

Solidification of Hydrocarbon Liquids using Polymer Blends

by

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A thesis submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Auburn, Alabama
August 09, 2010

Keywords: solubility parameter, solidifier, temperature-time plot, heat of solidification

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Abstract

Solidifiers are composed of dry, high molecular weight polymers that have a porous matrix and a large oleophilic surface area. They bond with the hydrocarbon liquids by molecular interaction (hydrogen bonding, London forces, etc.) and are employed as a method of preventing spill propagation and dispersion in order to minimize the impact of hydrocarbon liquid spills.

CIAgent© is a non-toxic, proprietary polymer blend listed in EPA National Contingency Plan Product Schedule as a “Solidifier” for use on oil spills in the navigable waterways of United States. CIAgent© can be used on oil, hydraulic fluid, transmission oil, or any petroleum-based fluids, solidifying the hydrocarbon liquid into a cohesive rubber-like, inert mass upon contact. Once solidified, the rubbery mass is easy to remove; keeping the spill contained and minimizing costs. The recovered solidified material can be reused as fuel or filler for other products or can be land filled.

Solidifier effectiveness is defined as the amount of agent required to solidify the hydrocarbon liquid under standard conditions. Hence, the solidifier needs to be characterized with respect to the effectiveness for the extensive hydrocarbon liquids that could be encountered.

This objective was achieved by measuring the heat of solidification using a solution calorimeter (Parr Instruments, Model No. 6755). Experiments were conducted at room temperature and atmospheric pressure. A Temperature–time plot was obtained, and the

temperature difference upon solidification was determined. The temperature change was correlated with the solubility parameters (δ_d , δ_p , and δ_h) of the hydrocarbon liquids and a three-dimensional map was generated to represent CIAgent© solidification effectiveness. The ease with which the CIAgent© solidifies the hydrocarbon liquid was determined from the calculated heat of solidification value. The release or adsorption of heat during the solidification process thus has implications for how CIAgent© applications should be conducted.

Acknowledgements

I would like to acknowledge my deep and sincere gratitude towards my advisor, Dr. Thomas Hanley, the best teacher and advisor I could have wished for, for his immense support, motivation, patience and continuous encouragement. I am thankful to him for his invaluable guidance and sound advice provided during the course of this study. His wide knowledge and logical school of thought have been of great value to me. I would like to thank Mr. Dan Parker, CIAgent Solutions, for his valuable time and help. I am deeply grateful to my committee members, Dr. Steve Duke and Dr. Virginia Davis for their valuable suggestions and time. During this work I have collaborated with many colleagues for whom I have great regard and I wish to extend my warm thanks to all those who have helped me with my work. I would also like to extend my heartfelt gratitude and appreciation to all my friends, especially Ms. Priyanka Dhage, for the patience, understanding and support that kept me sane during difficult times. The road to my graduate degree has been long and winding and I owe my most sincere gratitude and gratefulness to my parents, Mrs. and Mr. Mohanraj Solomon, for their enduring love and immense moral support and motivation. I thank the Almighty whose guidance and unchanging love has protected me and kept me going all these years.

“I can do all things through Him who gives me strength” – Philippians 4:13

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List of Symbols

δ	Solubility parameter
δ_t	Total solubility parameter
δ_d	Solubility parameter due to dispersion forces
δ_p	Solubility parameter due to polar forces
δ_h	Solubility parameter due to hydrogen bonding
χ	Interaction parameter
ΔG^M	Free energy of mixing
ΔH^M	Heat of mixing
ΔS^M	Entropy change of mixing
ϕ 's	volume fraction of solvent and polymer
V_M	Volume of the mixture
$\Delta G_{\text{noncomb}}^M$	Non-combinatorial free energy of solution
CED	Cohesive Energy Density
ΔH	Enthalpy of vaporization
R	Universal Gas Constant and Radius of sphere

V_m	molar volume
$D_{(S-P)}$	Distance between solvent and center of solubility sphere
f_d, f_p, f_h	Fractional parameters
ΔT	Temperature difference
T_S	Sample Temperature
T_E	Surrounding Temperature
m	mass of the solution
C_p	Specific heat of the solution
q, Q	Energy change
T_f	Final Temperature
T_i	Initial Temperature
QE	Energy Input
e	Energy equivalent of the calorimeter
E	molar cohesive energy

CHAPTER 1

Introduction

1.1- Oil Spills

An oil spill is the accidental petroleum release into the environment. Every year oil spills occur, often causing economical, social and environmental problems. Oil spills into rivers, bays and the ocean are caused by accidents involving tankers, barges, pipeline and refineries, usually while the oil is being transported. In addition to accidental spills, oily waters are found in petroleum production, numerous waste pits and manufacturing operations involving lubricating oils. Oil spills vary in magnitude, location and the degree of soil, water and debris contamination.

The sources of oil spills, the types of oil spilled into the sea and the causes of spills from any type of ship or vessel worldwide are shown in the Figure 1.1. About 24% of oil spilled into the sea comes from the transportation sector, which includes tankers, freighters, barges and the other vessels. Figure 1.1 also shows that grounding is the leading cause of oil spills from vessels (26%) followed by collision at 22%. Some other accidental causes of oil spills are explosion/fire (9%), ramming (9%) and sinking (7%), with human error (5%) and mechanical failure (2%) causing the least number of spills (Fingas 2001).

There is a need for cleanup of oil spills to reduce its many adverse environmental effects. 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. A number of factors must be considered to evaluate the adequacy of oil spill response. These include sea state, weather conditions, type of the oil, size of spill, elapsed time from spill to

response, presence of ice and level of response effectiveness. One of the basic methods for oil spill collection and clean up is by using solidifiers. Solidifiers are used to render the spill's oil phase viscous and suspended, thus immobilizing the spill's mass.

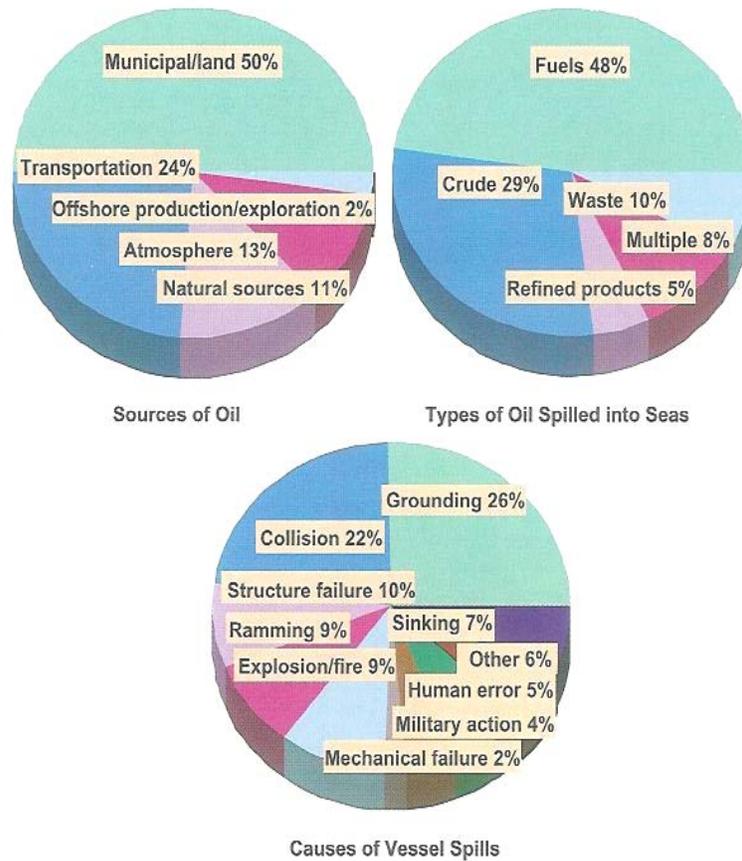


Figure 1.1- Statistical summary of oil spills into the seas worldwide (Fingas 2001)

1.2- Solidifiers

Solidifiers are a hydrophobic dry granular material made up of polymers. Unlike sorbents which physically absorb oil, solidifiers chemically bond with the oil to form a cohesive solidified mass with minimal volume increase (El-Nemr 2006). Firmly solidified oil has a

rubber-like consistency that tends to retain its shape and does not pull apart easily (Fingas 2008). Solidified oil floats on water and does not leave sheen when removed. Some incentives for using solidifiers include: rapid containment, application for land and water, non-toxic and non-leaching, reduced emulsion formation and lower cost alternatives for disposal.

The prime motivation for using solidifiers is to reduce the spread of oil and protect wildlife and receptor areas. To accomplish this, the solidifier application must be well targeted and effectiveness high. Furthermore, the recovery of the solidified oil must occur rapidly and efficiently. The second motivation for using the solidifiers is to reduce the impact on birds and mammals on the water surface.

Solidifiers might be best restricted to small spills on water near shore. Land-based spills are also treated using solidifiers. There are a number of issues involved in the utilization of the 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. Some of the commercially available solidifiers are ALSOCUP, CIAgent®, WASTE-SET 3200, WASTE-SET 3400, Nochar A650, AQUA N-CAP™ polymers, RAPIDGRAB 2000, RUBBERIZER®

1.3- Thesis Motivation

The solidifier of interest in this work is CIAgent®, a premier product of C.I. Agent Solutions, Louisville, Kentucky. CIAgent® is a non-toxic, non-hazardous, non-corrosive, non-carcinogenic, eco-friendly petroleum based blend of polymers, used to immobilize petroleum and related petrochemical emergency releases on land and water. It is a proprietary polymer blend, listed in the EPA National Contingency Plan Product Schedule as a “Solidifier” for use on

oil spills in the navigable waters of the United States. CIAgent© polymers have a long chain molecular structure that is highly cross-linking with organic liquid hydrocarbons, enabling it to solidify liquid hydrocarbons (sheen, gasoline, diesel and oils, including crudes) upon contact into an inert solid rubber-like mass that floats.

Solidifier effectiveness is defined as the amount of agent required to solidify the hydrocarbon liquid under standard conditions. Hence CIAgent© needs to be characterized with respect to the effectiveness for the extensive hydrocarbons that could be encountered.

This objective was achieved by measuring the heat of solidification using a solution calorimeter (Parr Instruments, Model No. 6755). Experiments were conducted at room temperature and atmospheric pressure. A temperature-time plot was obtained, and the temperature difference upon solidification was determined. The temperature change was correlated with the solubility parameters (δ_p , δ_d and δ_h) of the hydrocarbon liquids and a three dimensional map was generated to represent CIAgent© solidification effectiveness. The ease with which the CIAgent© solidifies the hydrocarbon liquid was determined from the calculated heat of solidification value. The release and absorption of heat during the solidification process has implications for how CIAgent© applications should be conducted. The mechanism by which the CIAgent associates with the hydrocarbon liquids was also studied.

CHAPTER 2

Literature Review

2.1- Theory on Solubility parameters

The solubility parameter, δ , indicates the relative solvency behavior of a specific solvent. The basic assumption in the solubility parameter concept is that a correlation exists between the cohesive energy density and mutual solubility. Liquids with similar solubility parameters dissolve the same solutes to be mutually compatible leading to an indirect method of measuring the solubility parameter of the polymer. When the polymer and the solvent have the same solubility parameter, maximum expansion of the polymer molecule will occur and therefore the highest viscosity would be obtained. If the polymer is cross-linked, the individual parts of the polymer chains (polymer segments) solvates to give a swollen gel. Maximum swelling will take place when the solubility parameter of the polymer matches that of the solvent and the interaction parameter, χ , is minimal. The interaction parameter accounts for the contribution of the non-combinatorial entropy of mixing and the enthalpy of mixing to the Gibbs energy of mixing (Rodriguez 2003)

2.1.1- Free Energy of Mixing

The free energy of mixing must be zero or negative for the solution process to occur spontaneously (Rodriguez 2003). The free energy change for the solution process is given by the expression

$$\Delta G^M = \Delta H^M - T\Delta S^M \quad (2.1)$$

where ΔG^M is the free energy of mixing, ΔH^M is the heat of mixing, T is the absolute temperature and ΔS^M is the entropy change in the mixing process.

Equation 2.2 gives the heat of mixing as proposed by Hildebrand and Scott (1950 and 1962).

$$\Delta H^M = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 \quad (2.2)$$

where φ_1 and φ_2 are volume fractions of solvent and polymer respectively and V_M is the volume of the mixture. This equation is often cited as a shortcoming in that only positive heats of mixing are allowed. Patterson and Delmas (1962) showed that the right-hand side of Equation 2.2 should be $\Delta G_{noncomb}^M$ and not ΔG^M .

$$\Delta G_{noncomb}^M = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 \quad (2.3)$$

The non-combinatorial free energy of solution $\Delta G_{noncomb}^M$ includes all free energy effects other than the combinatorial entropy of solution occurring because of simply mixing the components. This result is consistent with the Prigogine corresponding states theory of polymer solutions and can be differentiated to give expressions predicting both positive and negative heats of mixing (Hildebrand and Scott 1962; Patterson and Delmas 1962). Therefore, both positive and negative heats of mixing could be expected from theoretical considerations and have been measured accordingly. Solubility parameters can be used to predict both positive and negative heats of mixing.

2.1.2- Cohesive Energy Density: Solubility parameter is defined in terms of cohesive energy density (CED) per unit volume. The cohesive energy density is in turn derived from the heat of vaporization. The amount of energy (in calories) that was added from the onset of a reaction to the point of its completion would give a direct indication of the amount of energy required to

separate the molecules and thus the amount of Van der Waals forces that hold the molecules together (Burke 1984) . From the heat of vaporization, we can derive the cohesive energy density (CED) by the following expression

$$CED = \frac{\Delta H - RT}{V_m} \quad (2.4)$$

where ΔH = heat of vaporization, R = universal gas constant, T = temperature, V_m = molar volume

In other words, the cohesive energy density is a numerical value that is a direct reflection of the van der Waals forces holding the molecules together. This correlation between the vaporization and the van der Waals forces translates into a correlation between vaporization and solubility behavior as the same intermolecular attractive forces have to be overcome to vaporize a liquid as well as dissolve it (Burke 1984).

2.1.3- Solubility Parameter and Units of Measurement

In 1936 Hildebrand defined solubility parameter as the square root of the cohesive energy density indicating the solvency behavior of a specific solvent.

$$\delta = \sqrt{CED} \quad (2.5)$$

The solubility parameter is the measure of the strength of the interactions between the molecules of a substance, since vaporization involves increasing the average distance of separation between them. Two molecules are “like” one another if the strength of their interactions is similar. A widely used dimension for the solubility parameter is $(\text{cal}/\text{cm}^3)^{1/2}$ called the hildebrand. Other units used are $(\text{J}/\text{cm}^3)^{1/2}$ and $(\text{MPa})^{1/2}$ which are identical. One hildebrand is the equivalent of

$2.046 \text{ (MPa)}^{1/2}$. Solubility is likely to occur when a polymer and solvent have similar solubility parameters.

