viscosity of solidified oil for various solidifiers (offshore oil).

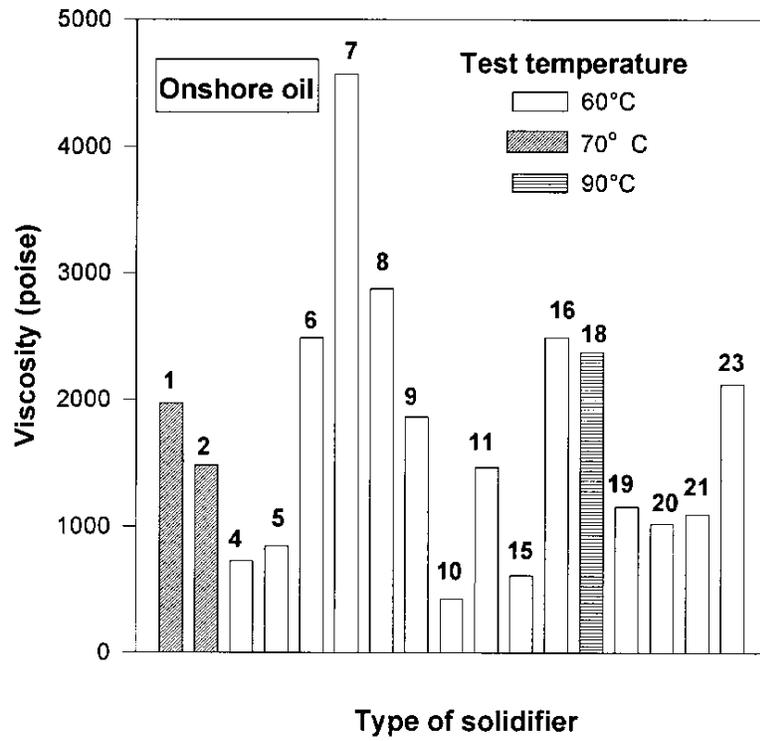


Figure 10 Viscosity of solidified oil for various solidifiers (onshore oil).

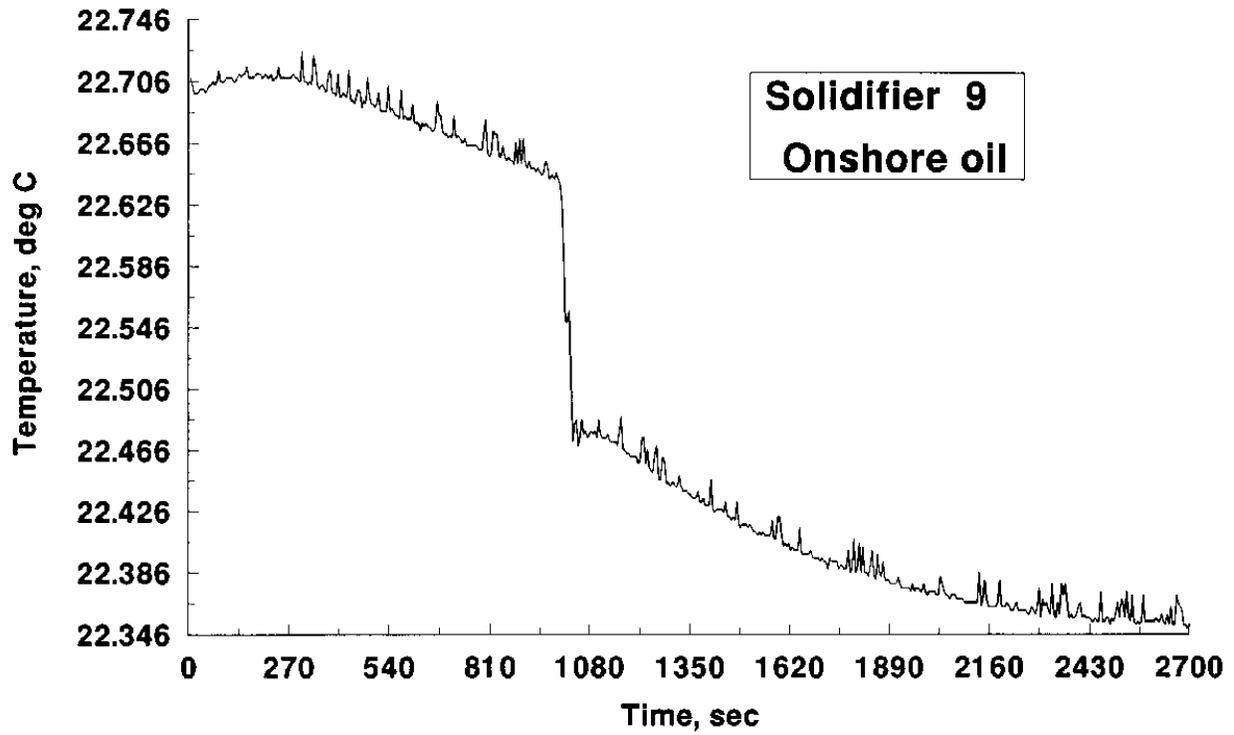


Figure 11 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-9, onshore oil).*

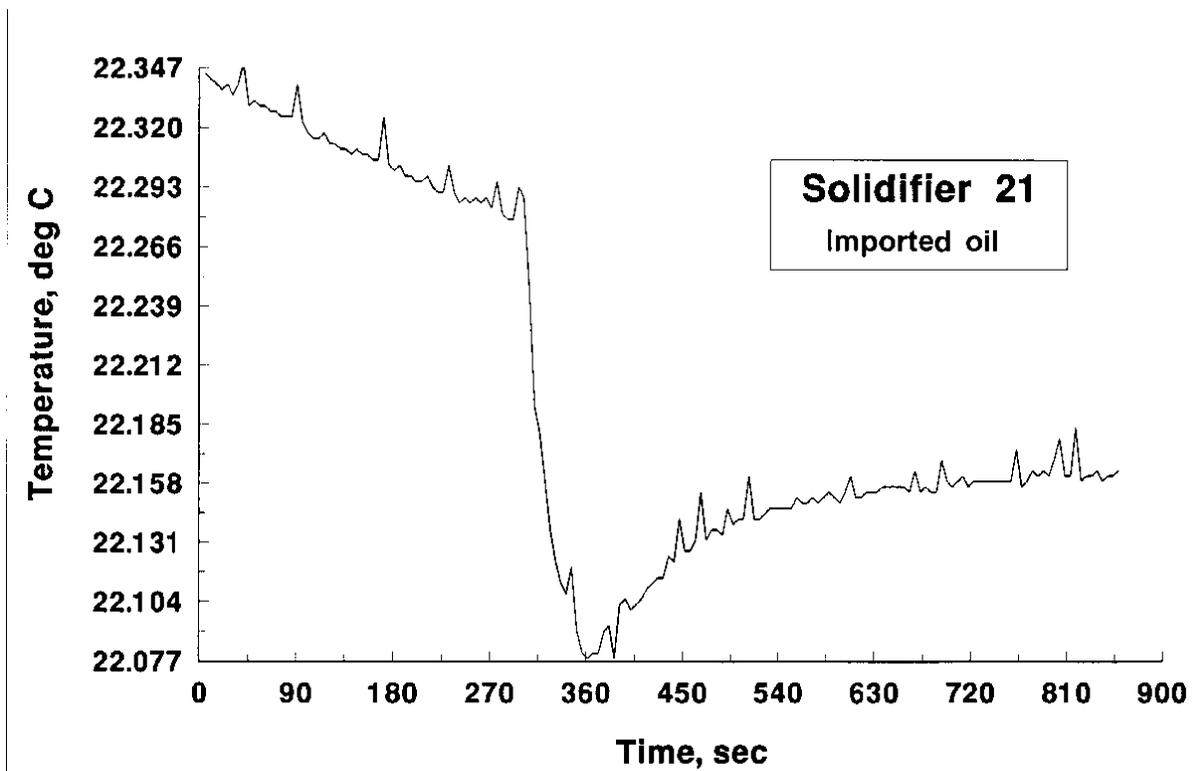


Figure 12 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-21, imported oil).*

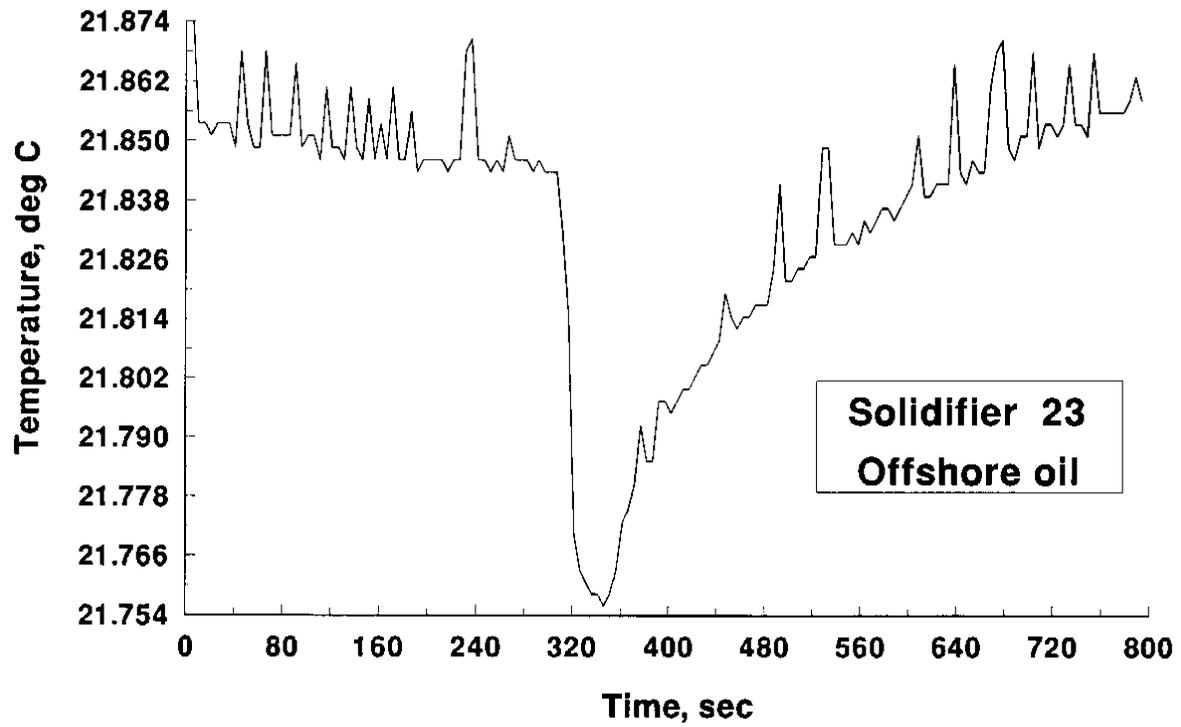


Figure 13 *Temperature changes with time of reaction of crude oil with solidifier (Solidifier-23, offshore oil).*

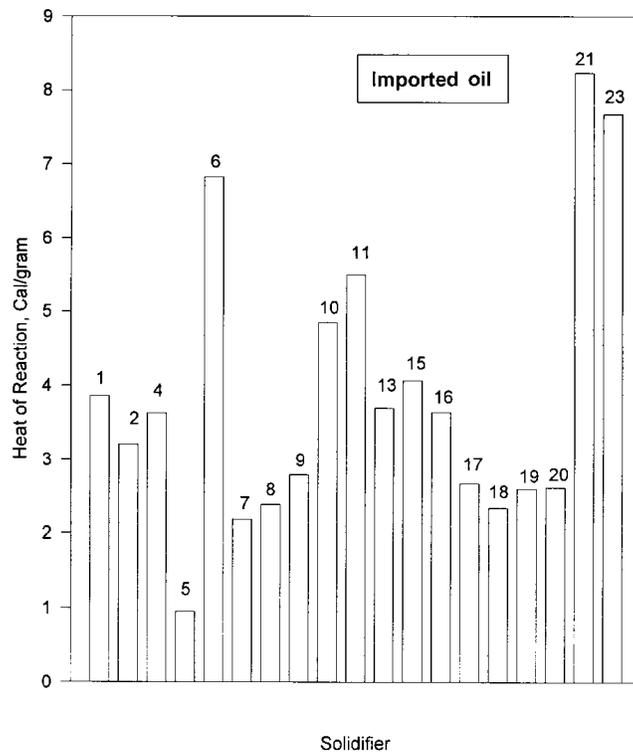


Figure 14 Heat of reaction for selected solidifiers (Imported oil).