2.1.4- Experimental Determination of Solubility Parameters, Solvents:

The determination of solubility parameter of a solvent is relatively easy. The molar volume is determined by pycnometry or a value can be found from literature. Since most solvents have significant volatility, their heat of vaporization can be determined calorimetrically. This is converted into the desired energy of vaporization through a conversion term that is simply the change in pressure-volume product for the process

2.1.5- Experimental Determination of Solubility Parameters, Polymers:

Indirect methods are used to determine the solubility parameters of a polymer. A series of solvents of known solubility parameters are tested to determine solvency for a polymer. The solvent solubility parameter value δ_1 , corresponding to the midpoint of the “good solvents” is taken to be the solubility parameter of the polymer δ_2 . Another approach is to measure the minimum temperature required to bring about dissolution of the polymer in a series of solvents of known solubility parameters. The solubility parameter of the polymer is taken to be the value of δ_1 that corresponds to the smallest required increase in temperature. If the polymer is cross-linked, the solubility parameter of the polymer is determined by the degree of swelling. A weighed amount of sample is placed in a series of solvents of known solubility parameters. The polymer is allowed to swell and after the swelling reaches equilibrium, the sample is reweighed and the value of the ratio of the swollen volume to the dry volume is calculated. The solubility parameter corresponding to the value of δ_1 at the highest degree of swelling is the solubility parameter of the polymer. Another method involves a theoretical approach called group

additivity scheme (Mark et al., 1992). The appropriate group contributions are added together to predict the solubility parameter of the substance.

2.1.6- Applications:

The fundamental idea is to determine the solubility parameter of the polymer and then use the results to identify a number of solvents that have solubility parameter close to this value. The application criteria would depend on the nature of the studies to be pursued. If the objective is to carry out light-scattering measurements, the need for maximizing the contrast factor would make the index of refraction of the solvent an important consideration. These predictions are for possible miscibility of two amorphous materials. They do not apply to crystalline polymers because of the positive heat of fusion. Polymer solvent interaction could also be characterized by the second virial coefficients A_2 (provides a measure of polymer-solvent interactions) and by the free energy of interaction parameter χ that appears in the Flory-Huggins theory of polymer solution thermodynamics (Mark et al., 1992).

2.2- Solubility Parameter Models

Solubility behavior can be adequately described using Hildebrand values, although, in some cases, the differences in polar composition can give unexpected results. To take into account the strong interactions, the total solubility parameter (Hildebrand value) is broken down into three different components: δ_d , for dispersion forces present in the regular solutions, δ_p , for polar interactions, and δ_h , for hydrogen bonding interactions. Values for the three components have been estimated by both experiments and calculations. When the total CED is estimated from the experimental enthalpy of vaporization, polar and hydrogen bonding parameters may be calculated using bond contribution models (Burke, 1992)

2.2.1- Two-Component Solubility Parameters:

Burrell proposed a scheme to overcome the inconsistencies caused by hydrogen bonding (Burrell 1968). This system of classification is quite successful in predicting solvent behavior and is still widely used in practical applications. The classification according to Burrell may be briefly summarized as follows:

Weak hydrogen bonding liquids: hydrocarbons, chlorinated hydrocarbons, and nitro hydrocarbons.

Moderate hydrogen bonding liquids: ketones, esters, ethers, and glycol monoethers

Strong hydrogen bonding liquids: alcohols, amines, acids, amides, and aldehydes

Specific values are assigned to hydrogen bonding capacity and the values are plotted against Hildebrand values on a two dimensional graph. Hydrogen bonding is a type of electron donor-

acceptor interaction and can be described in terms of Lewis acid-base reactions. For this reason other systems have attempted the classification of solvents according to their electron donating or accepting capability. Such extensions of the Hildebrand parameter to include acidity-basicity scales, and ultimately ionic systems are relatively recent and outside the scope of this paper.

2.2.2- Three-Component Solubility Parameters:

Crowley, Teague and Lowe developed the first three component system using the Hildebrand parameter, hydrogen bonding number and the dipole moment as the three components (Crowley et al., 1966, 1969). A scale representing each of these values is assigned to a separate edge of a large cube. Any point within the cube represents the intersection of three specific values. A small ball, supported on a rod, is placed at the intersection of values for each individual solvent as shown in Figure 2.1

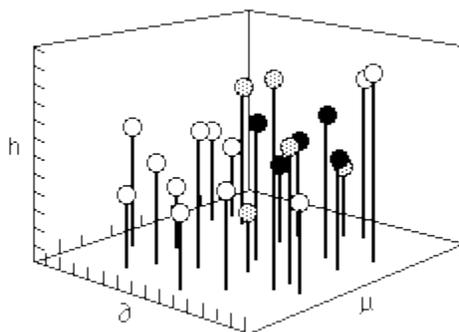


Figure 2.1- A three dimensional solubility parameter plot (Crowley et al., 1966, 1969)

Once the solvent positions have been located within the cube in this way, solubility tests are performed on individual polymers. The positions of the solvents that dissolve a polymer are

indicated by a black ball, non-solvents by a white one and partial solubilities by a grey ball. Once the volumes of solubility of a polymer has been established and drawn in three dimensions, it is translated into a two dimensional graph by a contour diagram.

2.2.3- Hansen Parameter and Model:

Hansen proposed that the concept of the solubility parameter could be extended to polar and hydrogen bonding as well as dispersion interactions (Hansen 1967; Hansen and Skaarup, 1967). The Hansen parameters are additive.

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.6)$$

where, δ_t^2 = total Hildebrand parameter; δ_d^2 = dispersion component; δ_p^2 = polar component and δ_h^2 = hydrogen bonding parameter

The total solubility parameter is estimated from the experimental enthalpy of vaporization, the polar and hydrogen bonding parameters may be calculated using bond contribution methods. Hansen used also used a three dimensional model to plot polymer solubilities. He found that by doubling the dispersion parameter axis, an approximately spherical volume of solubility would be formed for each polymer. This volume is described in Figure 2.2

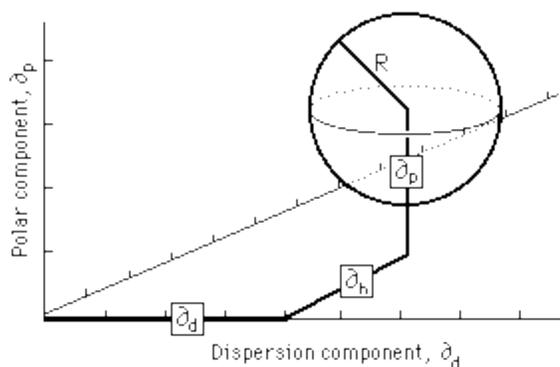


Figure 2. 2- The Hansen volume of solubility for a polymer (Hansen 1967)

The co-ordinates at the center of the solubility sphere are located by means of three component parameters (δ_d , δ_p , δ_h) and the radius of sphere, called the interaction radius (R). A polymer is soluble in a solvent or solvent blend when the Hansen parameters for the solvent lie within the solubility sphere for the polymer. In order to determine this, the distance of the solvent from the center of the polymer solubility sphere is calculated by the following expression,

$$D_{(S-P)} = [4(\delta_d S - \delta_d P)^2 + (\delta_p S - \delta_p P)^2 + (\delta_h S - \delta_h P)^2]^{1/2} \quad (2.7)$$

where $D_{(S-P)}$ = Distance between solvent and center of solubility sphere; $\delta_x S$ = Hansen component parameter for solvent and $\delta_x P$ = Hansen component parameter for polymer

If the distance ($D_{(S-P)}$) is less than the radius of interaction of the polymer, the solvent would be expected to dissolve the polymer. This method avoids reliance on graphic plots and can be effectively used in numerical form. The mathematics involved is tedious and it is perhaps the reason for the limited use of this system (Segarceanu et al., 1997)

2.2.4 -Triangular Model

Teas showed that, for several polymer-solvent systems, it was plausible to use fractional cohesive energy density plotted on a triangular chart to represent solubility limits (Teas 1968). A Teas graph is based on the hypothetical assumption that all materials have the same Hildebrand value. According to this assumption, the solubility behavior is determined by the relative amounts of the three component forces (dispersion force, polar force and hydrogen bonding force) that contribute to the total Hildebrand value. It is in terms of percentages rather than unrelated sums. Hansen parameters are additive components of the total Hildebrand value (Equation 2.6). Teas parameters are fractional parameters derived mathematically from the Hansen parameters and indicate the percent contribution that each Hansen parameter contributes to the whole Hildebrand value as shown in Equation 2.8

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \quad f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \quad f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \quad (2.8)$$

The sum will always be the same (100) if all the fractional parameters are added together.

$$f_d + f_p + f_h = 100 \quad (2.9)$$

This method has the advantage of spreading the points more uniformly over the triangular chart. The disadvantage is that it is completely empirical with a very limited theoretical justification of regular solution theory.

By means of a triangular graph, solvents may be positioned relative to each other in three directions. Alkanes, whose only intermolecular bonding is due to dispersion forces, are located in the far lower right corner of the Teas graph, the corner that corresponds to 100 percent

dispersion force contribution, and 0 percent contribution from polar or hydrogen bonding forces. Moving toward the lower left corner, corresponding to 100 percent hydrogen bonding contribution are the solvents that exhibit increasing hydrogen bonding capability. Moving upwards from the bottom of the graph are solvents of increasing polarity, due less to hydrogen bonding functional groups than to an increasingly greater dipole moment of the molecule like the ketones and nitro compounds.

Polymer Solubility Window: The polymer solubilities using the solvent positions are indicated using methods similar to those used by Crowley and Hansen (Crowley et al., 1966 and Hansen 1967). A polymer is tested in various solvents and the results are indicated on the graph. The edges of this area or the polymer solubility window as shown in Figure 2.3 can be determined in the following way. The liquids from diverse locations on the graph are mixed with the polymer and the degree of swelling or dissolution is noted using cloud point determinations. The mixture producing solubility is noted thus determining the edge of the solubility window. The procedure is repeated on various solvents and the boundaries can be accurately determined.

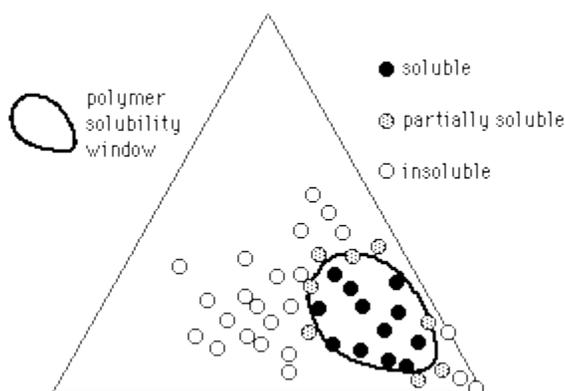


Figure 2.3- The solubility window of a hypothetical polymer (Burke 1984)

2.2.5- Effect of Physical Conditions on Solubility Parameters

Temperature:

From the Equation 2.10, it is found that the Hildebrand parameter decreases with the increasing temperature and gives a good approximation over a moderate temperature range for the simpler, non-polar liquids

$$\frac{d \ln \delta}{dt} = -k \quad (2.10)$$

where k is a constant. Hildebrand parameters for hydrocarbons may be fitted to an equation of the form

$$\delta = \delta_0 + mT \quad (2.11)$$

where m is of the order of $-0.03 \text{ MPa}^{1/2}\text{K}^{-1}$ (Barton 1991; Chee 2005). For hydrocarbon solvents the average decrease in δ for every 1°C temperature rise is ~ 0.01 , which has little effect on practical applications.

Mizerovski and Vansyatskaya used the literature data on enthalpy of vaporization and density to calculate the Hildebrand parameters of organic compounds over a wide temperature range (Mizerovskii et al., 1988). Temperature dependence of the dispersion component δ_d could be found by empirical evaluations (Hoy 1970). Various methods of calculating the variation of temperature with δ_d , δ_p , and δ_h have been reviewed (Hansen and Beerbower 1971). The effect of solubility parameter of solvent with changing temperature has also been utilized to provide a

solubility parameter spectrum for determination of polymer solubility parameter (Song et al., 1970)

Volume:

The effect of molar volume appears in the entropy term as well as in the solution parameter term. The plots of cohesion parameter against inverse molar volume are found to be approximately linear for particular classes of compounds. This correlation has been used in the determination of each liquid of a single recommended Hildebrand parameter from the wide range of reported values (Jayasri and Yaseen 1980). The slopes are positive, that is, the Hildebrand parameters decrease with increasing molar volumes in all series except aliphatic hydrocarbons, ethers and halogenated solvents. Hansen parameters with van der Waals was also correlated (Peiffer 1980). All other factors being equal, the solvent with the lower molar volume is superior thermodynamically. This is significant when the solvent has similar δ values and different molar volumes (Reynolds 1962). Fluorocarbons, with larger volumes have solubility parameters smaller than the corresponding hydrocarbons.

Concentration:

The importance of concentration has been emphasized in situations where there is a disparity in δ values (greater than about $2.3 \text{ MPa}^{1/2}$). It is clear that if the volume fractions (ϕ_i) are not taken into account, the apparent measured value of δ is incorrect. The heat of mixing per unit volume has a maximum value when ϕ_A and ϕ_B are 0.5 and at high volume fractions, the energy of mixing is much smaller. The concentration inconsistencies in experimental methods used to determine the solubility parameters are overcome by adjusting the concentration to

commercial usage. A practical problem is that a solvent system which is suitable at high solute concentration may produce phase separation at dilute concentration during clean up operations. Mizerovskii and Belova (1987) used the equation of Wrewsky (1929) for the composition dependence of the vaporization enthalpy of binary liquid mixtures. Current equations were shown to result in unacceptable errors in calculations when applied to binary mixtures involving benzene, tetrachloromethane, acetone, hexane and trichloromethane (Barton 1991).

2.3- Calorimetry

2.3.1- Principle and Applications

It is important to understand effort and money invested in an attempt to ensure quantification of the changes that occur. Calorimetry recognizes subtle differences in materials and quantifies change in terms of rate and the probability for a change to occur. The rate of change may be dependent on environmental conditions such as temperature, pressure, humidity and mechanical action. The enthalpy change that accompanies a reaction is found out by measuring the temperature rise or fall when a known amount of reaction takes place in a thermally isolated system, such as a calorimeter. Calorimetry is defined as the measurement of heat. The reactive systems were first studied by observing the respiration of guinea pig in an ice calorimeter in 1970 (Ewing 2005). Modern calorimeters could directly record, exothermic and endothermic reactions with signals as low as 5×10^{-8} W. Instruments have been designed to measure energy changes from temperatures little above absolute zero up to temperatures in excess of 2000 or 3000 K. Calorimetry has been widely used for day-to-day physical and chemical characterization of materials within a wide range of research applications.

Any calorimeter has basically two regions- the sample and the surroundings. The “sample” with a temperature (T_S) refers to the process under investigation (e.g., a phase change or a reaction) and also the associated containers, heater and thermometers. The “surroundings” refers to the controlled region around the sample with a temperature (T_E). The temperature control may be active as in the case of a Peltier unit; or passive, as in the case of a heat sink. A crucial element of calorimetry is the measurement of (T_S) and (T_E) and their difference (ΔT) as a function of time (t)

$$\Delta T = T_S - T_E \quad (2.12)$$

The applications of calorimeters are manifold offering a convenient and rapid means for chemical data with a precision that is adequate for most preliminary research and exploratory applications like pore size determination, oxidation of materials, clinical and biochemical analyses and purity determination etc (Ewing 2005). As an analytical tool it is used in industrial laboratories for product evaluation and quality control. Such applications also include tests in which there is a direct relationship between the heat of reaction and a chemical or physical property of the reactants in a system.

Heats of reaction, either endothermic or exothermic, could be determined in many different systems, ranging from simple acid- based reactions to more complicated redox, chelation, hydrolysis, hydrolysis and other reactions. It is effective for assays of weak acid and weak bases that do not respond readily to other detection methods. It could also be used for rapid specific ion determinations by thermo-chemical methods. The heat of solution produced when a solid dissolves in a liquid could also be measured. Similarly the heat of dilution produced by diluting a solution with solvent or with a solution of a lower concentration is also

measured using a calorimeter. The heat of mixing produced when two liquids are combined is also determined. The heat of wetting is used as a rapid method for determining the surface area of a powdered solid, since the heat released when a powder is treated with a wetting agent would be proportional to the exposed surface area.

2.3.2- Types of calorimeter

No standard system of classification exists because of the profusion of calorimeter designs. Hemminger and Hohne (1984) have suggested the following method based on three criteria: the measuring principle, the mode of operation and the principle of construction.

Measuring Principles:

- 1) Heat conduction calorimeters operate at constant temperature. Heat liberated from a reaction is a good approximation, entirely diluted within a heat sink. Modern isothermal calorimeters measure the conduction of heat as it travels between the reaction ampoule and the surroundings and often have a very high degree of sensitivity
- 2) Heat accumulation calorimeters allow a rise in temperature reaction system for exothermic reactions or a decrease in temperature for endothermic reactions. A reaction is followed by measurement of temperature change as a function of time. Modern calorimeters allow the signal to be converted into power. An adiabatic solution calorimeter is typical of this class.

- 3) Heat exchange calorimeters actively exchange heat between the sample and surroundings often during a temperature scanning experiment. The heat flow rate is determined by the temperature difference along the thermal resistance between the sample and surroundings.

Modes of Operations:

Three modes of operation are important.

- 1) Isothermal where the sample and surroundings are held at a constant temperature ($\Delta t = 0, T_S = \text{constant}$)
- 2) Isoperibol, or constant temperature jacket, where the surroundings stay at a constant temperature and the sample temperature may alter ($\neq \Delta T, T_E = \text{constant}$)
- 3) Adiabatic, where ideally no heat exchange takes place between the sample and surroundings because they are both maintained at the same temperature, which may increase during the reaction ($\Delta T = 0, T_S \neq \text{constant}$)

Construction:

The construction of a calorimeter may have a single measuring system or a twin or differential measuring system. Simple solution calorimeters have a single cell whereas the DSC has twin cells and operates in a scanning mode. The use of twin cells reduces the effects of internal and external noise and transient fluctuations.

Although calorimeter is intimately associated with the thermodynamics, iso-thermal or adiabatic conditions are never exactly achieved. Allowances are made for the slight differences between theoretical and actual behavior. Systematic errors can also cause problems. A specific instrument must be always calibrated in some way. The results should be checked by measurements of a known standard system that is similar to the system under investigation.

2.3.3- Solution Calorimeter

A solution calorimeter is an instrument that is used to measure the heat evolved or absorbed by chemical reactions in a liquid media. They are usually adiabatic calorimeters, mainly used for the study of rapid reactions like heats of solution, heat capacity of liquids, solids or the enthalpy change of rapid reactions in solution. A schematic diagram is given in Figure 2.4. The principle of a solution calorimeter is simple. A liquid reactant is contained in a Dewar flask, which is itself immersed in a thermostatic bath, usually kept at 298.15 K. Another reactant, either a liquid or a solid, is put in a small glass cell and immersed in the first liquid. Mixing is achieved mechanically. After the system comes to thermal equilibrium, the reaction is started by breaking the glass cell, to release the reactant inside the Dewar cell.

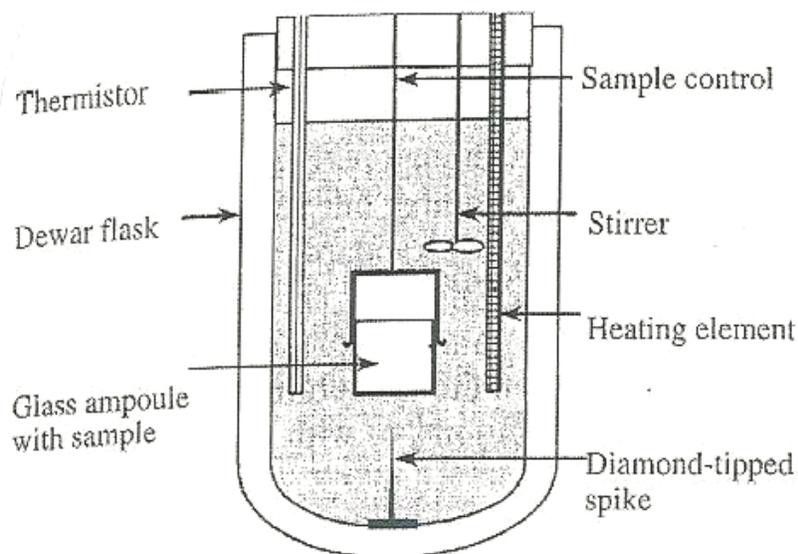


Figure 2.4- Schematic Diagram of a Solution Calorimeter (Ewing 2005)

The heat released or absorbed causes the temperature of the system to rise or drop, depending on the exothermicity or endothermicity of the process. The reaction is allowed to go to completion and the temperature change is measured. The heat capacity of the solution calorimeter is calibrated by studying the reaction of a standard system. Once the heat capacity of the calorimeter is known, any process in solution (reaction, mixing, precipitation, etc.) can be determined. The amount of heat absorbed by or removed from the solution can be calculated by the following equation.

$$q = mC_p\Delta T \quad (2.13)$$

where q represents the amount of heat transferred, c the specific heat of the solution, m the mass of the solution, and ΔT the temperature change associated with the process.

2.4- Overview of Oil Spill Solidifiers

The general purpose of countermeasures implemented during an oil spill response is to control the oil release and/or spread reducing its impact on the environment. Solidifiers are an existing technology that has potential to be applied to marine spills especially for protecting shorelines. Since 1968 Exxon has invested heavily in developing new technologies for responding to oil spills. U.S EPA and Exxon conducted research on the potential use of solidifiers in a scenario where the vessel was loaded to capacity was in imminent danger of sinking or breaking up (Goldstein 1974). The strategy was to solidify the oil in the vessel to prevent its release to the water. In early 1992, Exxon initiated a program to identify solidifiers that potentially could be used to protect shorelines from oil spills. Past evaluations of solidifiers concluded that the cost of application to large spills would be prohibitive due to the large amount of material required to solidify the entire spill. Environment Canada has commented that the use of solidifiers on open waters is questionable due to the large amount of solidifier required (Fingas 1992). Solidifiers have been available for over 20 years; however their applications have been primarily for handling small laboratory spills. The possibility of reducing the spread of waterborne oil by solidifying it, together with increasing the recovery and removal rates, is a concept with significant potential benefit (Walker 1994)

Solidifiers are used to render the spill's oil phase viscous and thus immobilizing the spill's mass. The desirable characteristics of the solidifiers are: buoyancy, low water pick up, high oil pick up, low rate of release and re-use potential. Solidifiers consist of polymerization catalysts and cross-linking agents and are available in dry granular form. They bond with the liquid into a solid rubber-like mass with minimal volumetric increase and retain the liquid for

easy removal. The bonded material eliminates a dripping-sponge effect by not allowing the material to be squeezed out, thereby minimizing residue or contamination (PERF 1992)

Solidifiers should meet the following criteria:

- 1) Insoluble in water
- 2) Specific gravity of less than 1
- 3) Composed primarily of polymers (with few other additives)
- 4) Contains less than 5 ppm of heavy metals and chlorinated hydrocarbons
- 5) Have a physical reaction with oil whereby at the prescribed application rate, the oil is sorbed by the product in a manner where the oil is resistant to leaching
- 6) Should not release the solidified liquids under pressure
- 7) It should be non-toxic to wildlife and other species

2.4.1- Solidifier Chemistry

There are three types of solidifiers: polymer sorbents, cross-linking agents and polymers with cross-linking agents. These types have unique characteristics and properties. Some of them form chemical bonds; others work only by adsorbency into polymer chains

Polymer Sorbents:

This is the most common type of 'solidifier'. In this type there is no chemical bonding. Figure 2.5 shows the schematic representation of polymeric adsorption. Polymers have spaces between them that can hold oil. The oil is adsorbed into these spaces and held together by van der Waals forces, which are weak attractive forces between molecules. The oil could be

removed by applying pressure to the completed solid. The success of this reversal would depend on the time, as the solidified oil becomes more stable with time. Generally, block co-polymers are more efficient and hold oil better. The most common materials used are styrene butadiene and related polymers, polytertiary- butyl styrene, polyacrylo-nitrile butadiene, polyisopropene (rubber), polyethylene and polypropylene, poly isobutylene and related polymers. The advantages of these kinds of solidifiers are relatively simple, lower toxicity and are slower to react and thus mix better. The disadvantages are that they are more like sorbents and oil can be released from these products especially under some pressure.

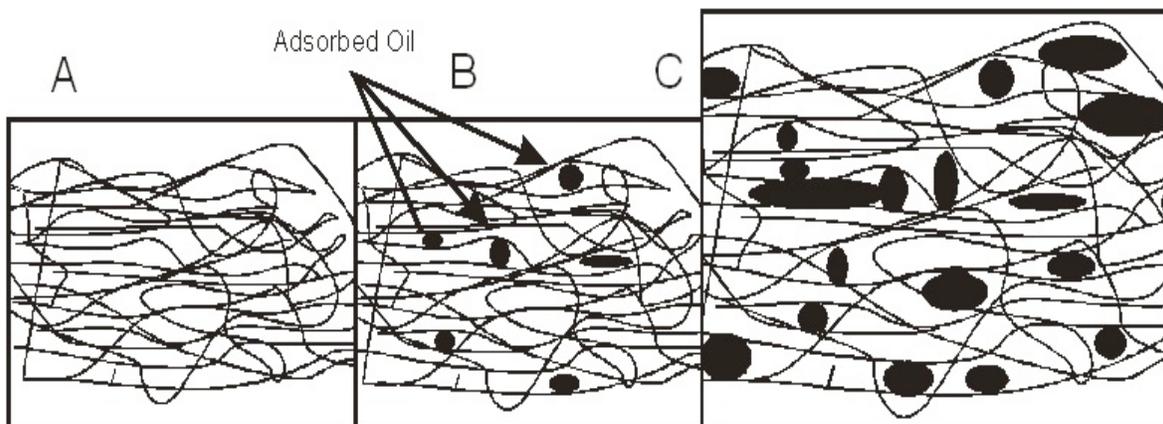


Figure 2.5- Schematic Process of Polymeric Adsorption (Fingas 2008)

Cross-Linking Agents:

Cross-linking agents are chemical products that chemically form bonds between two hydrocarbons to solidify the oil. It is typically a chemical reaction releasing a small amount of heat or absorb heat depending on the chemical that is used. Figure 2.6 shows that the starting

reagent, shown as X's, mixed with the black oil to form the cross links as shown by the jagged line. Most cross-linking agents react quickly and thus do not penetrate very thick oil. Crosslinking agents that have been used include norbornene and anhydrides. Pelletier and Simon (1999) made a new series of oil treating agents which solidify oil. These agents were prepared by reacting surfactants, alcohols or carboxylic acids with alkylchlorosilanes in light hydrocarbon solvents (Pelletier and Simon, 1999).

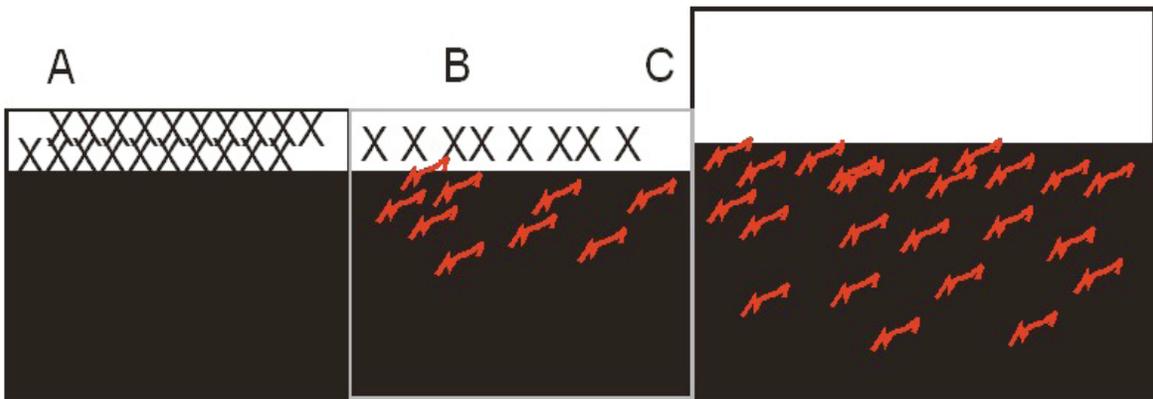


Figure 2.6- Schematic Process of Cross-Linking Agents (Fingas 2008)

The advantages of cross-linking agents are that the final product is fully solidified and forms a durable mat which is easy to recover. The disadvantages of this technology is that it is difficult to get complete solidification, especially of a thicker slick as the product is reactive and reacts with the first hydrocarbon it comes to contact with. It also has the disadvantage of linking with the other hydrocarbons such as in containment booms, organic matter, etc.