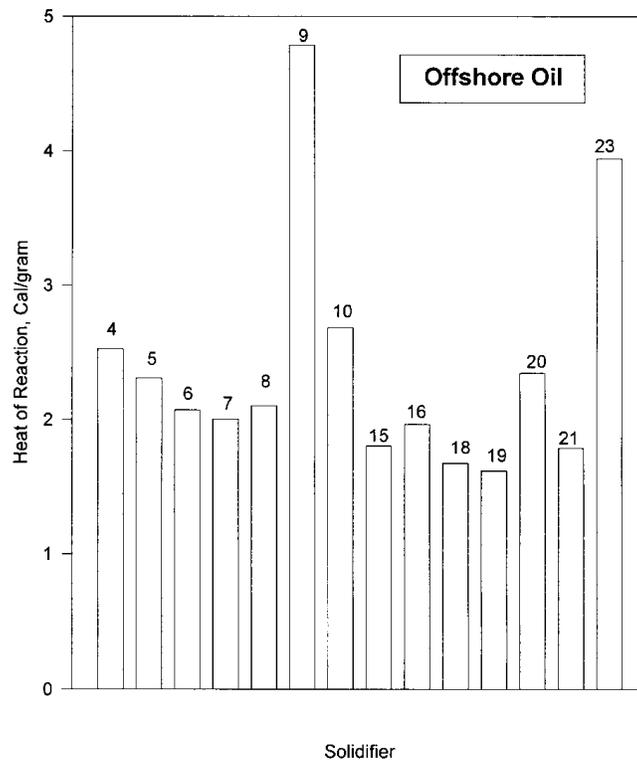


Figure 15 Heat of reaction for selected solidifiers (offshore oil).

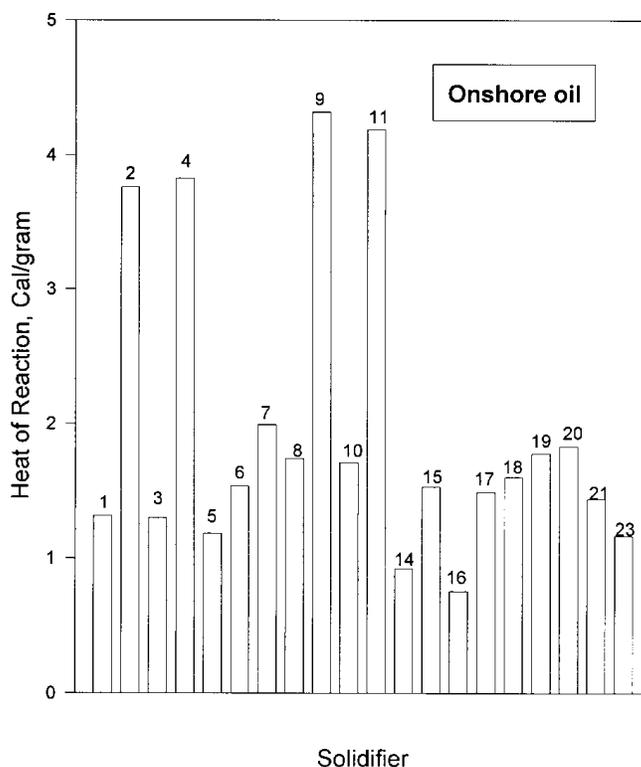


Figure 16 Heat of reaction for selected solidifiers (onshore oil).

4.5 Effect of Crude Oil Characteristics on Solidification

The effectiveness of a solidifier may depend on various factors such as acid number, base number, API gravity, paraffin wax content, and sulfur content in the oil samples. Furthermore, heat of reaction, viscosity, consumption level, and viscosity/consumption level, play a major role in determining the solidifier's effectiveness. The higher the reaction heat and viscosity/consumption level, the better the integrity of the product. A plot of reaction heat, viscosity and viscosity/consumption ratio has been plotted for selected solidifiers that showed a similar trend.

As concerns the acid number, Solidifier 7 had the highest heat of reaction for the onshore oil. Similarly, the highest heat of reaction for imported oil was shown by Solidifier 21. The highest heat of reaction for offshore oil was shown by Solidifier 23 (Figure B.1). Thus, by monitoring the acid number, the effectiveness of the solidifier can be improved. For the selective solidifiers that showed the same trend in behavior it was observed that Solidifier 23 had the highest heat of reaction for offshore oil. Similarly the highest heat of reaction for imported oil was that of Solidifier 21; the highest heat of reaction for onshore oil was that of Solidifier 7. Figure B.2 shows the base number versus heat of reaction for the three crude oil samples.

As the API gravity data decreased, the heat of reaction decreased (Figure B.3). The lower the API gravity, the more efficient the reaction. Optimally, the value of the API gravity should match that of the imported oil. For the selective solidifiers that showed the same trend in behavior, Solidifier 8 had the highest heat of reaction with the imported oil. Similarly the highest heat of reaction with offshore oil was that of Solidifier 23. The highest heat of reaction with onshore oil was that of Solidifier 7.

From the graph of heat of reaction versus percent by weight of asphaltenes, it was observed that as the percent by weight of asphaltenes increased, the value of the heat of reaction increased (Figure B.4). The higher the weight percent of the asphaltenes, the higher the heat of reaction and the better the reaction product. For the selective solidifiers that showed the same trend in behavior, Solidifier 7 had the highest heat of reaction with the onshore oil. Similarly, the highest heat of reaction with offshore oil was that of Solidifier 23. The highest heat of reaction with imported oil was that of Solidifier 21.

From the graph of heat of reaction versus percent by weight of paraffin wax content, it was observed that as the percent by weight of paraffin wax content increased, the heat of reaction increased (Figure B.5). The higher the weight percent of the paraffin wax, the higher the heat of reaction and the better the reaction product. For the selective solidifiers that showed the same trend in behavior, Solidifier 7 had the highest heat of reaction with the onshore oil. Similarly the highest heat of reaction for offshore oil was that of Solidifier 23. The highest heat of reaction for imported oil was that of Solidifier 21.

From the graph of heat of reaction versus percent by weight of sulfur content, it was observed that as the percent by weight of sulfur content increased, the heat of reaction increased (Figure B.6). The higher the weight percent of the sulfur content, the higher heat of reaction and the better the reaction product. For the selective solidifiers that showed the same trend in behavior, Solidifier 7 had the highest heat of reaction with the onshore oil. Similarly, the highest heat of reaction for offshore oil was that of Solidifier 23. The highest heat of reaction for imported oil was that of Solidifier 21.

4.6 Solidification Viscometry

We investigated this phenomena (initial/instantaneous viscosity of the crude oil-solidifier mixture) by using a 39B model Fann Viscometer to develop shear rate-shear stress relationships. This model viscometer is normally used in the oil field for rheological determination of oil field drilling fluids. Our instrument was modified to perform shear stress-shear rate measurements on low viscosity fluids such as crude oil and fuel products. The preliminary results show that the shear rate-shear stress relationship will likely uncover the mechanisms of the solidification process. The initial viscosity may have critical ramifications for the effectiveness of the solidifier as an oil spill remediation method. Due to instrument limitations, this study remained incomplete (see section 3.2.6).

4.7 Effectiveness of Solidifiers

The effectiveness of the solidifiers may depend on many factors. For example, the characteristics of the crude oil or fuel and the solidifier chemistry will combine in a synergistic effect. Therefore, although the parametric study of solidification may prove beneficial to optimize the process, it should not be considered the ultimate tool for that purpose. As a result of this study, we recommend using the ratio of viscosity and consumption rate to screen and estimate the effectiveness of the solidifiers (Figures 17-19). The dispersion and removal of solidified byproducts are very important in the utilization of solidifiers. The solidified oil should be stable so that it will not disperse. Therefore, we want as high a viscosity as can economically be achieved. Once the oil is solidified, it must be removed from water or land for final disposal. In this phase, the solidified byproduct must be strong enough to remain intact during pick up and disposal. In this case, the viscosity again plays a major role.

The experiments have shown that consumption of solidifier does not necessarily have a direct relationship with the production of a high viscosity byproduct. Therefore, the ratio of viscosity to solidifier consumption can be used as a measure of solidifier effectiveness. Based on this parameter, Figures 17-19 have been developed.

Figures B.7-B.12 show the plots of various crude oil characteristics versus byproduct viscosity. The plots of the same crude oil characteristics versus a viscosity/consumption ratio are shown in Figures B.13-B.18. The data set for these plots is not large enough to arrive at a definitive conclusion regarding the role of these parameters in the solidification process. It is evident that these parameters may play a role since they follow similar trends for the same solidifiers. Further work in this area is recommended.

The results from the heat of reaction, viscosity/consumption level tests show that we must consider the final product on the basis of additional relationships that are not evident to us. But, with the study of the structural properties of the final product, we may come to a conclusion at a later time which may reveal many more interesting facts.

From our laboratory and data analysis, we have observed the following results while comparing the impact of viscosity, consumption, and viscosity/consumption ratio versus the type of the solidifier for all products:

Using onshore oil, we have observed the following results:

- Viscosity/consumption level is high for Solidifier 16.
- Viscosity is high for Solidifier 7.
- Consumption level is high for Solidifier 7.

Using offshore oil, we have observed the following results:

- Viscosity/consumption level is high for Solidifier 20.
- Viscosity is high for Solidifier 2.
- Consumption level is high for Solidifier 22.

Using imported oil, we have observed the following results:

- Viscosity/consumption level is high for Solidifier 20.
- Viscosity is high for Solidifier 20.
- Consumption level is high for Solidifier 18.

Similarly, the following trends are observed for the effect of such parameters as sulfur, paraffin wax, asphaltenes, API gravity, base number and acid number on onshore oil, offshore oil and imported oil for two factors: viscosity and viscosity/consumption level.

For Viscosity:

Crude Oil type

Imported Offshore Onshore

1. Acid number High Low Very Low
2. Base number High HighLow

3. API gravity High High Low
4. Asphaltenes Low High Very Low
5. Paraffin wax Low High Very Low
6. Sulfur Low High Very Low

For Viscosity / Consumption level:

Crude Oil type

Imported Offshore Onshore

1. Acid number High Low Very Low
2. Base number High Low Very Low
3. API gravity High Low Very Low
4. Asphaltenes HighLow Very Low
5. Paraffin waxLowHighLow
6. SulfurLowHighLow

The above results show that the solidification process could be highly dependent upon the crude oil characteristics. Further work in this area is highly recommended.

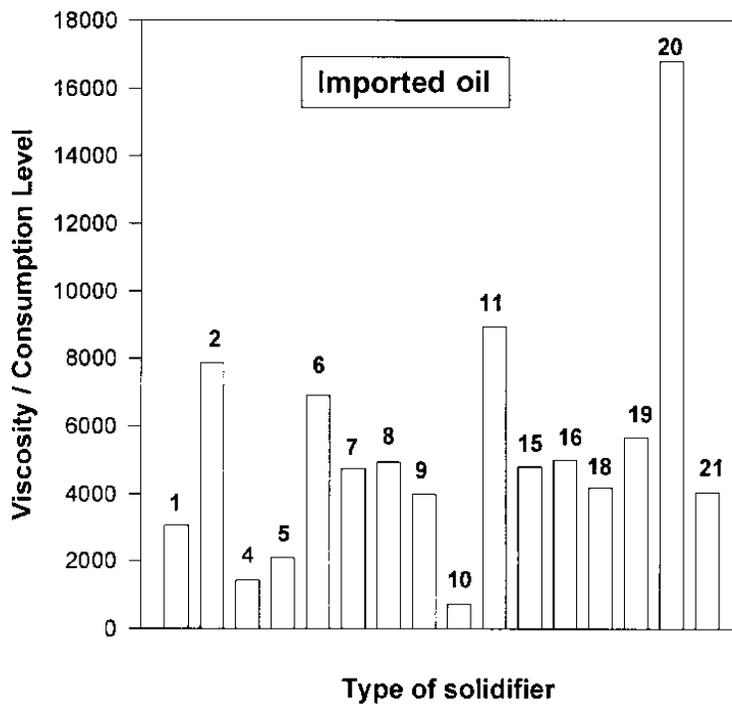


Figure 17 The ratio of viscosity/consumption level for various solidifiers (imported oil).

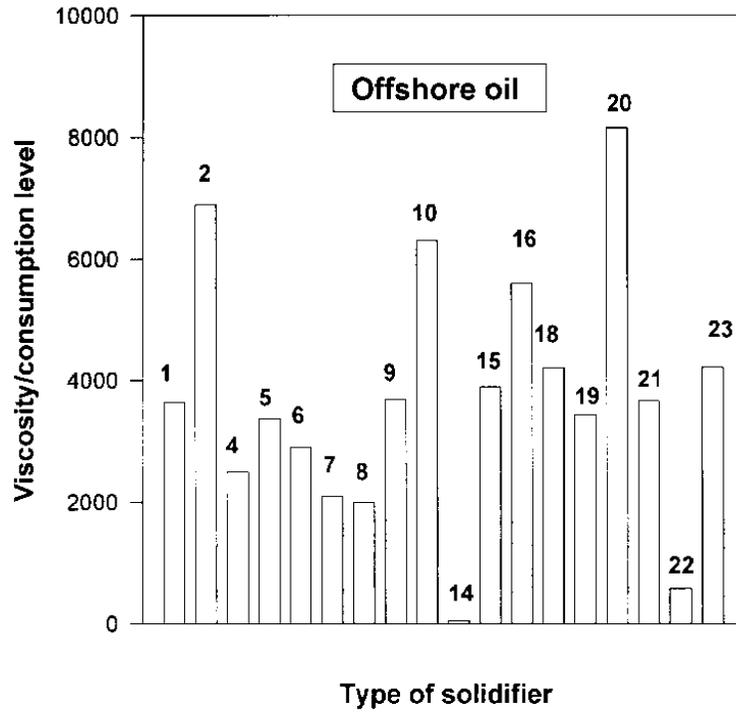


Figure 18 The ratio of viscosity/consumption level for various solidifiers (offshore oil).

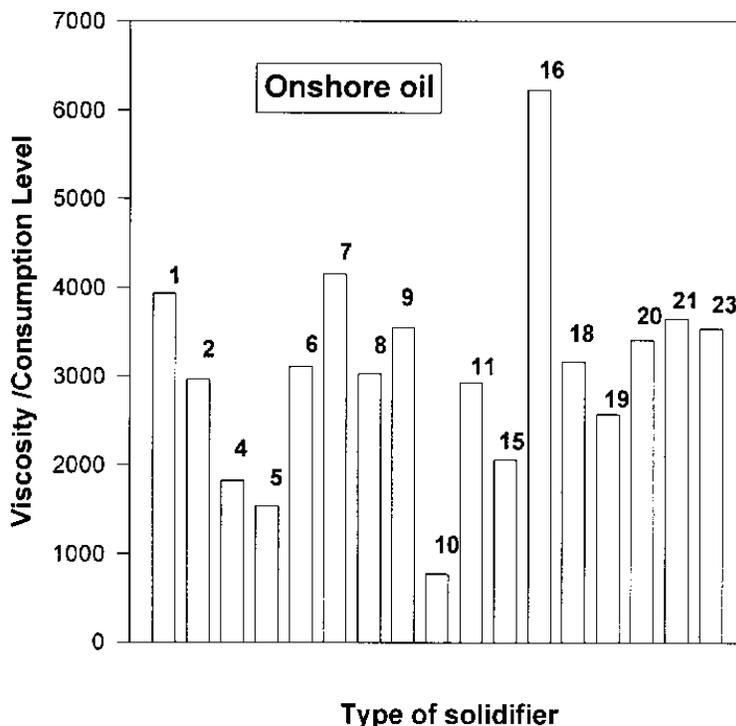


Figure 19 The ratio of viscosity/consumption level for various solidifiers (onshore oil).

5.0 Conclusions

On the basis of the foregoing discussion the following conclusions are made:

1. Solidifiers render oil viscoelastic.
2. Solidified byproducts performed satisfactorily in a sink/float test.
3. A static test can screen solidifiers and provide quick optimum dosage.
4. A dynamic test provides the energy level needed to determine consumption level and byproduct uniformity.
5. Capillary rheometry provides a measure of byproduct integrity which can be applied to recovery/disposal and material characterization.
6. The viscosity of solidified oil cannot be evaluated at a uniform temperature due to the solidifier's chemistry.
7. The solidifier's effectiveness may depend upon the level of oil asphaltenes, the paraffin wax content, and the sulfur content.
8. The measurement of phase viscometry (initial/instantaneous viscosity) using sensitive instrumentation will likely uncover the mechanism of the solidification process.
9. The solidifier consumption level varied with type of crude oil.
10. The modified calorimetry screened the products based on the energy absorption and can determine their effectiveness based on the heat of reaction.
11. Phase viscometry will show the initial solidification mechanism of solidifiers, which will affect the length of time needed for solidification.
12. The ratio of viscosity to consumption level can be a measure of solidifier effectiveness and an

economic factor.

13. Integration of the methods and procedures developed in this study will help users screen and select solidifiers and decide on recovery and disposal techniques.
14. The results of this work can potentially form the basis for arriving at new ASTM procedures for evaluation and characterization of solidifiers.

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Appendix A. Plots of Temperature Changes with Time of Reaction of Crude Oil with various solidifiers

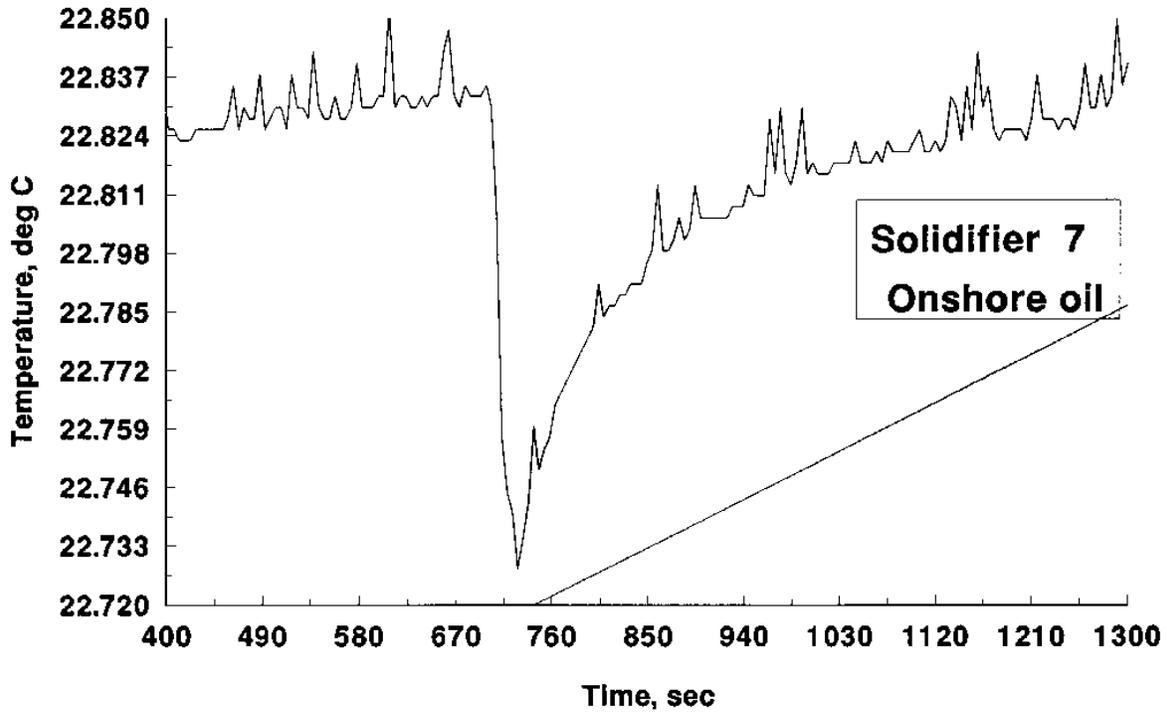


Figure A.1 *Temperature changes with reaction time of crude oil with solidifier(Solidifier-7, onshore oil).*

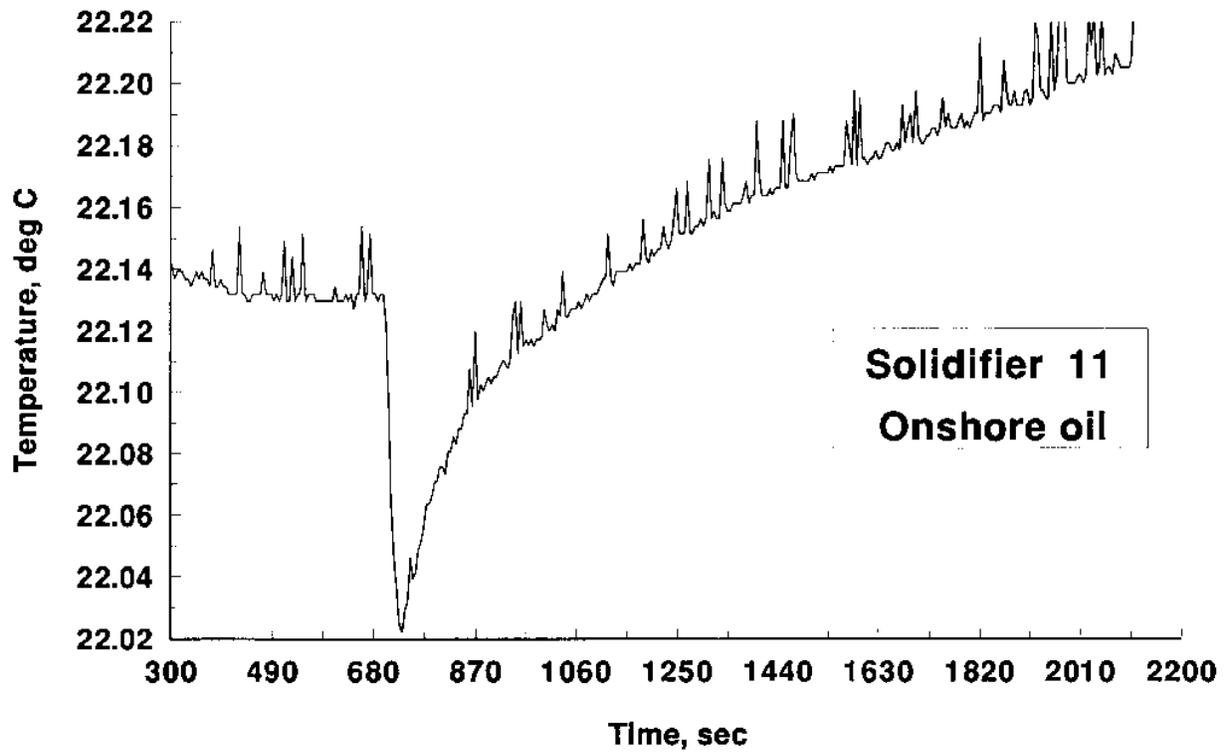


Figure A.2 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-11, onshore oil).*