Cross-Linking Agents and Polymeric Sorbents Combined:

This type of agent combines a polymeric sorbent with a cross-linking agent. The cross-linking agent is attached to a polymer end. The purpose is to gain the advantages of both types of agent. A schematic of how this agent type works is shown in Figure 2.7. Figure 2.7A shows the schematic of oil with the cross-linking agents (X's) on the ends of the polymers. Once added to oil, these agents start to adsorb oil and cross-link the oil components as shown by the jagged lines in Figure 2.7B. The final product, where the agent has adsorbed and cross-linked a portion of the oil is shown in Figure 2.7C

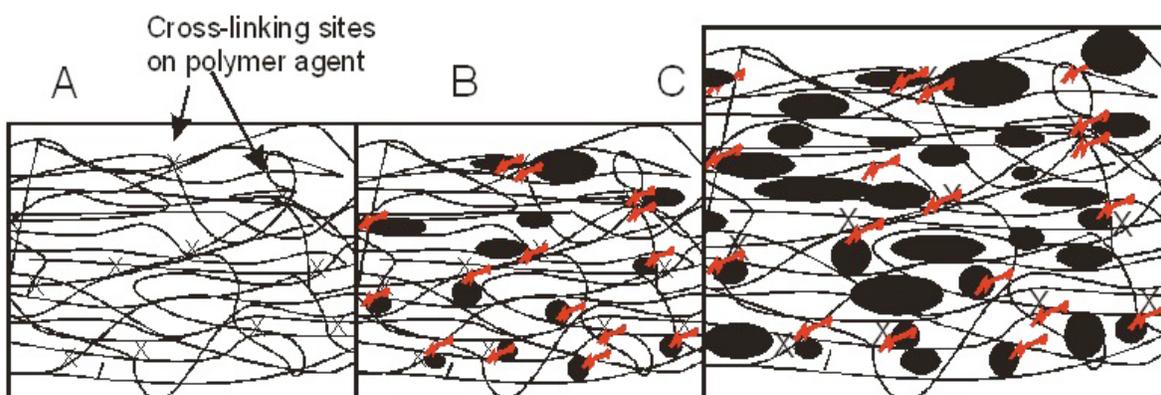


Figure 2.7- Schematic of the Process of Polymeric Sorption Combined with Cross-Linking
(Fingas 2008)

The polymers used are generally styrene butadiene and related polymers, while the cross-linking agents are typically anhydrides. An example of this type of agent is RigidOil by British Petroleum whose composition was widely disclosed by Meldrum et al. (1981). The advantages of this type of solidifier agent are that the product mixes with oil better than cross-linking agent alone and that solidification is better than for polymeric sorbents alone. The disadvantages are

that generally it has two components which must be mixed immediately before application and that solidification may be difficult to achieve because the product may form a crust with the oil on the top.

2.4.2- Major Solidifier Issues

A number of issues must be considered in the utilization of solidifiers to combat oil spills. Their impact on the habitat, application rates, development of application techniques and guidance on pick up and disposal of treated oil should be investigated. Solidifying the oil without recovering it immediately can cause major problems. Another major issue was the completeness of solidification. A solidifier can potentially react with the oil it first comes in contact with, leaving the remaining oil untreated (Walker 1994).

Effectiveness:

Solidifier effectiveness is defined as the amount of agent that is required to solidify oil under standard conditions. The factors that influence solidifier effectiveness include oil composition, sea energy, state of oil weathering and type of solidifier used and the amount applied. While it is easier to measure the effectiveness in a laboratory than in the field, they may not be representative of the actual conditions. Factors like sea energy and mixing may not be accurately reflected in laboratory tests.

Laboratory Tests:

Laboratory tests were carried out by Exxon, Rea, Pelletier and Ghalambor. Most used a similar procedure with the end point being the disappearance of free oil. Rea tested seven polymer cross-linking chemicals with diesel fuel (Rea 1991). Mixing was carried out and then

the products were tested with a penetrometer and the products tested for diesel fuel vaporization as well as leachability. It was found that the gelled fuel continued to solidify over time, but eventually approached a constant level. The ratio of solidification was proportional to the mass of agent added. The gelled fuels emitted volatile organics at a declining rate over time. Ghalambor tested 23 solidifiers (Ghalambor 1996). These solidifiers were: Elastol 1, Elastol 2, Envirobond # 403, Nochars A 610, Nochars A 650, OARS, OSSA, Omni-Zorb #2000, Omni-Zorb # AZ1N, Omni-Zorb # BZ, Omni-Zorb # PZ, Petro-Lock, Rubberizer, Seamate - 3mm, Seamate - 4 mm, Seamate fine, SPI particulate 1, SPI particulate 2, Spill Gel (Fractech), Waste-set PS # 3200, and Waste-set PS # 3400. Various test oils were used. The 'consumption level' of solidifier or the quantity of agent needed to solidify varied from 25 to 120 percent. The viscosity of the resulting products varied from about 1000 poise to about 8000 poise. Calorimetry was carried out on the reactions and the heats of reaction varied from 0.9 to 4.3 cal/g. Negative values would indicate an endothermic reaction and positive values would indicate an exothermic or heat-releasing value. Both types of reactions were found. The Exxon laboratory test included application of solidifier to oil until no visible oil remained on the water surface (Dahl 1996). The oils tested were gasoline, diesel, Bunker C and 3 different crude oils. Most of the products were able to solidify some of the oils into a firm mat; however, none of the solidifiers formed a firm solid mat with all of the oils tested. The solidifiers used range from a ratio of about 1.5 to about 3.5. Pelletier and Simon (1999) tested their new silicone solidifier using a light crude oil, Brent (Pelletier and Simon, 1999). The ratio needed to solidify was 1:7, agent to oil. The solidified oil contained water up to 85 percent by weight of the total mass. It was found that the silicone coated solid surfaces and rendered them less adhesive to oil. The

solidification process was found to be independent of temperature and salinity effects. Throughout this testing no end point other than the disappearance of free oil was used. Measurement of viscosity and penetration was used, but an acceptable procedure was not found. It should be noted that all researchers felt that the disappearance of free oil method did result in good repeatability.

Field Trials:

In 1981, tests were carried out using RigidOil on light fuel oil and topped crude. Some tests resulted in partially solidified oil with some free oil floating beside (McGibbon 1982). The lack of mixing was the reason for the incomplete solidification. In mid 1980's, the solidifier was tested on a larger scale offshore Newfoundland (Fingas 1995) by Canadian Coast Guard and Canadian Oil Industry. The agent reacted with the oil on the surface and when the oil was sampled, it was soft with some portions almost liquid. It was concluded that this technology was not practical for offshore oil spills. Delaune et al. tested the solidifier product, Nochar A 650 and found that the solidifier did react with South Louisiana Crude forming a cohesive solid mass with no dripping. It was found that more solidifier was required to achieve the end result than the laboratory tests (Delaune 1999).

Tank Tests:

The tank test by Exxon in 1995 (Dahl et al., 1997) was carried out in the Imperial tank and a specialty insulation blower was used. The oils tested were gasoline, diesel, Bunker C and 3 different crude oils. The primary purpose was to assess the overall applicability of the technology on larger scale. The findings of the field application were that the application rate was about 1:1 but the material broke into clumps; solidification increased with time. Disposal

was found to be an issue and solidified diesel was still flammable and it was noted that vapours were released from the solidified oils (Dahl 1997).

Analytical Methods:

Analytical means in any test system is a major concern. Penetrometers and viscometers are used to determine an end point for noting the presence of liquid oil by several researchers (Rea 1991; Fingas 1995). These methods did not yield consistent results. Sampling a heterogeneous material is difficult.

Toxicity:

Another important issue with solidifiers is toxicity, both of the solidifier and the treated oil. The LC_{50} of a substance is the 'Lethal Concentration to 50 percent of a test population' usually given in mg/L, which is approximately equivalent to parts per million. The smaller the LC_{50} number, more toxic the product.

Potential for Sinking:

Another concern is that the solidified oil might sink (Michel 2008). No studies of the density of the final products have been performed, although no observations of sinking have been made.

Recovery of Solidified Oil:

Most solidified oil was recovered using hand tools such as shovels, rakes and pool nets. Dahl et al., suggests the use of fishing nets or nets that were developed for the recovery of heavy oil (Dahl 1997). Recovery is another factor that may restrict the use of solidifiers to small, near shore spills.

Solidification Time:

Solidification time is very important and is partially dependent on the reactivity of the treating agent itself. If the reaction time is very fast, crusting occurs and the oil will not be completely solidified. If the reaction time is too slow, the product would not be useful. It is suggested that solidification time might best occur between 10 to 60 minutes to have optimal use on typical small spills.

2.4.3- Methods of testing the effectiveness of the solidifier

The effectiveness of a solidifier is based on the amount of product and time it takes to “fix” a given volume of oil. Preliminary tests of a few products found that 13 to 44 percent by weight of the product of oil was required to solidify a sweet crude oil over a 30 minute period (Walker 1993).

Static Testing:

A procedure was developed to test the solidifiers under static conditions using a known amount of oil on a known volume of water. This test determined the optimum dosage of each product. A cell container with a known volume of water and oil was used for this test. A known amount of solidifier was weighed using an analytical balance. The procedure used 1 gram of solidifier to the maximum extent of absorption of oil for that particular solidifier. The solidifier was added in increments of 1 gram. The maximum efficiency of the solidifier was noted.

Dynamic Testing:

This test involved using a mechanical stirrer to simulate wave conditions and homogeneous mixing (200 to 400 rpm depending upon the consistency of the sample). As the

oil was stirred, the solidifier product was added using the optimum dosage determined in the static test.

Byproduct Viscometry :

This test used 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 3835-90: *Standard Test Method for Determination of Properties of Polymeric Materials by means of a Capillary Rheometer*. This method describes measurement of the rheological properties of polymeric materials at various temperatures and shear rates. The results showed that the capillary rheometer provides high viscosity readings. The results help us arrive at an effective and economical dosage for the solidification treatment of oil spills.

Calorimetry Test:

This test was conducted to measure the ease with which the reaction takes place between the reactants, by measuring the heat of reaction. A solution calorimeter was used to measure the heat of evolved or absorbed in a liquid media. The greater the heat value, faster the reaction proceeds and better the integrity of the final byproduct. The application of this process determined how and to what extent solidifiers can be applied in oil spill scenarios. The heat of solidification thus has implications as to how the solidifier applications should be conducted.

Crude Oil Characterization:

The determination of acid components was the major focus of this test. The solidification process was related to the acid components of the oil. Asphaltenes, paraffin, pour point, API gravity, TPH distillation, sulfur content, acid number and base number were also determined.

Solidification Viscometry:

Three phases of viscosity were determined during the solidification process. An initial viscosity develops after introduction of the solidifier. The effect depends on the characteristics of oil and solidifier as well as secondary factors such as atmospheric conditions. A 39B model Fann Viscometer was used to develop shear rate- shear stress relationships. This instrument is designed to provide absolute viscosity measurements. Preliminary results showed that the shear rate – shear stress relationship will uncover the mechanisms of the solidification process. The viscosity may have critical effects on the effectiveness of the solidifier as an oil spill remediation method.

2.4.4- Recovery and Removal

A number of options were reviewed for recovery and removal of the solidified material. These options were tested at Calgary using the solidified oil generated during application testing. Fish nets, containment booms, spill shovels and wire screen nets are some of the recovery and removal methods. The fish netting was found to work extremely well for removing the solidified oil and also unused solidifier material. Advantages of using fish netting include: easy deployment from shore to boat, lower towing stresses for the nets than for similar rigid containment booms, reuse of the nets and recovery of the solidified material in the water or on the shore.

Containment booms also worked well in containing both the solidified oil and the free solidifier material. Booms filled with solidifier material would also work well in containing and herding the solidified oil to an area for pickup. Once recovered, the solidified oil is removed using spill shovels or wire screen nets. These have the advantage of removing the solidified oil

without water. Part of the recovery process is the selection of the proper container for storage and transportation to the disposal facility

2.4.5- Disposal

The disposal facility should be conducted in order to determine the type of containers their facility can handle. An important determinant of disposal is whether the solidified material is classified as hazardous and non-hazardous. Solidified material from each spill must be tested in order to determine if the material is characteristically hazardous or non-hazardous. Applicable local regulations for handling and disposal must also be followed. To determine if the solidified oil is characteristically hazardous in the U.S analyses for ignitability, toxicity, corrosivity and reactivity were carried out. Several disposal options were investigated to determine the feasibility of integrating solidified petroleum into the disposal process. The options that were identified included: landfill, thermal reuse, incineration and waste conversion to energy such as in cement kilns, municipal incinerators. The only option considered to be non-viable was the use as boiler fuel for the electric utility industry as it requires materials on a consistent, steady basis. Cost of disposal varies depending on the disposal option and facility. Table 1 presents the range of costs for the different options evaluated (Dahl 1996). These costs are only the facility costs and do not include transportation or pre-treatment.

SOLIDIFIER DISPOSAL COSTS	
Disposal Options	Cost Range (\$/ ton)
Non-hazardous Material	
Cement Kiln	\$ 350 to \$ 600
Municipal Incinerator	\$ 150 to \$ 200
Hazardous Material	
Landfill	\$ 50 to \$ 200
Incineration	\$ 1000 to \$ 1800

Table 2.1- Costs of different options and facilities of disposal (Dahl, 1996)

2.5- CIAgent©

CIAgent© is made from a group of proprietary polymers that are non-toxic, non-hazardous, non-corrosive and environmentally friendly petroleum bonding agents, primarily used as chemical countermeasure against water borne spills. Petroleum-based products include oils, transportation fuels, solvents, oil-based paints, etc. CIAgent© is listed as a “**Solidifier**” in EPA National Contingency Plan Product Schedule for use on oil spills in the navigable waterways of United States.

CIAgent©, formerly known as CI Agent, Cheap Insurance and Petro Capture, is a dry granular material specifically designed to immobilize petroleum based liquid spills by coagulating and bonding the liquid. Unlike the adsorbents that soak up the liquid through expansion, CIAgent© bonds the liquid into a removable mass with minimal volumetric increase and retains the liquid for easier removal eliminating the *dripping effect* by not allowing the liquid to escape and thus minimizing any residue or contamination.