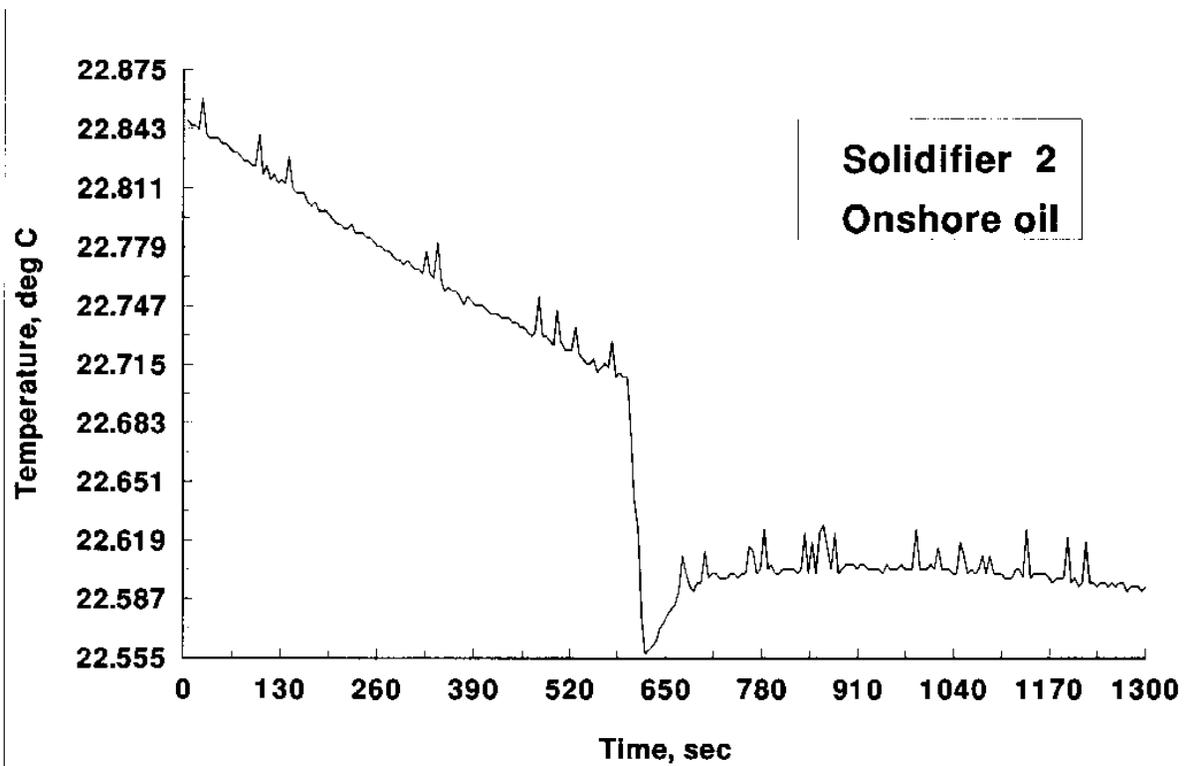


Figure A.3 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-2, onshore oil).*

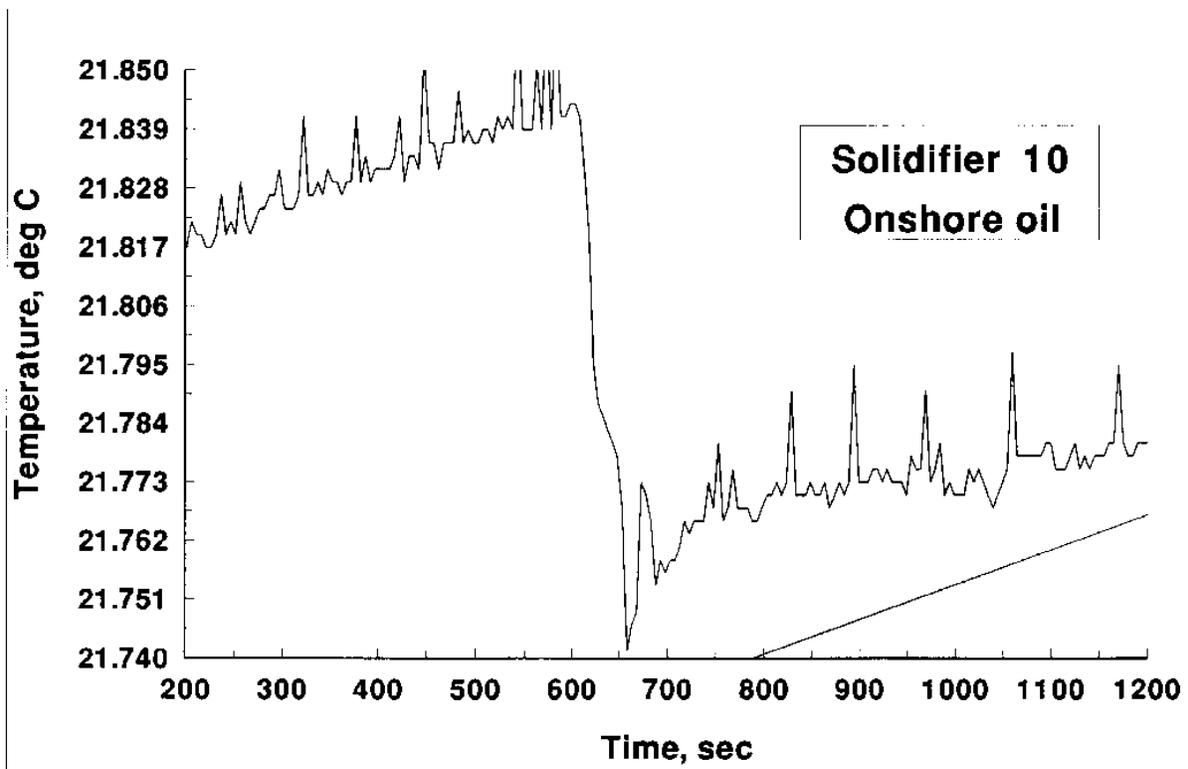


Figure A.4 Temperature changes with reaction time of crude oil with solidifier (Solidifier-10, onshore oil).

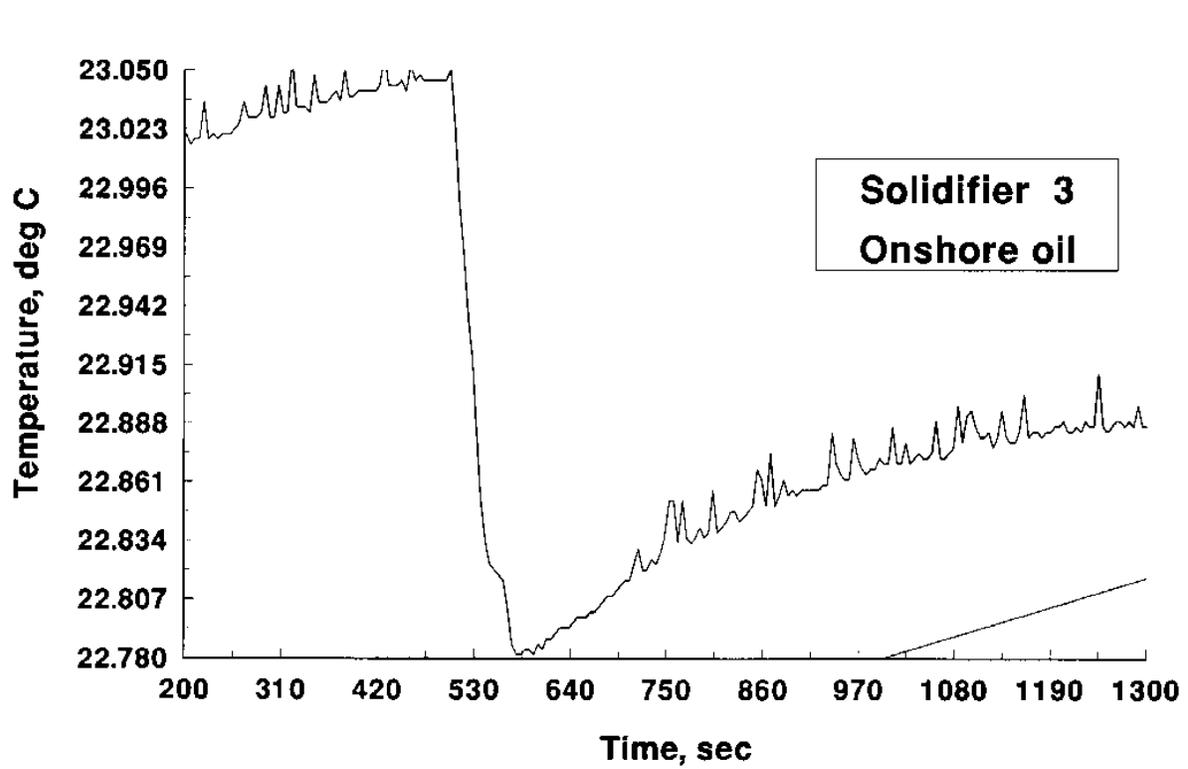


Figure A.5 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-3, onshore oil).*

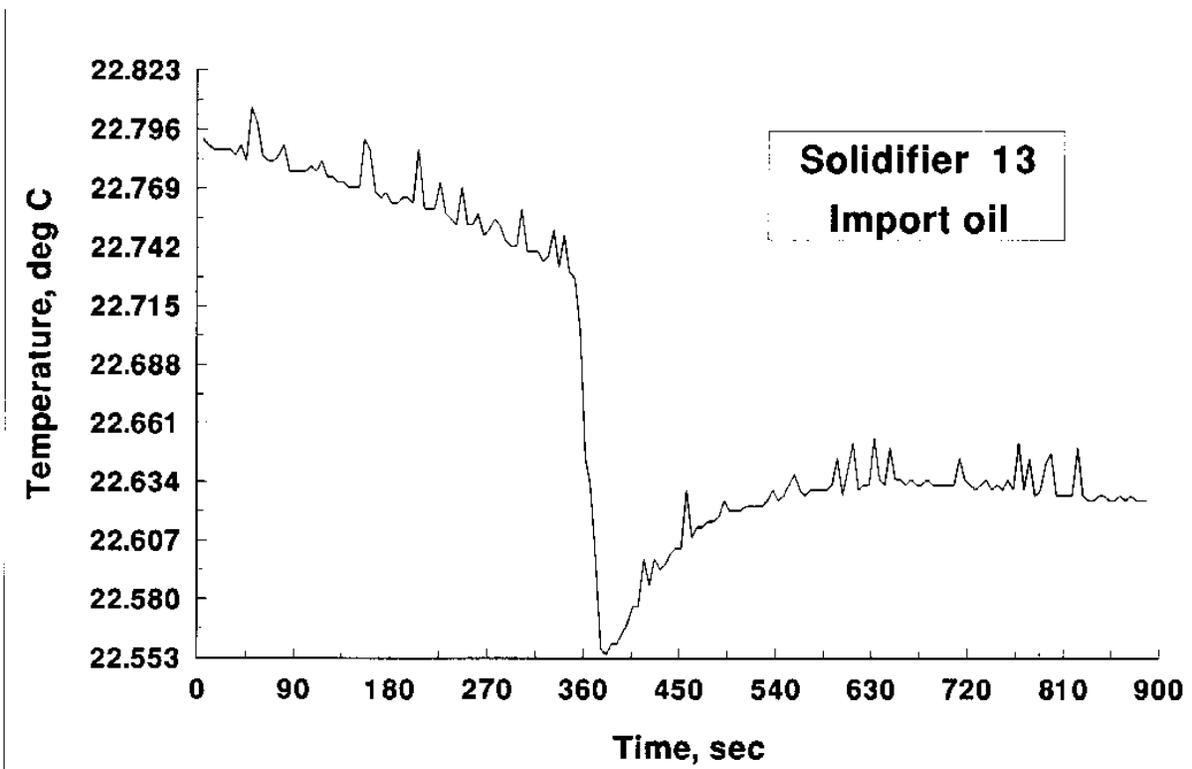


Figure A.6 Temperature changes with reaction time of crude oil with solidifier (Solidifier-13, imported oil).

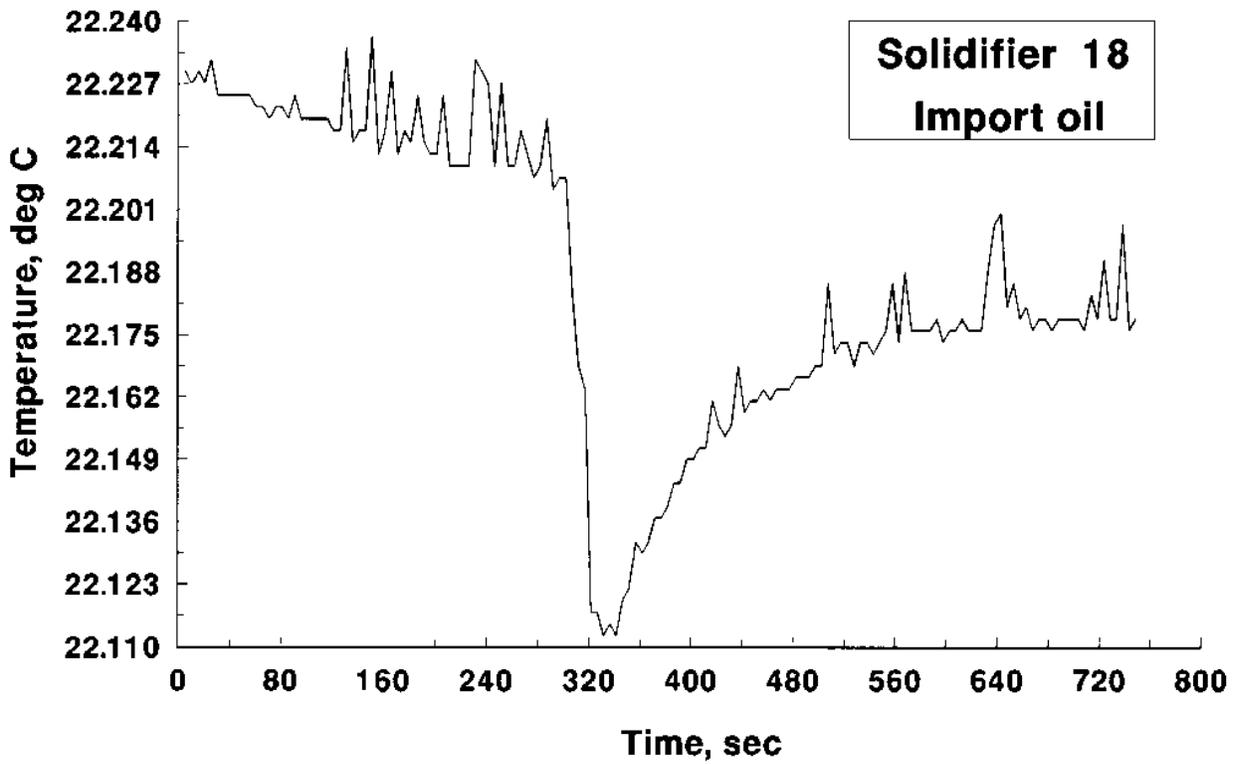


Figure A.7 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-18, imported oil).*

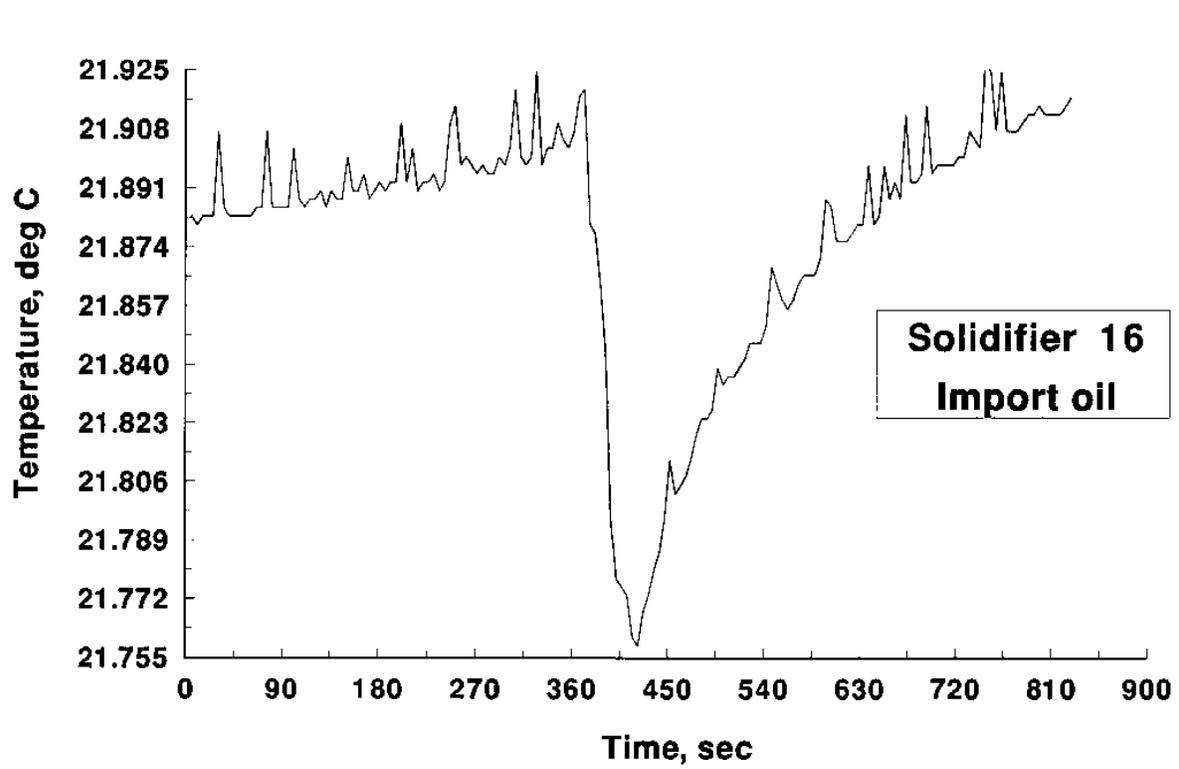


Figure A.8 Temperature changes with reaction time of crude oil with solidifier (Solidifier-16, imported oil).

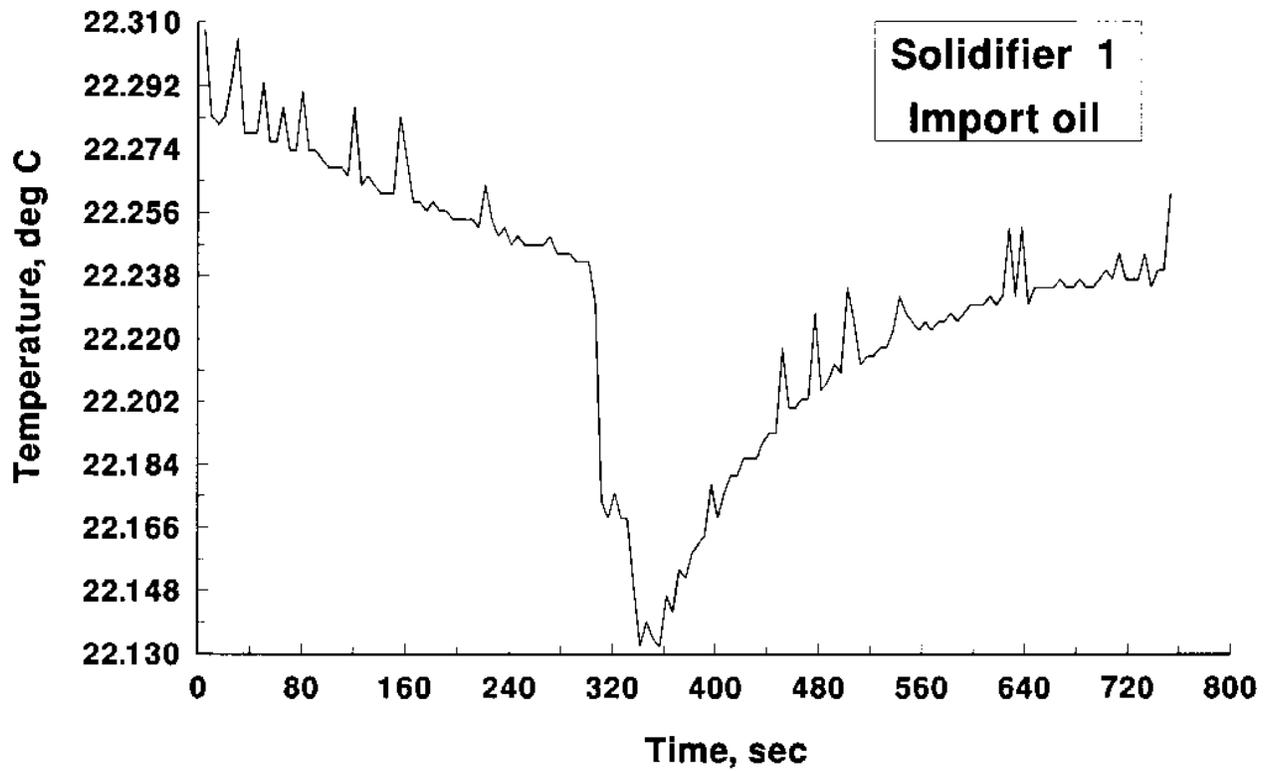


Figure A.9 *Temperature changes with reaction time of crude oil with solidifier (Solidifier-1, imported oil).*

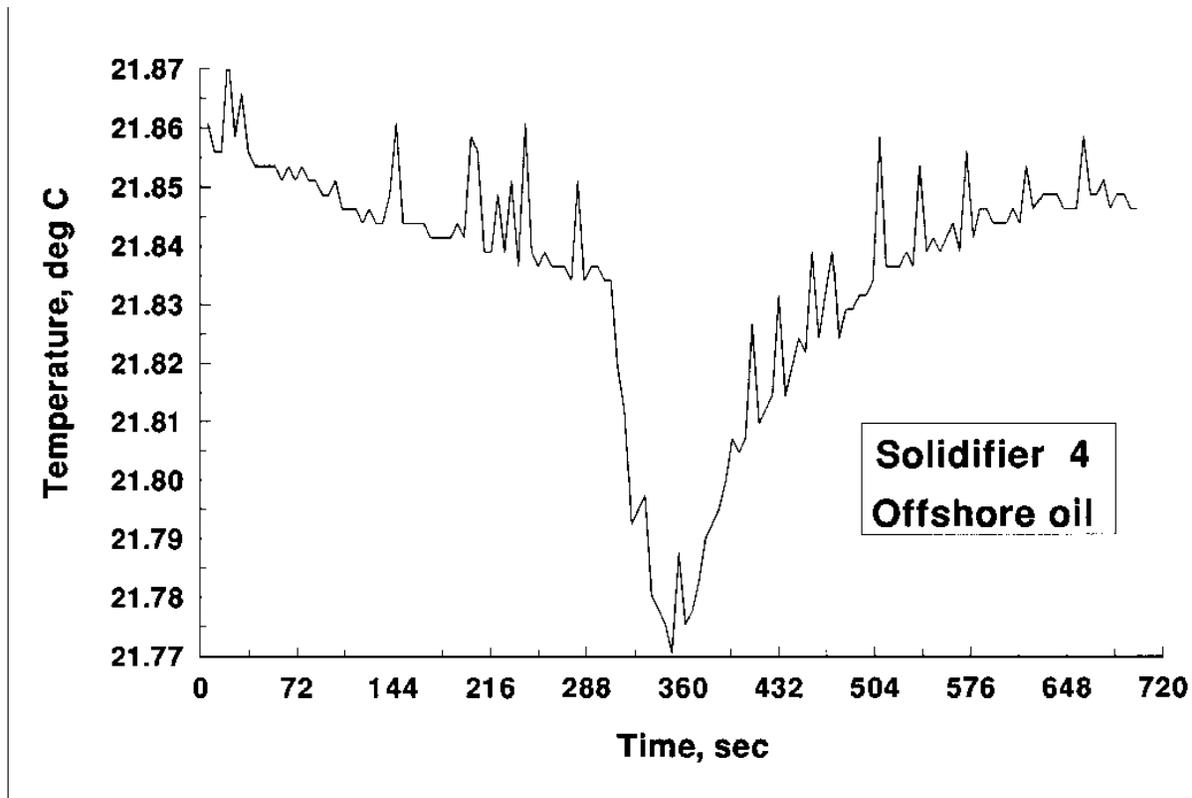


Figure A.10 Temperature changes with reaction time of crude oil with solidifier (Solidifier-4, offshore oil).