CIAgent© polymers are composed of lightly cross linked polymer chains. Because of the cross linking, CIAgent© displays an unusual behavior with organic materials. Unlike most plastics that dissolve readily in an appropriate solvent, CIAgent© solidifies the organic liquid through “*micro-encapsulation*” which basically converts the original liquid into a non-leachable solid waste. When CIAgent© is contacted by an active organic liquid, it begins to solidify through the cross linking of the **seven different polymers** used in its unique blend. No other chemical or mechanical action is necessary. The organic liquids are absorbed and entrapped in its molecular network forming a cohesive *rubber-like* mass, which may be easily removed in most clean up situations. In addition it does not pick up any water in the process of solidifying

the petroleum-based spill. This allows CIAgent© *Pillows* and *Booms* to be used on land as a preventive measure prior to possible release of a hydrocarbon. CIAgent© is extremely stable and the toxicity of the material *encapsulated* is reduced considerably. The application rate, pick up ratio and speed of solidification varies with the viscosity of the liquid, type of hydrocarbon, the amount of volatiles remaining and temperature. In order to solidify a hydrocarbon, a ratio of 4 to 1 CIAgent© is required. There are a number of applications for spent CIAgent©, eliminating the formulation of a waste product and allowing the material, if acceptable via TCLP and other Environmental Protection Agency (EPA) and/or state testing procedures, to become an intermediate for introduction into another downstream process.

2.5.1- Properties of CIAgent©

Some of the properties of the CIAgent© are listed as follows:

- 1) Non-toxic, non-hazardous, non-carcinogenic, non-corrosive and environment friendly
- 2) Works in both fresh and salt water. It has a specific gravity of 0.94 g/cm³ and a pH of 7.81
- 3) It has no temperature limitations. Can work in extreme heat and cold. The maximum storage temperature is 190 °F. Optimum storage temperature is 50 – 80 °F
- 4) Buoyant. No expensive mechanical equipment is required for recovery.
- 5) Can be disposed in landfills, eliminating the “Cradle to Grave Liability” and the fees associated with the hazardous waste disposal
- 6) The spent CI Agent can be recycled as raw materials for the following types of end-use applications:
 - i) Asphalt modification to improve flexibility and stability characteristics

- ii) Plastics and rubber additions to extend raw material and provide various characteristics enhancements
 - iii) Additives for adhesives, sealants and coating to extend and improve flexibility
 - iv) Oil viscosity modification to change the characteristics of various petrochemical products
 - v) Additives for general rubber compounding to modify prosperities and extend rubber make up
 - vi) Alternatively, the encapsulated material can be used as a fuel creating 7000 BTU/lbs with an extremely small (0.2 percent) ash residue
- 7) It has an indefinite shelf life

2.5.2- Mechanism of CIAgent©

CIAgent© solidifies the organic liquid through “**microencapsulation**” which basically encapsulates petroleum-based liquid spills through the rapid transformation of a liquid material into an inert cohesive rubber like mass upon contact. It solidifies the liquid into a removable mass with minimal volumetric increases and retains the liquid for easier removal. CIAgent© will cure instantly or in a relatively short period of time (depending on the viscosity of the material) and will form an interlocking network with a rubber-like consistency. The concept of microencapsulation was first developed by the National Cash Register Co. during the 1930’s. Southwest Research Institute entered the microencapsulation field in 1950, developing techniques for the encapsulation of gasoline (Ranney 1969). This is a modified entrapment where a hydrocarbon liquid is immobilized within microcapsules prepared from food grade organic polymers. The entrapped hydrocarbon liquid once within the cross-linked polymer,

cannot escape the matrix (Weetall 1975). The molecular structure of CIAgent© is such that it associates strongly with the liquid hydrocarbons (e.g. gasoline, diesel fuel, crude oils etc.), solidifying them into an inert mass upon contact. The physical attraction between the oil and the polymer is attributed to the hydrogen bonding and London's forces. Not only does CIAgent© solidifies the hydrocarbon, it also retains it for easier removal and disposal. The entrapped hydrocarbons can be disposed in a landfill as per the EPA regulations or used as raw material.

2.5.3- Procedure for Application of CIAgent©

For small scale spills on water (salt or fresh), CIAgent© can be broadcasted directly onto the spill, spreading a thin layer from the outer edge into the middle of the spill. Agitation is not necessary. The product is also available as oil absorbent, water repellent booms and pillows. CIAgent© may be deployed with an air or water stream directed at the leading edge of the spill in case large scale spills. Static buildup may occur because of its fine particulate nature, if the product is applied in dry form at a high rate of delivery. Dispensing material should be properly grounded to prevent the static buildup. The product is relatively non-abrasive and should not harm machinery or pumping systems. The polymer has a specific gravity of less than one and will tend to separate and move to the surface when mixed with water. Therefore, in the case of water carrying media, agitation will be necessary to keep the product suspended. CIAgent© encapsulates and solidifies the oil, while continuing to float even after saturation. The solidified oil or hazardous material may be removed from water using a vacuum pump or fish net. The material should be put into appropriate containers and disposed of in accordance with federal, state and local regulations.

For spills on land, the product would be applied in the same manner as in the water-based spill situation. To recover solidified oil or hazardous materials from spills on land, the spent material may be collected and swept up using an industrial vacuum cleaner, broom, or shovel. The material should be put into appropriate containers and disposed of in accordance with federal, state and local regulations.

2.5.4- Uses of CIAgent©

CIAgent© can be used in loose granular form, dissolvable film packs, pillows, booms and hydrocarbon flow filters as a spill prevention and clean up tool. It has become the engineered spill prevention solution for the electric utility industry for SPCC secondary containment and for oil contamination removal in underground vaults and manholes. CIAgent© Barrier Booms are the ideal solutions for providing secondary containment. They are also used in pad-mounted transformers, oil filled equipment storage areas and bulk fuel storage areas all without the use of concrete walls, sump pumps and water separator systems. CIAgent© Marine Pillows are ideal for cleaning water in both recreational and commercial vessels. The CIAgent© Sheen Bag is used in a situation which requires sheen to be removed from water. CIAgent© Hydrocarbon Flow Filters, storm drain inserts and sheen bags can remove hydrocarbons from water to levels below 5 ppm without impeding the flow of water. These are used in electrical substations, storm water run-off, contaminated cooling tower water, retention pond out-flows and bulk storage tank farms rain water out-falls. Hydrocarbon flow filters and barrier booms are used to replace concrete bunding. It can solidify and remove any liquid hydrocarbon (gasoline, diesel and oils, including crudes) from both fresh and salt water without processing any water. Hydrocarbon Detection Strips are used to detect hydrocarbon contaminated water in elevator

shafts, underground utility vaults and manholes, retention and secondary containment vessels. It is also used on the CIAgent© EVAC Filtration system to determine whether the filter is nearing its maximum hydrocarbon retention level.

CHAPTER 3

Characterization by using a Solution Calorimeter

3.1 - Experimental Set-up and Procedure

In order to characterize the effectiveness of CIAgent© with a variety of hydrocarbons that could be encountered, a solution calorimeter was used. A Parr Instrument Solution Calorimeter Model No. 6755 was used in this work. The purpose of this experiment was to measure the heat of solidification which can be related to the ease of the solidification. Figure 3.1 shows a schematic drawing of the calorimeter. The calorimeter is adiabatic and operates at ambient pressure. The glass Dewar is loaded with the solidifier volumetrically. The hydrocarbon liquids are pipetted and loaded in the rotating sample cell. The sample cell has two parts: a lower bell and a stem. The stem is thin-walled and fragile, resulting in a low heat capacity. The thermistor probe is used to measure the temperature change. The cell was attached to the stirring shaft and the push rod was inserted into the sample dish.

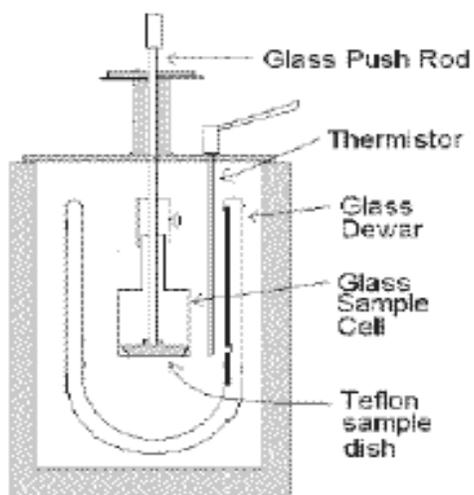


Figure 3.1- Parts of a Solution Calorimeter (Operation manual, Parr Instruments)

Each test in a solution calorimeter was divided into three distinct time periods:

- 1) A pre-period where the solidifier and the hydrocarbon liquids were allowed to come to an initial thermal equilibrium. At the end of the pre-period, the solidification was started by depressing the push rod quickly.
- 2) A solidification period during which the solidifier and hydrocarbon liquid are combined and an enthalpy change occurs in the system.
- 3) A post-period during which the solidified hydrocarbon liquid is allowed to attain a post period equilibrium.

The solidification temperature in the Dewar flask was measured using a calorimetric thermometer (Parr Inst., Model No. 6722) which was connected to the calorimeter. A computer was connected to the RS232 serial port of the calorimeter to record the data. Figure 3.2 shows the schematic representation of the experimental apparatus.

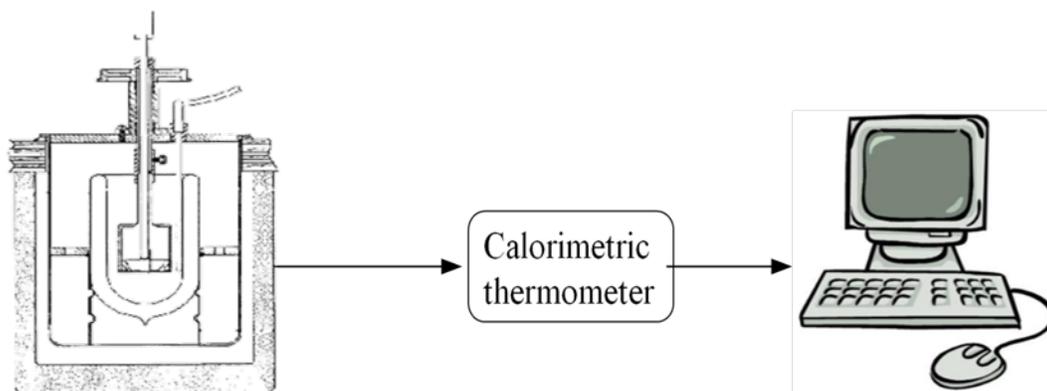


Figure 3.2- A Schematic representation of the experimental apparatus

A bench scale study was conducted to calculate the optimum solidifier to hydrocarbon liquid ratio. The same ratio was used in the solution calorimeter to find the heat of solidification for the process. Hydrocarbon liquids used included gasoline, diesel oil, kerosene, motor oil,

mineral oil, biodiesel, n-octane, iso-octane, n-heptane, toluene, Crude A, Crude B, methyl methacrylate, JP-4 and JP-8. All measurements were made at room temperature and at atmospheric pressure. Results were obtained for the various combinations of the solidifier and the hydrocarbon liquids and the readings were plotted to obtain the heat of solidification. The excess solidifier was weighed to determine the required solidifier mass, m

3.2- Temperature -Time Plot

In order to determine the net temperature change produced by the solidification, it is necessary to interpolate a point on the thermogram at which the temperature reached 63 percent of its total rise. The point 63 percent of the total rise was chosen because it represents two time constants of maximal temperature change and therefore allows for better mathematical characterization of the thermogram. This process is illustrated in Figure 3.3

- 1) The pre period drift line was extended well past the point at which the solidification was initiated.
- 2) The post period drift line was extrapolated backward to the firing time.
- 3) The vertical distance, R , between the two extrapolated lines at a point near the middle of the solidification period was measured
- 4) The distance, R , is multiplied by 0.63
- 5) A vertical intercept with the thermogram which is exactly $0.63R$ above the pre-period drift line is located and a vertical line is drawn through this point to intercept both drift lines
- 6) The initial temperature and the final temperature (at the points of intersection with the drift lines) were subtracted to determine the corrected temperature rise, ΔT_c .

$$\Delta T_c = T_f - T_i \quad (3.1)$$

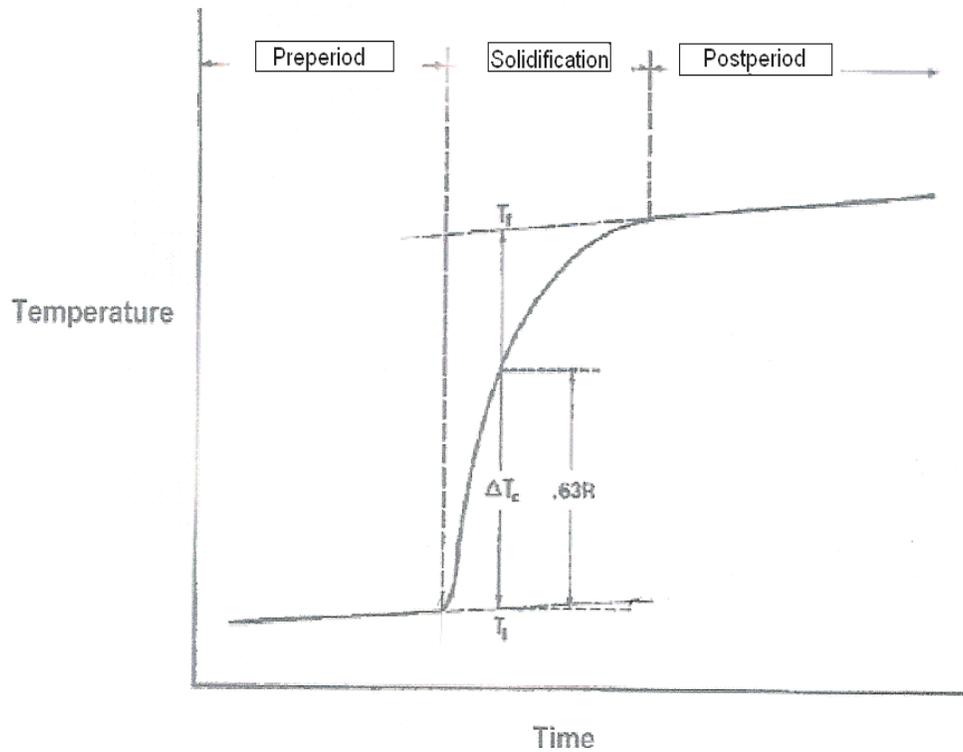


Figure 3.3- Temperature – Time Plot (Operation Manual, Parr Instruments)

3.2.1 Using MS EXCEL

The net temperature rise was determined by the following method using MS EXCEL.