Appendix B. Plots of Crude Oil Characteristics versus Heat of Reaction, Crude Oil Characteristics versus Viscosity, and Crude Oil Characteristics versus Viscosity/Consumption Level

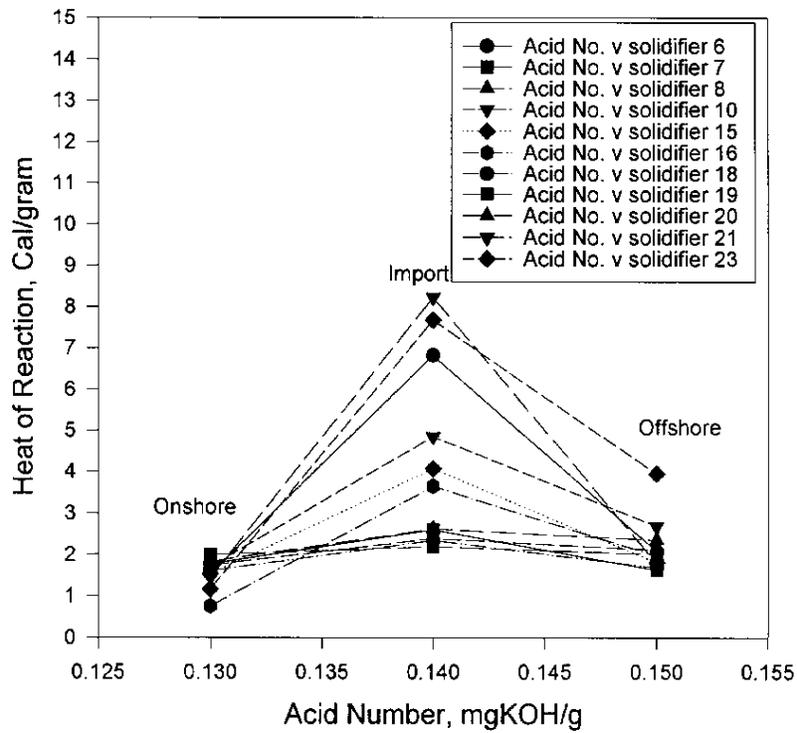


Figure B.1 Heat of reaction versus acid number for selected solidifiers.

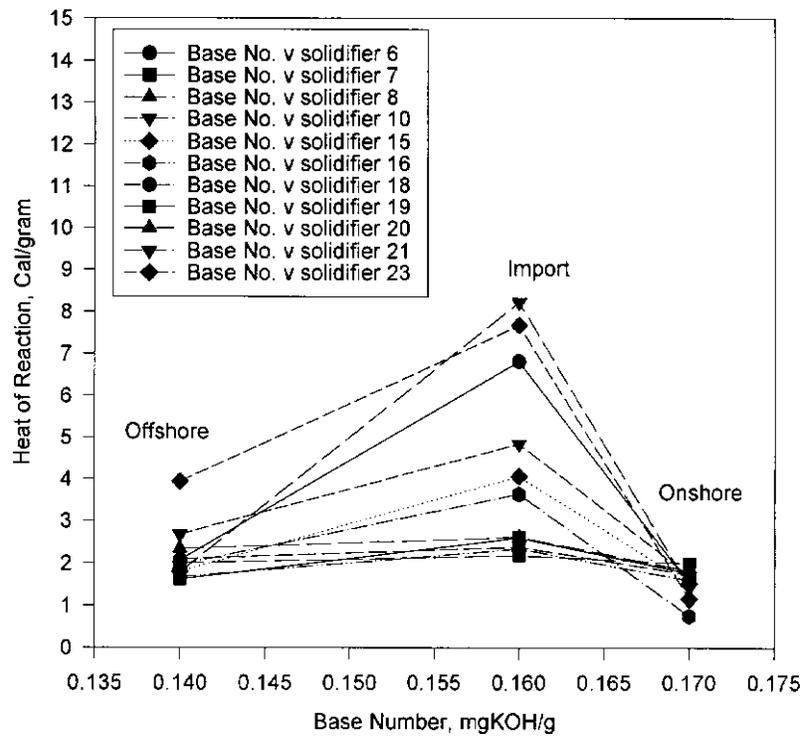


Figure B.2 Heat of reaction versus base number for selected solidifiers.

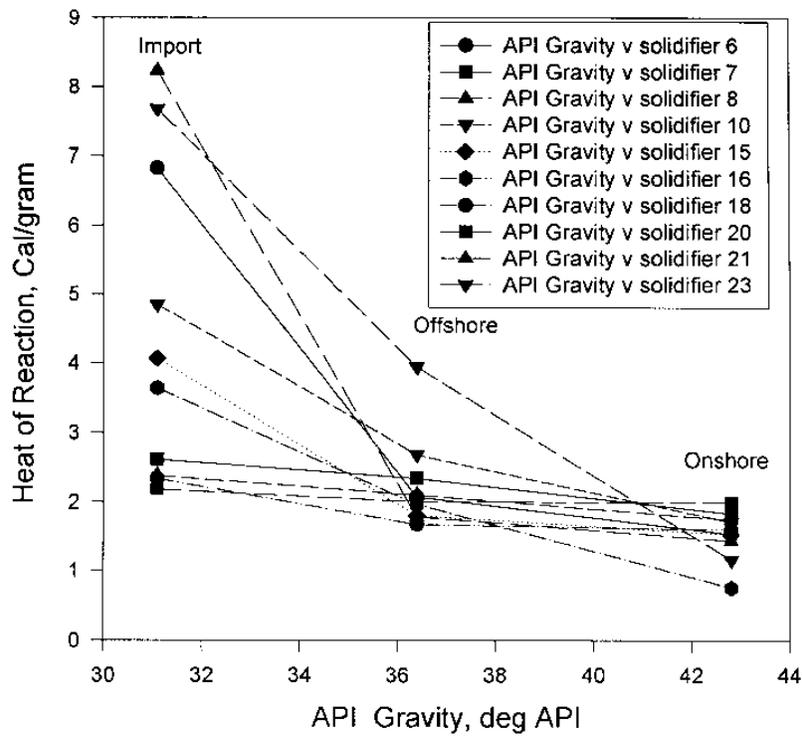


Figure B.3 Heat of reaction versus API gravity for selected solidifiers.

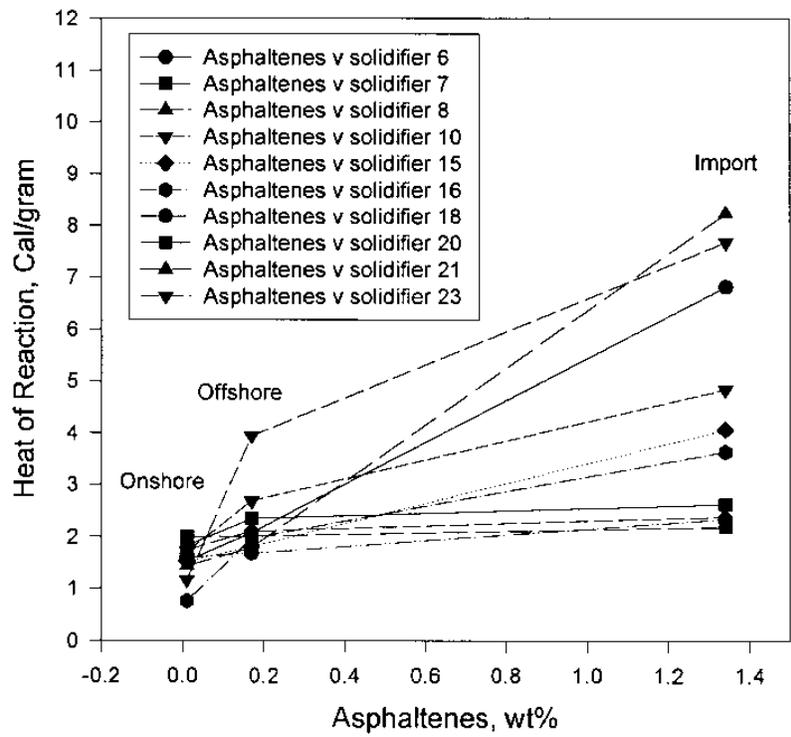


Figure B.4 Heat of reaction versus asphaltenes for selected solidifiers .

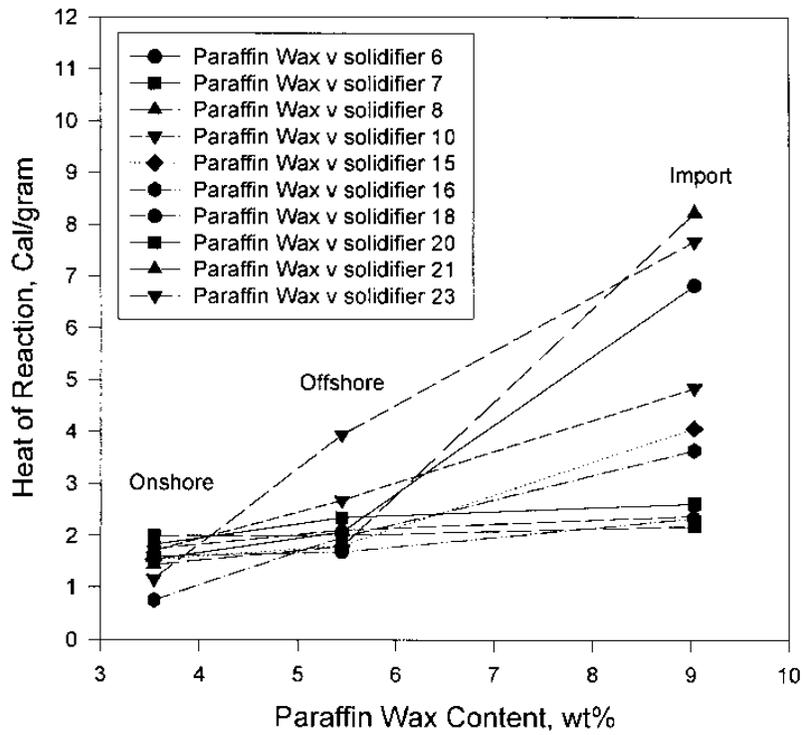


Figure B.5 Heat of reaction versus paraffin wax content for selected solidifiers.

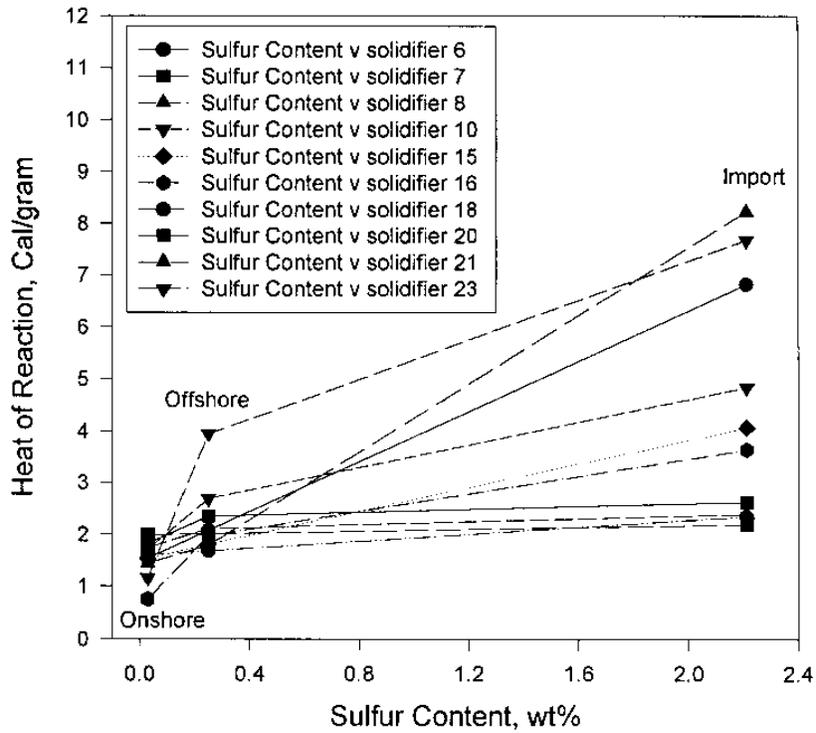


Figure B.6 Heat of reaction versus sulfur content for selected solidifiers.