- 1) An x vs. y chart of the time temperature data was created.
- 2) Linear regression lines for both the pre-period and post period drift lines were constructed and the slope and intercept are determined.
- 3) New temperature data points were calculated using the determined slopes and intercepts.

- 4) The difference between the calculated pre- and post period temperature values was calculated (A)
- 5) The difference between the observed temperature and the calculated pre-period temperature divided by the difference between calculated pre- and post-period solidification temperatures (B)
- 6) The values of (B) are examined for a value closest to 0.63. The value in (A) at the same time was the ΔT for the solidification
- 7) This value for ΔT was used to determine the heat of solidification

3.3 - Standardization of the Calorimeter

For standardizing the 6755 Solution Calorimeter, solid tris (hydroxymethyl) aminomethane, commonly called TRIS, was dissolved in dilute hydrochloric acid in a controlled process for which the amount of heat evolved was well established. 0.5 grams of TRIS was dissolved in 100 ml of 0.1 N HCl to generate 58.738 calories per gram of TRIS at 25°C.

- 1) 100 ml of 0.1 N HCl was added to the Dewar flask.
- 2) 0.5 grams of TRIS was weighed into the Teflon Dish on an analytical balance.
- 3) The rotating cell was assembled and placed in the calorimeter. The calorimeter is allowed to achieve equilibrium and the solidification was initiated by depressing the push rod.
- 4) The thermogram was then analyzed to determine the net corrected temperature rise ΔT_c .
- 5) The energy input is calculated by substituting in the equation

$$QE = m[58.738 + 0.3433(25 - T(0.63R))] \quad (3.2)$$

where QE = the energy input in calories, m = weight of TRIS in grams and $T(0.63R)$ = temperature at point 0.63R on the thermogram

Note: The term, $0.3433(25-T (0.63R))$, adjusts the heat of solidification to any temperature above or below the 25°C reference temperature.

The energy equivalent of the calorimeter and its contents were calculated by substituting in the equation

$$e = - \frac{QE}{\Delta T_c} \quad (3.3)$$

where e is expressed in calories per °C

The energy equivalent of the empty calorimeter is determined by subtracting the heat capacity of 100 grams of 0.1 N HCl from e, as follows

$$e' = e - (100)(0.99894) \quad (3.4)$$

where e' = energy equivalent of the empty calorimeter in calories per °C, 100 = mass of 0.1 N HCl in grams, 0.99894 = specific heat of 0.1 N HCl at 25° C

3.4- Data Analysis

The energy change, Q was calculated by the product of the corrected temperature change, ΔT_c and the energy equivalent of the calorimeter and its contents, e.

$$Q = (\Delta T_c)(e) \quad (3.5)$$

where Q = energy change (calories), ΔT_c = corrected temperature change (°C) and e = energy equivalent of the calorimeter and its contents (calories per °C)

The change in enthalpy, ΔH_T , at the mean solidification temperature expressed in calories per gram was obtained from the energy change, Q , in calories divided by the amount of solidifier used, m , expressed in grams.

$$\Delta H_T = -Q/m \quad (3.6)$$

where T is the temperature at the 0.63 R point on the thermogram

The temperature change can be correlated to the solubility parameter difference between the polymer and hydrocarbon liquid. CIAgent© associates with the hydrocarbon liquids solidifying them into an inert, rubber-like mass through a physical process. This physical attraction could be attributed to the secondary forces such as hydrogen bonding and London forces. A measure of the strength of the secondary bonds is given by the cohesive energy density (CED).

$$CED = -E/V \quad (3.7)$$

where E is the molar cohesive energy and V is the molar volume. The cohesive energy density is equal to the square of the solubility parameter as given by Equation 2.5.

The molar cohesive energy, $-E$ is the energy associated with all the molecular interactions in a mole of the material. According to Polak (1966), this energy can be expressed as

$$-E = \Delta_1^g U + \int_{V=V_{vap}}^{V=\infty} (\partial U / \partial V)_T dV \quad (3.8)$$

It can also be subdivided according to the relationship as

$$-E = \Delta_1^g H + \Delta H - RT + p_s V \quad (3.9)$$

where $\Delta_1^g H$ is the molar vaporization enthalpy, ΔH is the enthalpy change, p_s is the saturation vapor pressure at temperature T , V is the molar volume of the liquid and R is the gas constant. At pressures below atmospheric pressure $\Delta_1^g H$ and $p_s V$ are usually negligible compared to ΔH and RT :

$$-E \approx \Delta H - RT \quad (3.10)$$

It is customary to distinguish three modes of interaction between the molecules which collectively produce the cohesive energy density: dispersive forces present in regular solutions δ_d , polar interactions δ_p and hydrogen bonding interactions δ_h .

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3.11)$$

The total CED is estimated from the experimental enthalpy of vaporization and the polar and hydrogen bonding parameters are calculated using bond contribution methods. A three dimensional map is used to represent the solvent interaction with a polymer.

Chapter 4

Characterization of the Effectiveness of CIAgent©, a Hydrocarbon Liquid Solidifier

Abstract

Solidifiers are dry, granular hydrophobic polymers that form a physical bond with the oil by molecular interaction (van der Waals forces, London's forces, etc.) and are used to immobilize oil spill propagation and dispersion. CIAgent© is a non-toxic, proprietary polymer blend listed as an "Oil Solidifier" on the EPA's National Contingency Plan Product Schedule. CIAgent© solidifies the liquid hydrocarbons through rapid transformation into a cohesive rubber-like inert mass upon contact. This rubbery mass retains the liquid for easier removal and disposal.

The characterization of the effectiveness of CIAgent© for the variety of hydrocarbon spills (e. g., gasoline, diesel fuel, crude oil) that could be encountered was achieved by measuring the heat of solidification using a solution calorimeter (Parr Instruments, Model No.6755) at room temperature and atmospheric pressure. A Temperature-Time plot was obtained and the heat of solidification was calculated using the temperature difference upon solidification. The temperature change and the degree of swelling in the solidifier were correlated to the solubility parameters (δ_d , δ_p and δ_h). A triangular graph was generated to represent the effectiveness of CIAgent© solidification for the solvents that were tested. The heat of solidification value is used to determine extent of CIAgent© application in case of an oil spill scenario.

4.1 - Introduction

Oil spills are a frequent occurrence particularly because of the heavy use of oil and petroleum products in our everyday lives. In the United States, more than half of the approximately 2.6 million tons of oil and petroleum products used per day is imported from countries like Saudi Arabia, Canada and Venezuela. There are about 25 spills per day into navigable waters and an estimated 75 spills on land (Fingas 2001). Reducing the adverse environmental effects of oil spills has always been the goal of the response efforts in United States. Oil spill responders try to optimize net environmental benefits when considering how to deal with a spill. This simply means that the effects on the environment of any cleanup techniques used are weighed against the damage to the site.

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. The basic methods for oil spill collection and clean up are containment and recovery, sorbents, dispersants, in-situ burning, bioremediation, shoreline cleanup and use of solidifiers.

Solidifiers are used to render the spill's oil phase viscous and suspended, thus immobilizing the spill's mass. Solidifiers are a hydrophobic dry granular material made up of polymers. Unlike sorbents that physically absorb oil, solidifiers chemically bond with the oil to form a cohesive solidified mass with minimal volume increase. CIAgent© is listed as an "oil spill solidifier" in the EPA's National Contingency Plan Product Schedule, to be used on oil spills in the navigable waterways of the United States. Unlike absorbents that soak up a liquid through expansion, CIAgent© solidifies the liquid into a removable mass with minimal volumetric increase and retains the liquid for easier removal.

The objective of the research was to characterize the effectiveness of CIAgent© for a variety of hydrocarbon liquids that could be encountered. This has implications on how CIAgent© applications should be conducted in case of an oil spill scenario.

4.2 - Literature

4.2.1 - CIAgent©

CIAgent©, also known as C I Agent, Cheap Insurance and Petro Capture, is a proprietary, dry granular material specifically designed to immobilize petroleum based liquid spills by coagulating and bonding the liquid. CIAgent© polymers are composed of lightly cross-linked polymer chains. Because of the cross linking, CIAgent ©displays an unusual behavior with organic materials. Unlike most plastics that dissolve readily in an appropriate solvent, CIAgent© solidifies the organic liquid through “*micro-encapsulation*” which converts the original liquid into a non-leachable solid waste. When CIAgent© is contacted by an active organic liquid, it begins to solidify through the cross linking of the seven different polymers used in its unique blend. No mixing is necessary. The organic liquids are absorbed and entrapped in its molecular network forming a cohesive *rubber-like* mass that may be easily removed in most clean up situations. In addition, it does not pick up any water in the process of solidifying the petroleum-based spill. CIAgent© is extremely stable and the toxicity of the material encapsulated is reduced considerably. The application rate, pick up ratio and speed of solidification varies with the viscosity of the liquid, type of hydrocarbon, the amount of volatiles remaining and temperature. In order to solidify a hydrocarbon, a ratio of 4 to 1 CIAgent© is required. There are a number of applications for spent CIAgent©, eliminating the formulation of a waste product and allowing the material, if acceptable via TCLP and other Environmental

Protection Agency (EPA) and/or state testing procedures, to become an intermediate for introduction into another downstream process such as Asphalt modification, Plastic and rubber and adhesive additives etc. It is non-toxic, non-hazardous, non-carcinogenic and non-corrosive and has no temperature limitations. CIAgent© has a specific gravity of 0.94 g/cm³ and a pH of 7.81.

4.2.2 - Solubility Parameters

Solubility parameters have been found to aid in the selection of solvents. They are used to predict compatibility of polymers, chemical resistance, and permeation rates and even to characterize the surfaces of pigments, fibers and fillers. They have been applied to the study of polymer solubility and swelling, biological materials, barrier properties of polymers, surfaces etc. The skill with which solvents can be optimally selected with respect to cost, solvency, workplace environment, external environment, evaporation rate, flash point etc. has improved over the years as a result of a series of improvements in the solubility parameter concept. (Hansen, 2000).

The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. The basic assumption in the solubility parameter concept is that a correlation exists between the cohesive energy density and mutual solubility. Liquids with similar solubility parameters will be miscible and the polymers will dissolve in solvents whose solubility parameters are not too different from their own. The basic principle has been “like dissolves like”. In case of cross-linked polymers this has been modified to “like seeds like” as a solution cannot occur, but individual parts of the polymer chain can solvate to give a swollen gel.

Maximum swelling would take place when the value of δ_2 matches δ_1 of the solvents and the interaction parameter is at its minimum (Rodriguez 2003).

Solubility parameter is defined in terms of cohesive energy parameters. The energy of vaporization is a direct measure of the total (cohesive) energy holding the liquid's molecules together. The Hildebrand solubility parameter is defined as the square root of cohesive energy density (Hildebrand, 1962)

$$\delta = \sqrt{CED} \quad (4.1)$$

and the cohesive energy density is defined as

$$CED = \frac{\Delta H - RT}{V_m} \quad (4.2)$$

A widely used dimension for the solubility parameter is $(\text{cal}/\text{cm}^3)^{1/2}$ called the hildebrand. Other units used are $(\text{J}/\text{cm}^3)^{1/2}$ and $(\text{MPa})^{1/2}$ which are identical. One hildebrand is the equivalent of $2.046 (\text{MPa})^{1/2}$

Polymer Solubility Window: The polymer solubility using the solvent positions are indicated using methods similar to those used by Crowley (1966) and Hansen (1967). A polymer is tested in various solvents and the results are indicated on the graph. These edges of this area or the polymer solubility window can be determined in the following way. The liquids from diverse locations on the graph are mixed with the polymer and the degree of swelling or dissolution is noted using cloud point determinations. The mixture producing solubility is noted thus

determining the edge of the solubility window. The procedure is repeated on various solvents and the boundaries can be accurately determined (Burke, 1984).

4.3 - Experimental Procedure

A Parr Solution Calorimeter (Model No. 6755) was used to characterize the effectiveness of CIAgent© for a variety of hydrocarbon liquids that could be encountered. The instrument was used to measure the heats of solidification. All measurements were made room temperature and atmospheric pressure. The experimental set-up consisted of a glass Dewar in which the CIAgent© was loaded volumetrically. The hydrocarbon liquids were placed in a sealed glass cell. Both the reactants are allowed to reach a thermal equilibrium. The reaction was started by depressing the push rod and emptying the contents of the cell into the Dewar flask and system was allowed to attain a post-period equilibrium.

Each test in a solution calorimeter was divided into three distinct time periods.

- 1) A pre-period during which the solidifier and the hydrocarbon liquids were allowed to come to an initial thermal equilibrium. At the end of the pre-period, the reaction was started by depressing the push rod quickly.
- 2) A solidification period during which the reactants are combined and an enthalpy change occurs in the system.
- 3) A post-period during which the reactants are allowed to attain a post period equilibrium.

A bench scale study was conducted to calculate the optimum ratio of the CIAgent© to the hydrocarbon liquids. The same ratio was used with the same test conditions in the solution calorimeter to find the heat of solidification during the process. A temperature – time plot was

obtained from the calorimeter for the various combinations of the solidifier and the hydrocarbon liquids and the readings were plotted to obtain the reaction heat. The excess solidifier was weighed to determine the required solidifier mass, m

4.4 - Results and Discussions

4.4.1 - Research Objective

The effectiveness of the solidifier CIAgent© was characterized with respect to the large variety of hydrocarbons that could be encountered.