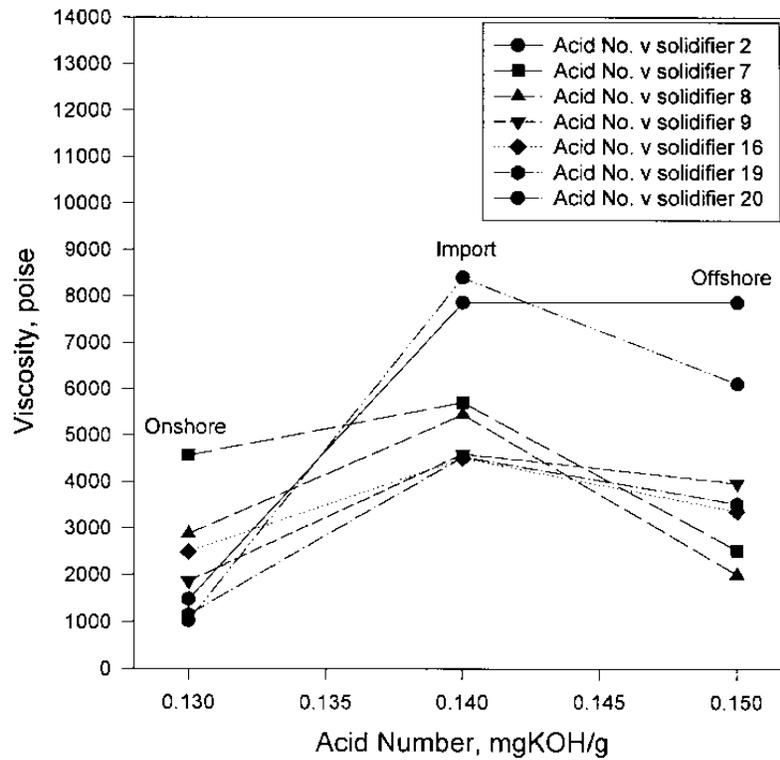


Figure B.7 Viscosity versus acid number for selected solidifiers.

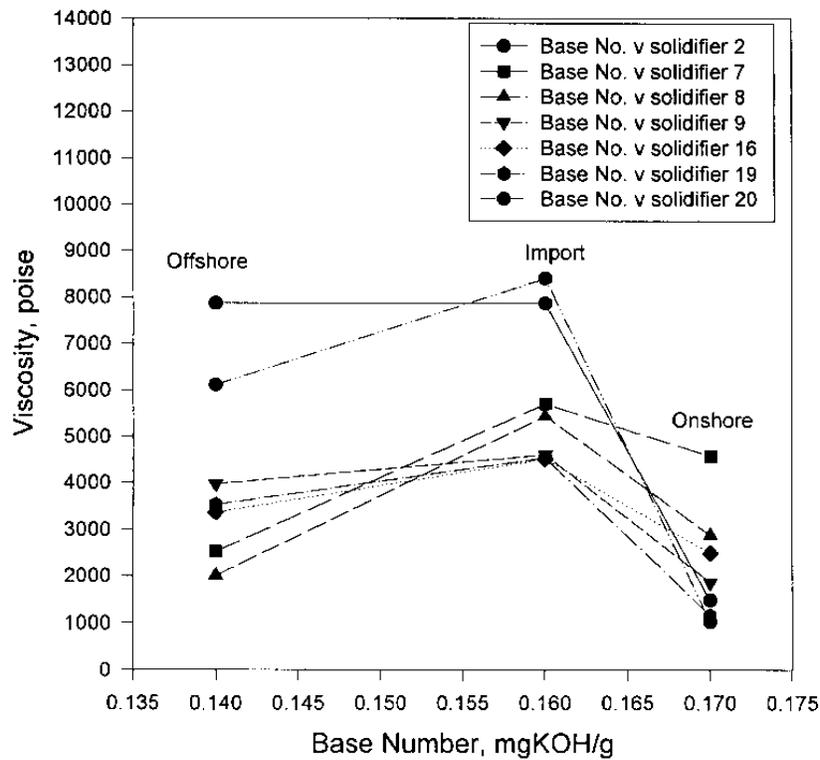


Figure B.8 Viscosity versus base number for selected solidifiers.

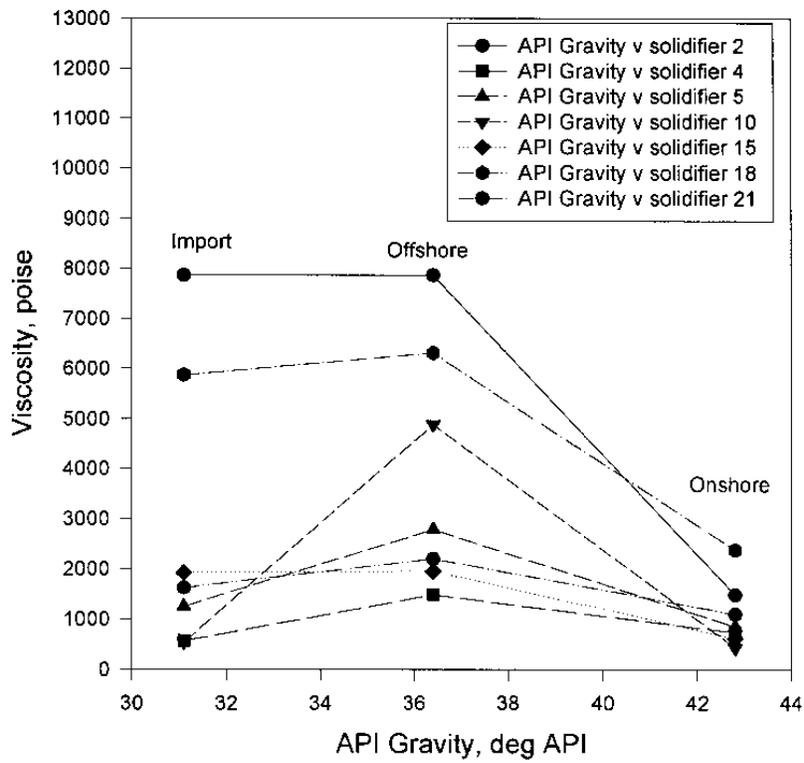


Figure B.9 *Viscosity versus API gravity for selected solidifiers.*

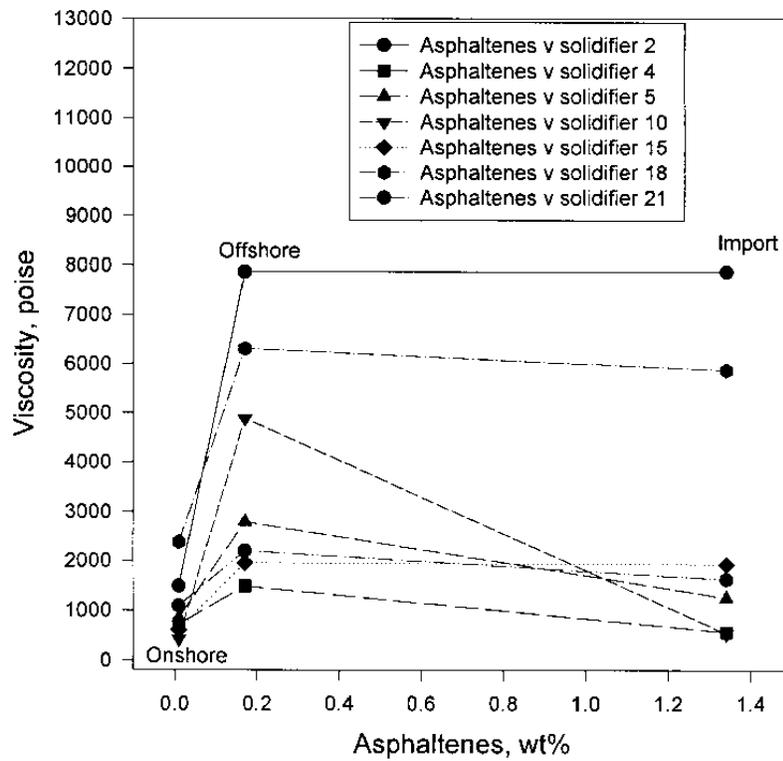


Figure B.10 Viscosity versus asphaltenes for selected solidifiers.

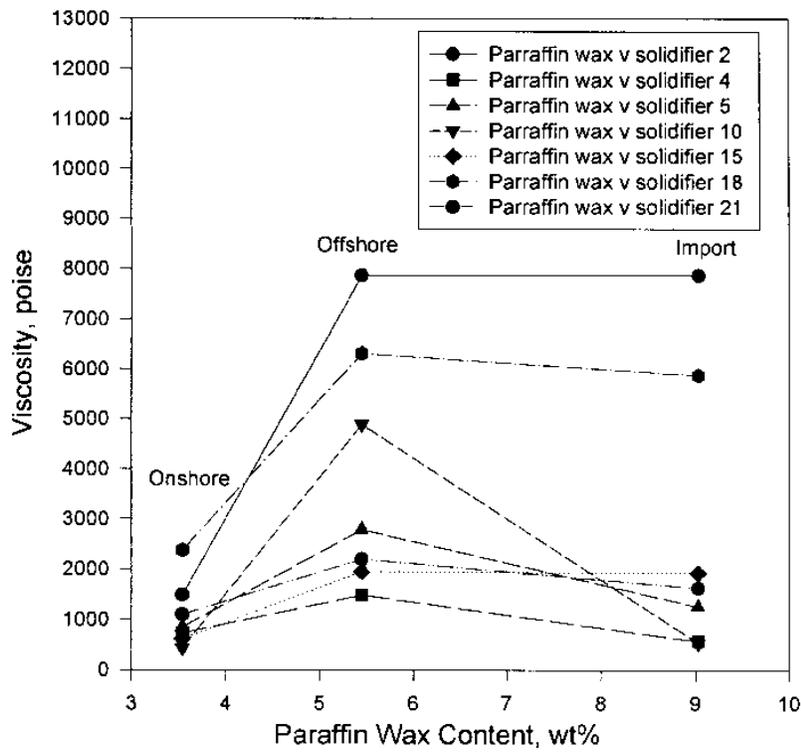


Figure B.11 Viscosity versus paraffin wax content for selected solidifiers.

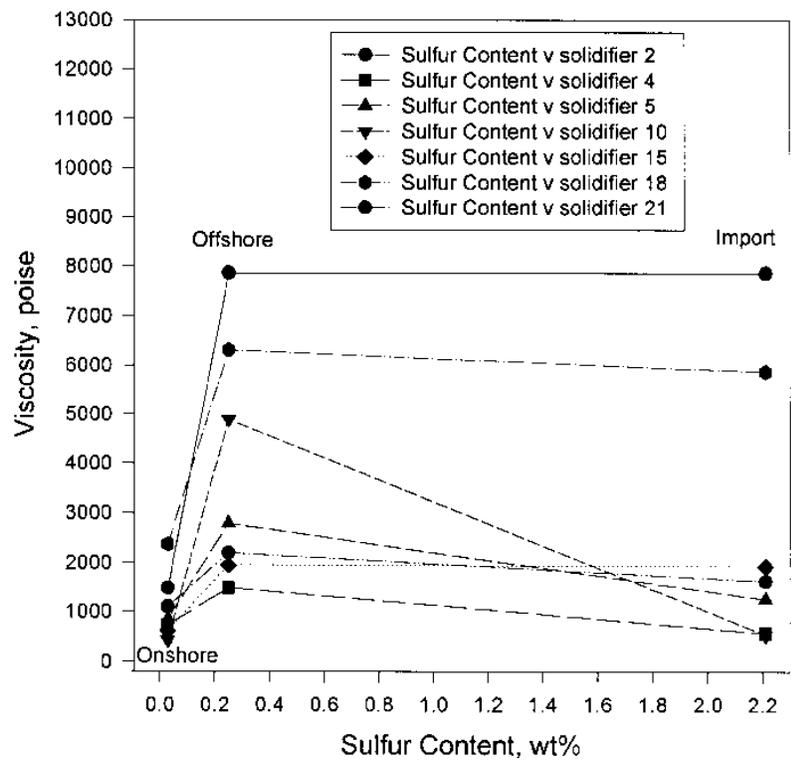


Figure B.12 Viscosity versus sulfur content for selected solidifiers.

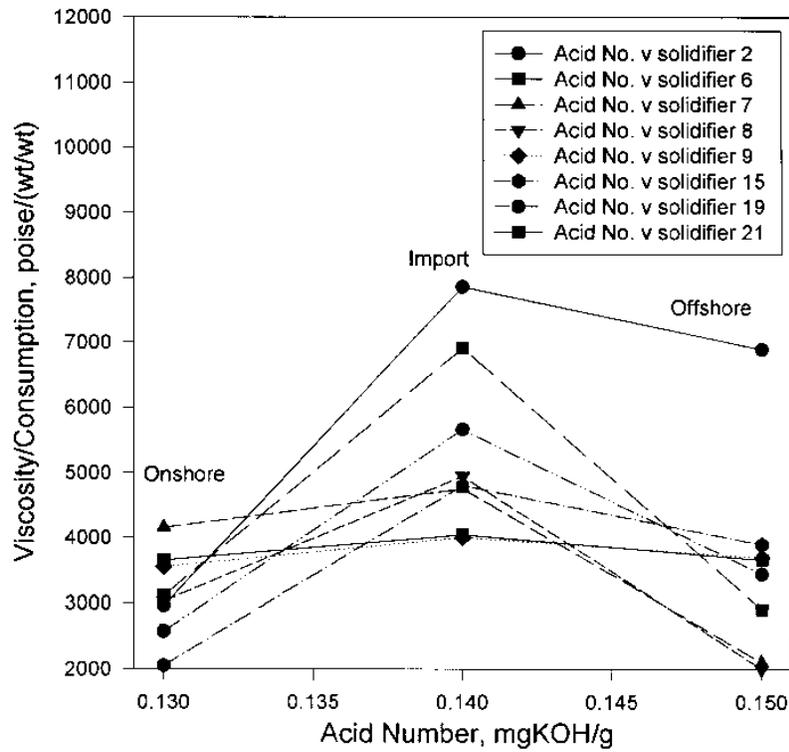


Figure B.13 Viscosity/consumption level versus acid number for selected solidifiers.

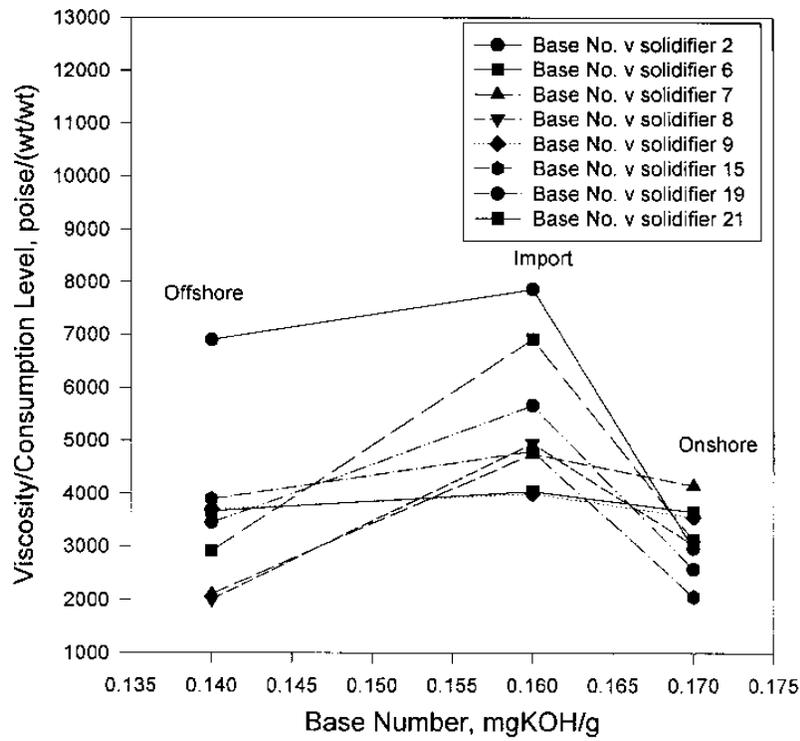


Figure B.14 Viscosity/consumption level versus base number for selected solidifiers.

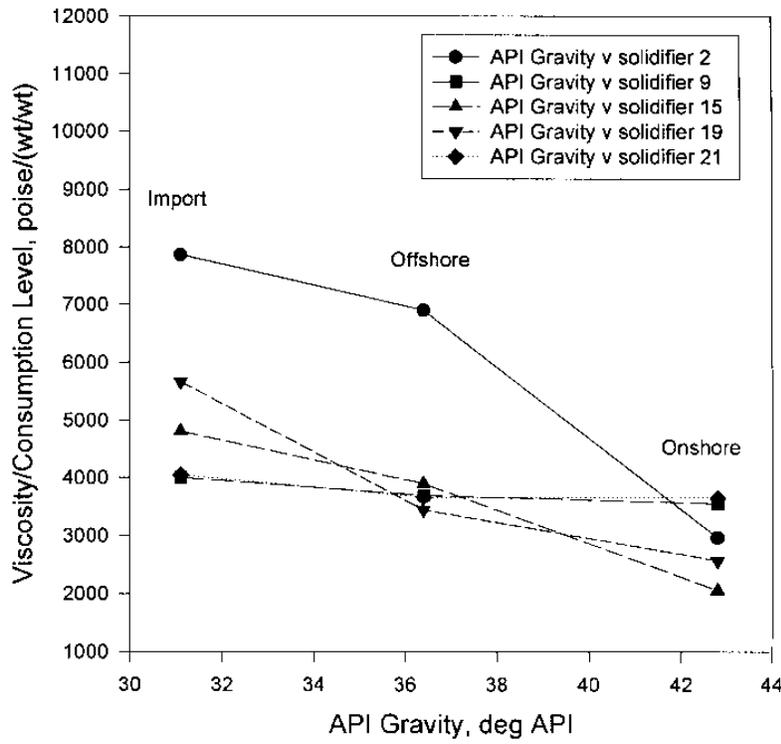


Figure B.15 Viscosity/consumption level versus API gravity for selected solidifiers.

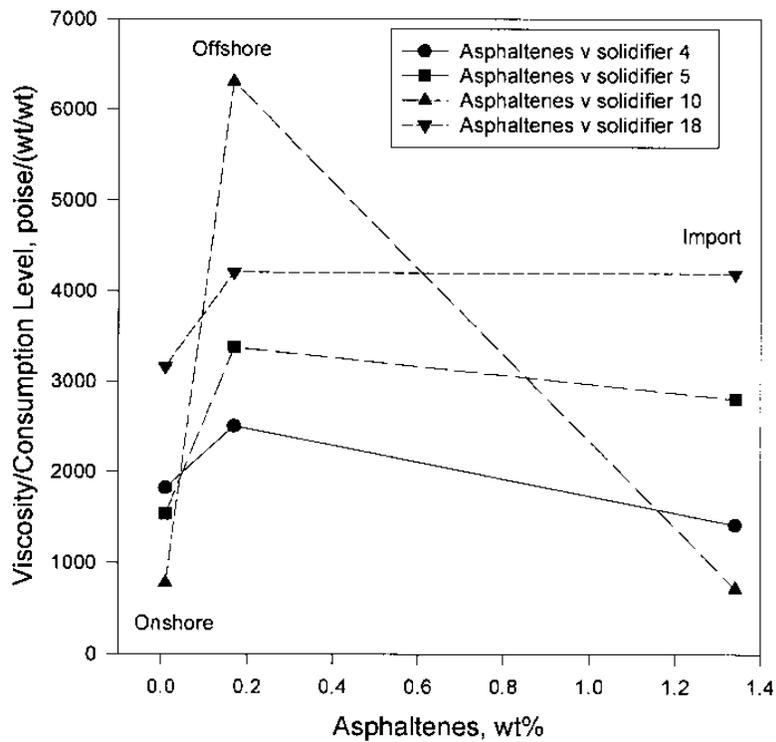


Figure B.16 Viscosity/consumption level versus asphaltenes for selected solidifiers.

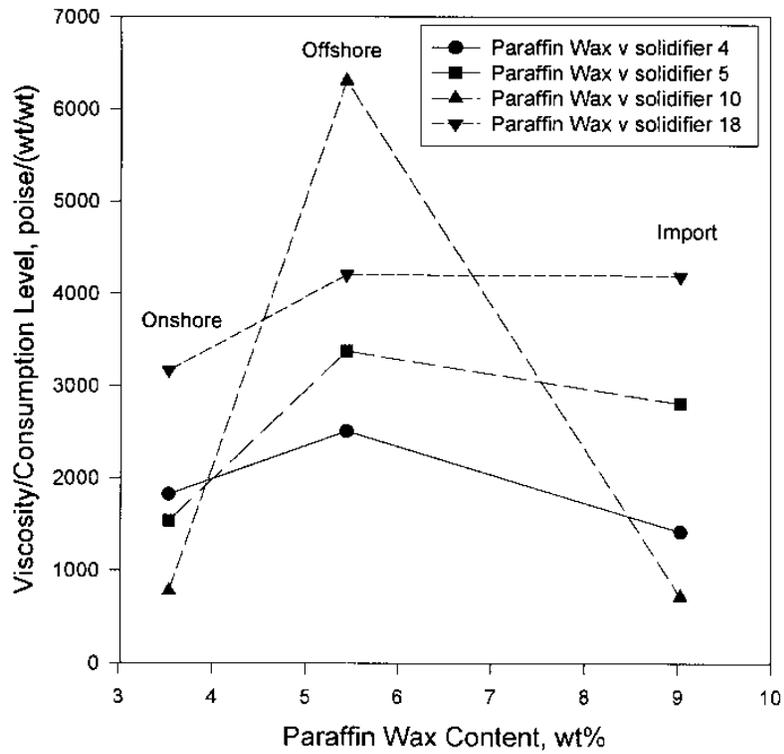


Figure B.17 Viscosity/consumption level versus paraffin wax content for selected solidifiers.

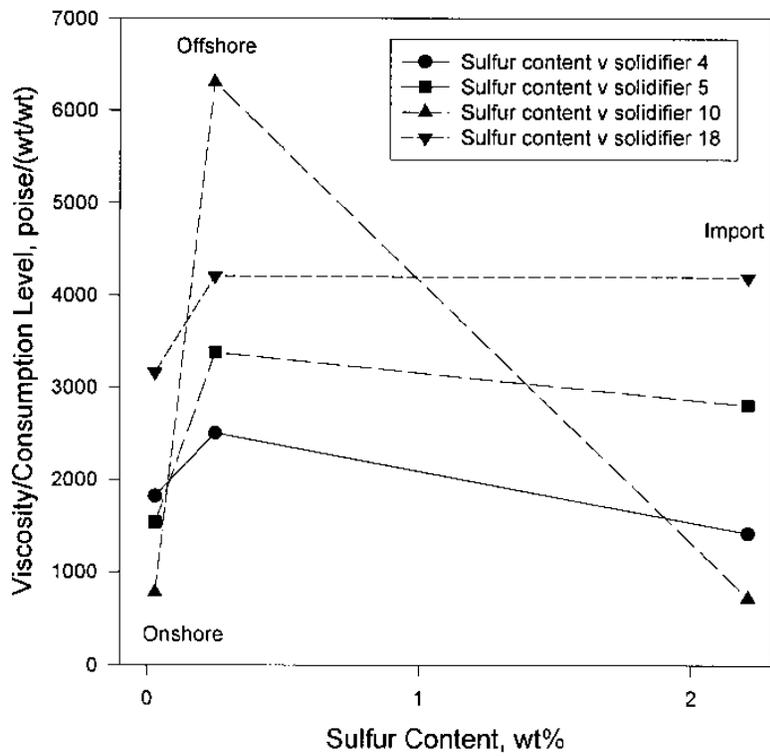


Figure B.18 Viscosity/consumption level vs. sulfur content for selected solidifiers.