The effectiveness of a solidifier could be defined by

- 1) The temperature change
- 2) The solidification time
- 3) Weight ratio of solidifier and hydrocarbon liquid

4.4.2 - Solvents and their Properties

Sixteen different solvents were tested with the solidifier. The solvents and their relevant data are as shown in Table 4.1:

Solvent	Specific gravity	Notes
Gasoline	0.71 – 0.77	Consists of hydrocarbons between 4 to 12 carbon atoms per molecule
Diesel	0.81-0.85	Chemical formula ranges from C ₁₀ H ₂₀ to C ₁₅ H ₂₈ . The

Solvent	Specific gravity	Notes
		viscosity is 32.6 – 40 SUS @100 F
Kerosene	0.78 - 0.81	Clear liquid obtained from fractional distillation of petroleum. Viscosity 2.71 centistokes @ 20 °C
Motor Oil	0.8856	Heavy Duty motor oil. SAE 15W-40, API CJ-4
Crude A	0.9176	Heavy Crude oil. API 22.66. Oily Black liquid.
Crude B	0.8555	Light crude. API 33.90. Less viscous
Isooctane	0.692	2,2,4 –Trimethylpentane. Mol. wt 114.23. Chemical formula $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$
n-Heptane	0.6795	Mol. wt 100.21. Clear colorless liquid. viscosity 0.4 mPas @ 20 °C. Chemical formula C_7H_{16}
n-Octane	0.703	C_8H_{18} . Mol. wt 114.23. Viscosity 0.542 mPas @ 20 °C
Toluene	0.8636	C_7H_8 . Mol. wt. 92.17 g/mol, Boiling point 110.6 °C
JP-4(Ross 1974)	0.81 @68 F	Jet Fuel, 50-50 kerosene and gasoline blend.
JP-5 (Ross 1974)	0.788 - 0.834	Complex mixture of hydrocarbons, containing alkanes, naphthenes and aromatic hydrocarbons. Has a higher flash point than commercial aviation fuel.

Solvent	Specific gravity	Notes
JP-8	0.775-0.84	Kerosene based. In addition it has icing inhibitor, corrosion inhibitor, lubricants and antistatic agents
Mineral Oil	0.84-0.90	Mineral oil, light. Clear liquid.
Methyl methacrylate (MMA)	0.939	Colorless liquid, C ₅ H ₈ O ₂ , Mol. wt. 100 g/mol
Biodiesel	0.88	100% biodiesel (From AU Biosystems Engineering)

Table 4. 1 - Solvents and their properties

4.4.3 - Solidification Temperature Change

The temperature change is measured by the Parr solution calorimeter. All measurements were made at room temperature and atmospheric pressure. The temperature change should be related to the solubility parameter difference between the polymer and hydrocarbon liquid. Both endothermic and exothermic responses were observed.

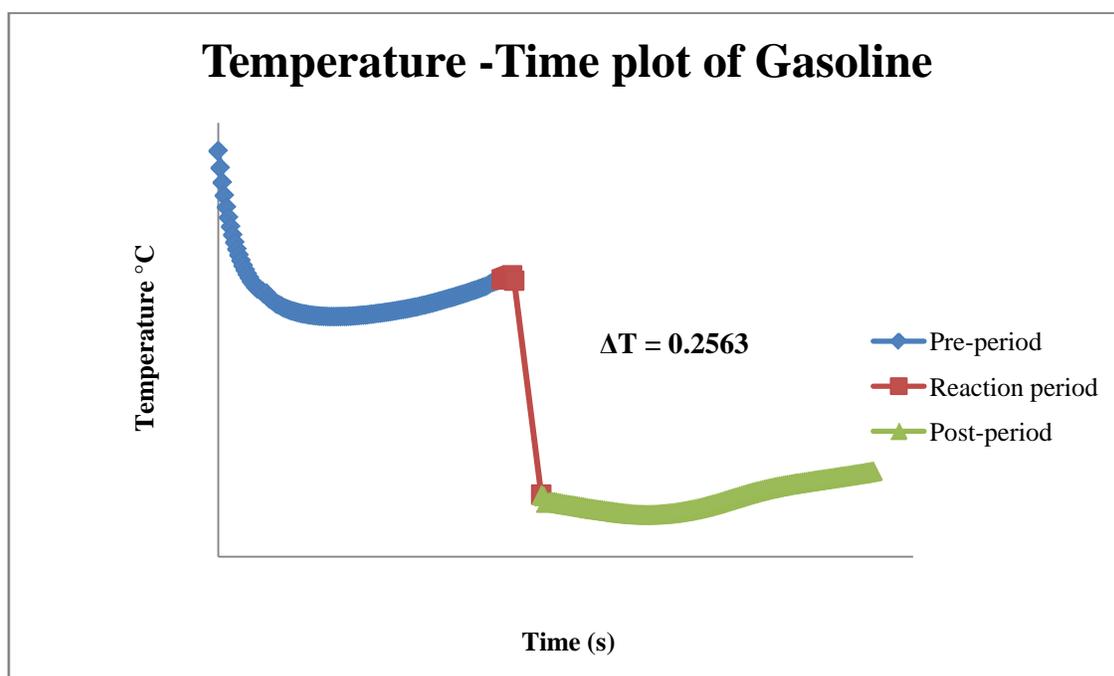


Figure 4. 1 - Temperature - Time Plot of Gasoline

Figure 4.1 shows an example of a temperature-time plot of gasoline. Gasoline spills are common. The experimental tests with CIAgent© and gasoline showed that when the reaction began, the temperature of the oil dropped and then came to a thermal equilibrium with its surroundings. The drop in temperature is calibrated from the difference in temperature of the pre-

period and the post period reaction. The heat of solidification is calculated from the corrected temperature change by the following equation

$$\Delta H_T = -(\Delta Tc)(e)/m \quad (4.3)$$

where e = energy equivalent of the calorimeter and its contents, calories per °C, found by a standardization procedure. This value indicates the speed of the reaction and the integrity of the byproduct.

Endothermic Response

Figure 4.2 shows the solvents that showed an endothermic response. CIAgent© consists of polymerization catalysts and cross-linking agents. Thus for the reaction to take place, these cross-links should be broken. The polymer molecules and hydrocarbon liquids reconfigure to form closer physical bonds, requiring energy from the surrounding and therefore the reduction in temperature (endothermic response). Mineral oil, gasoline, crudes and biodiesel follow an endothermic response. Crudes and gasoline have a greater association with the polymer; hence they show a greater temperature change.

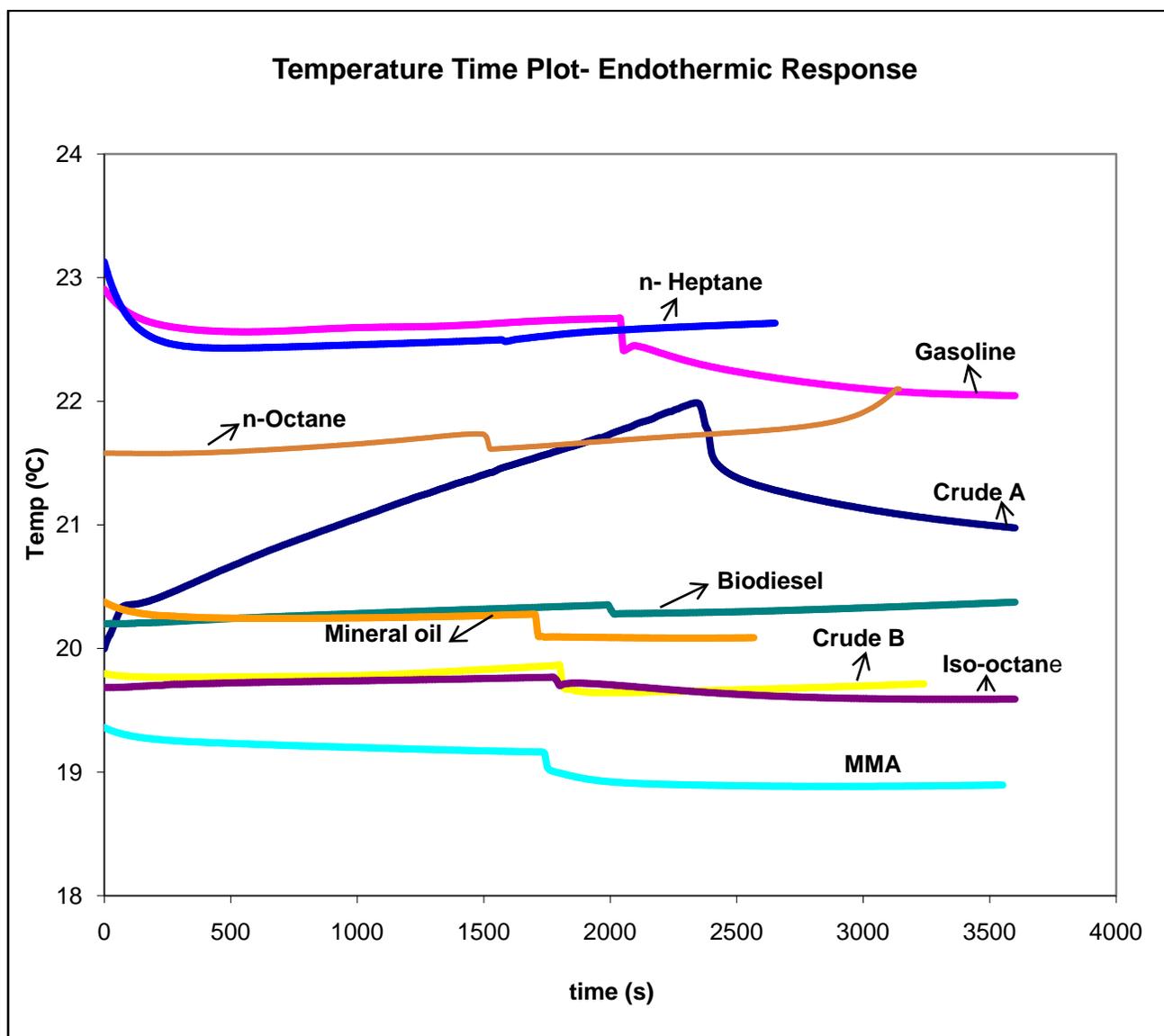


Figure 4. 2 - Temperature-Time Plot of Solvents Showing Endothermic Response

Exothermic Response

An exothermic response was observed when CIAgent© was tested with solvents like diesel, kerosene, motor oil, JP-4, JP-5, and JP-8. In these hydrocarbon liquids, the polymer molecules relax after its association thereby releasing energy. The energy from this relaxation exceeds the energy needed for the polymer and solvent to associate, hence resulting in a very slight exothermicity that is observed in Figure 4.3. Most of the solvents like JP-4, JP-5, JP-8 are specific blends and have higher densities. Even though solidification occurs, the association is not as pronounced as the solvents that show an endothermic response.

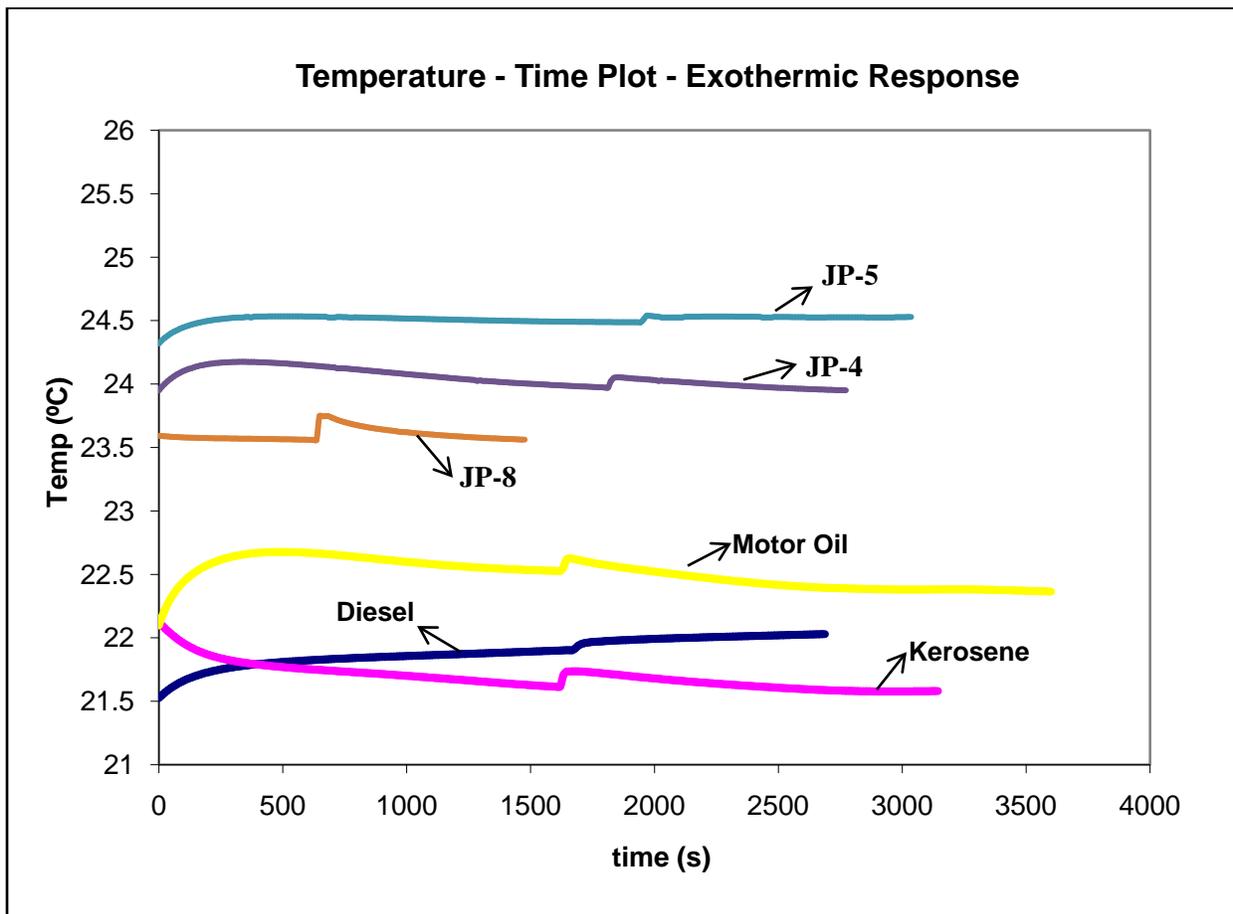


Figure 4.3 - Temperature-Time Plots of Solvents Showing Exothermic Response

Comparative Change in Temperature Plot for the Hydrocarbon Liquids.

The change in temperature, ΔT , was calculated from the difference between the calibrated pre period and post period values as explained in Section 3.2. Figure 4.4 gives the ΔT values of the various hydrocarbons that were tested. The ΔT value was greatest for crude oil, gasoline, MMA and mineral oil.

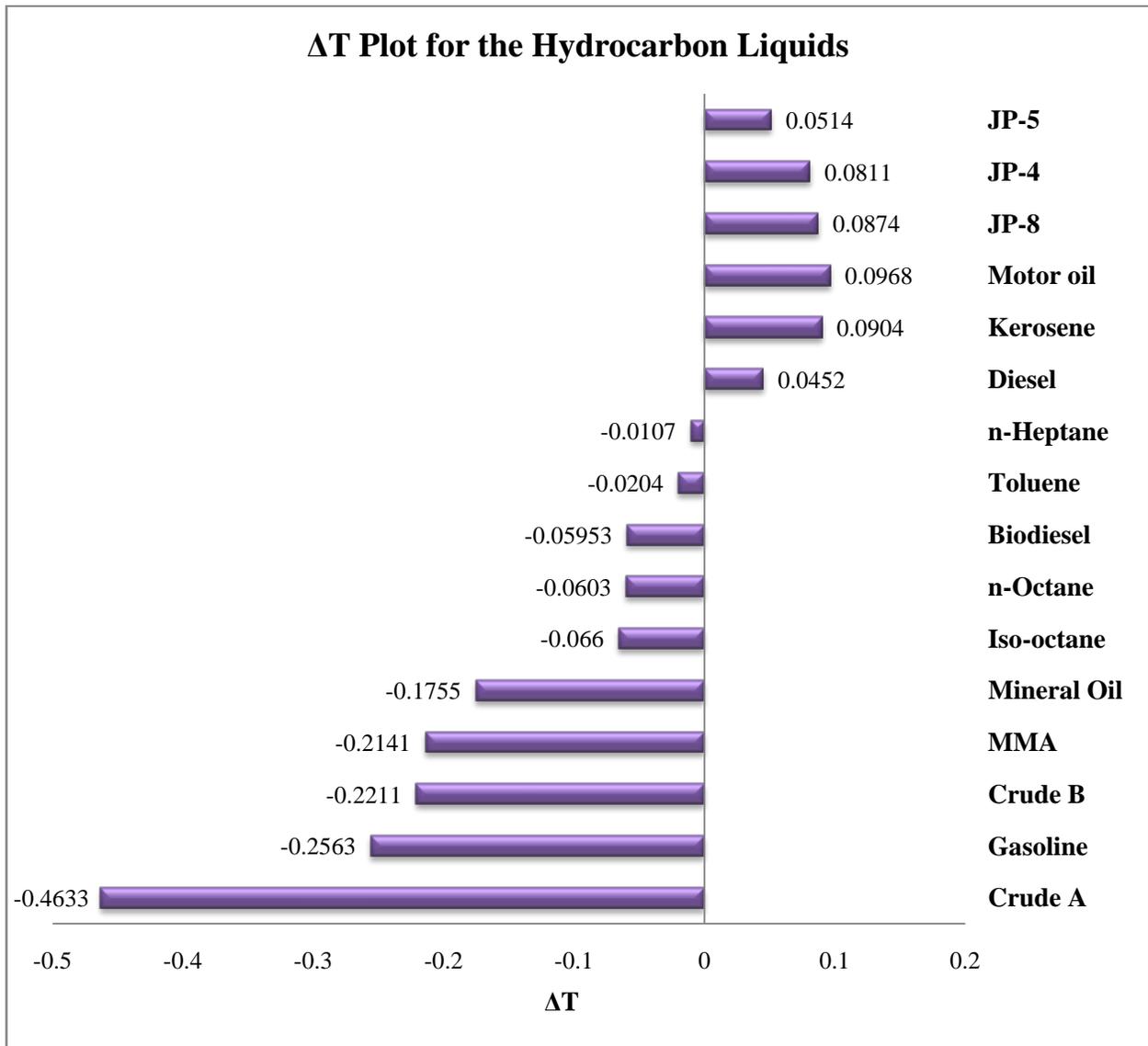


Figure 4. 4 - ΔT Plot for the Hydrocarbon Liquids

Comparative ΔH_s plots for the Hydrocarbon Liquids

The heat of solidification ΔH_s was calculated from the ΔT values, the energy equivalent of the calorimeter and the mass of the solidifier, m , as described in Section 3.3. Figure 4.5 shows the ΔH_s plot for the hydrocarbon liquids. From these ΔH_s values, the ease with which the solidifier reacts with the hydrocarbon liquids was determined. A greater value of the heat of solidification indicates a faster solidification and a better integrity of the byproduct. The byproduct integrity plays an important role in removal and disposal methods.

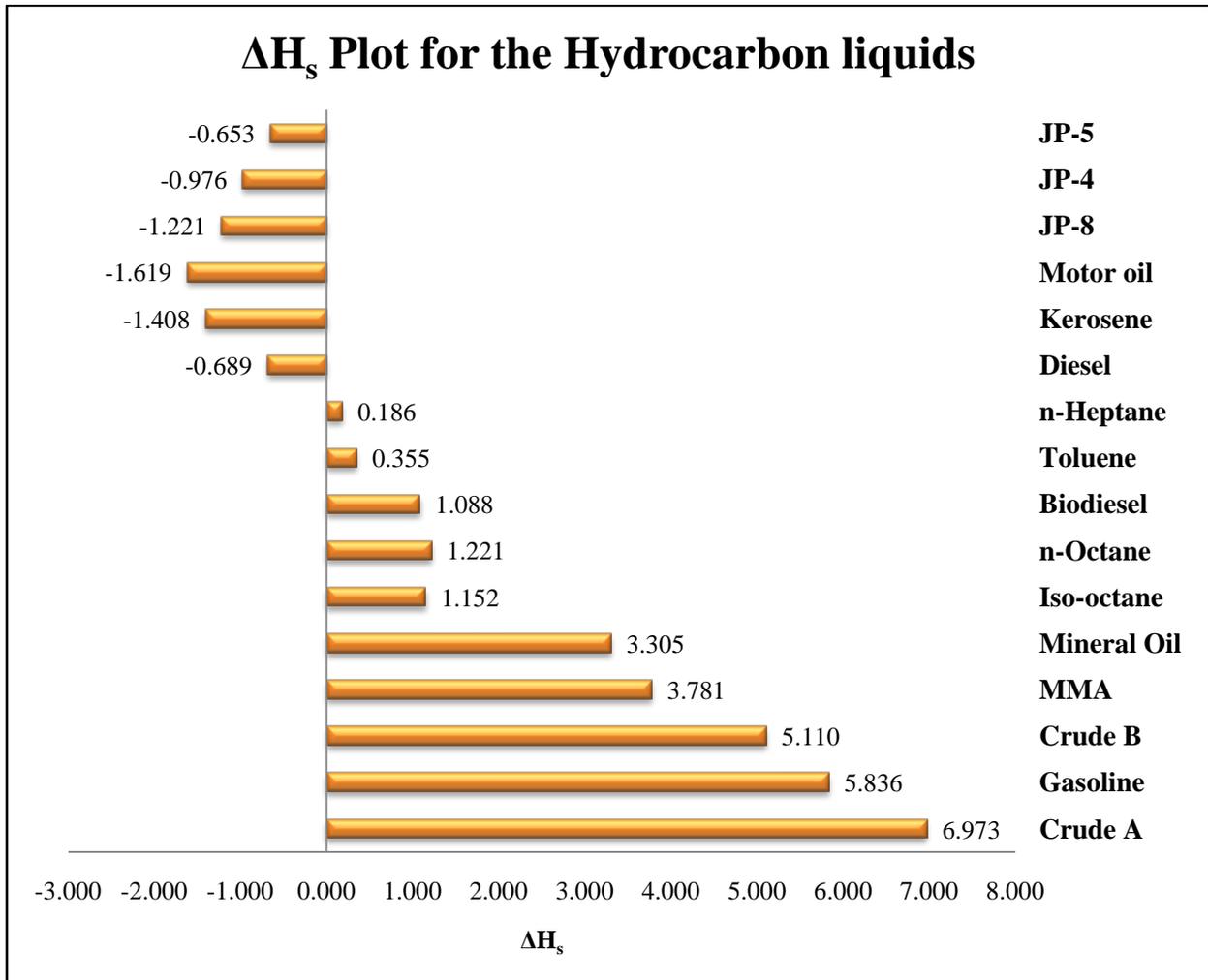


Figure 4.5 – Heat of Solidification for the Hydrocarbon Liquids

The ΔH_s plot shows both positive and negative responses depending on the endothermic and exothermic temperature differences. Crudes, gasoline, MMA and mineral oil have a greater heat of solidification values. The impact of these values on the integrity of the by-product is as shown in Figure 4.6.

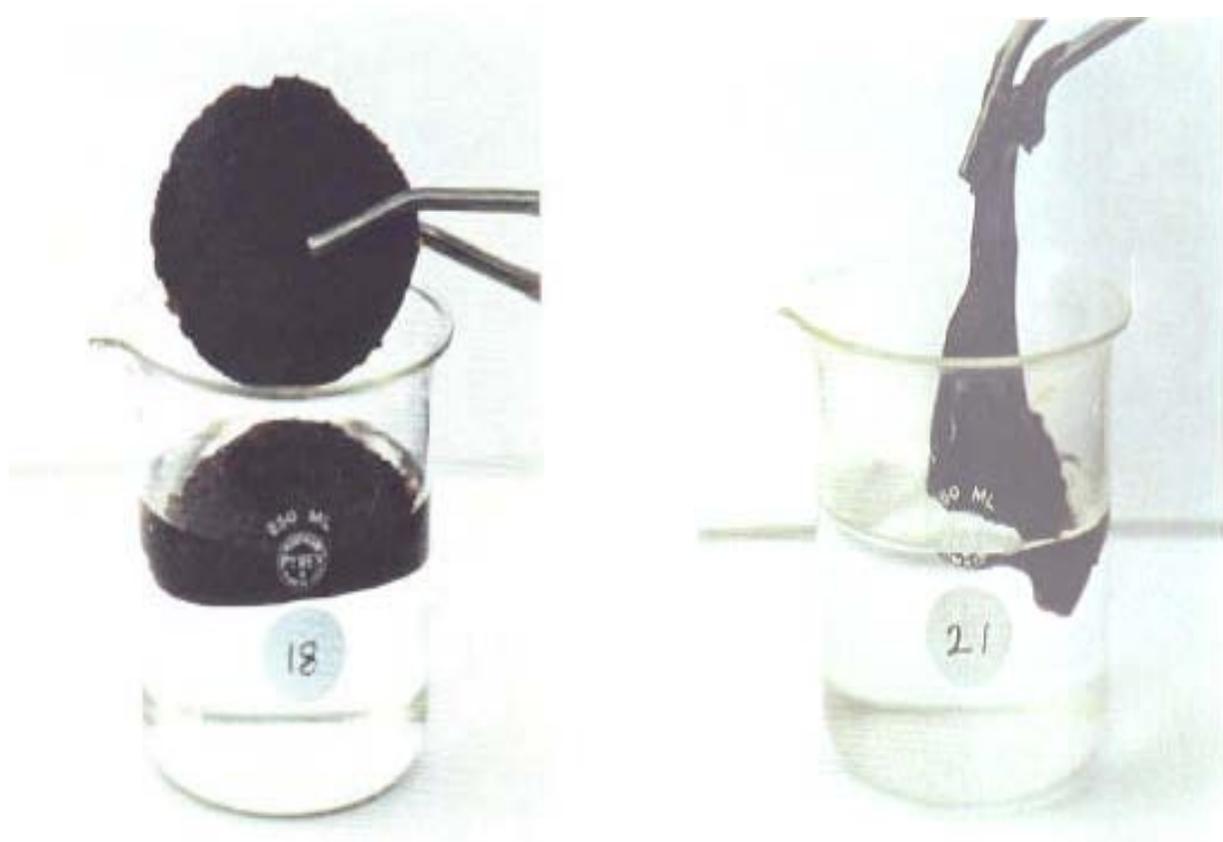


Figure 4.6 - By-product integrity of crude oil samples based on the heat of solidification values

Solidifier Mass:

The mass of the solidifier used to solidify the hydrocarbon liquids was plotted against the heat of solidification values. From the Figure 4.7, it could be inferred that the reactions with a positive ΔH_s consumed less solidifier than the reactions with a negative ΔH_s . Since δ is proportional to the ΔH_s , this information is particularly useful in determining the amount of solidifier that should be applied in hydrocarbon spill scenarios. Thus, the heats of solidification have implications for how the solidifier applications should be conducted.

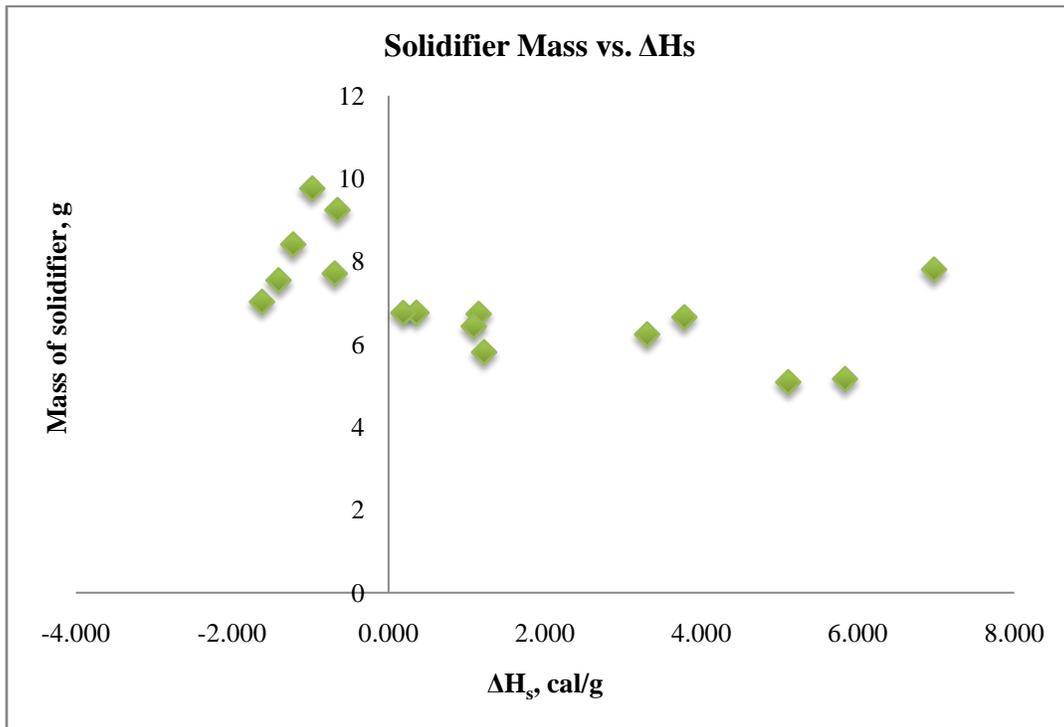


Figure 4. 7 - Solidifier Mass versus. ΔH_s

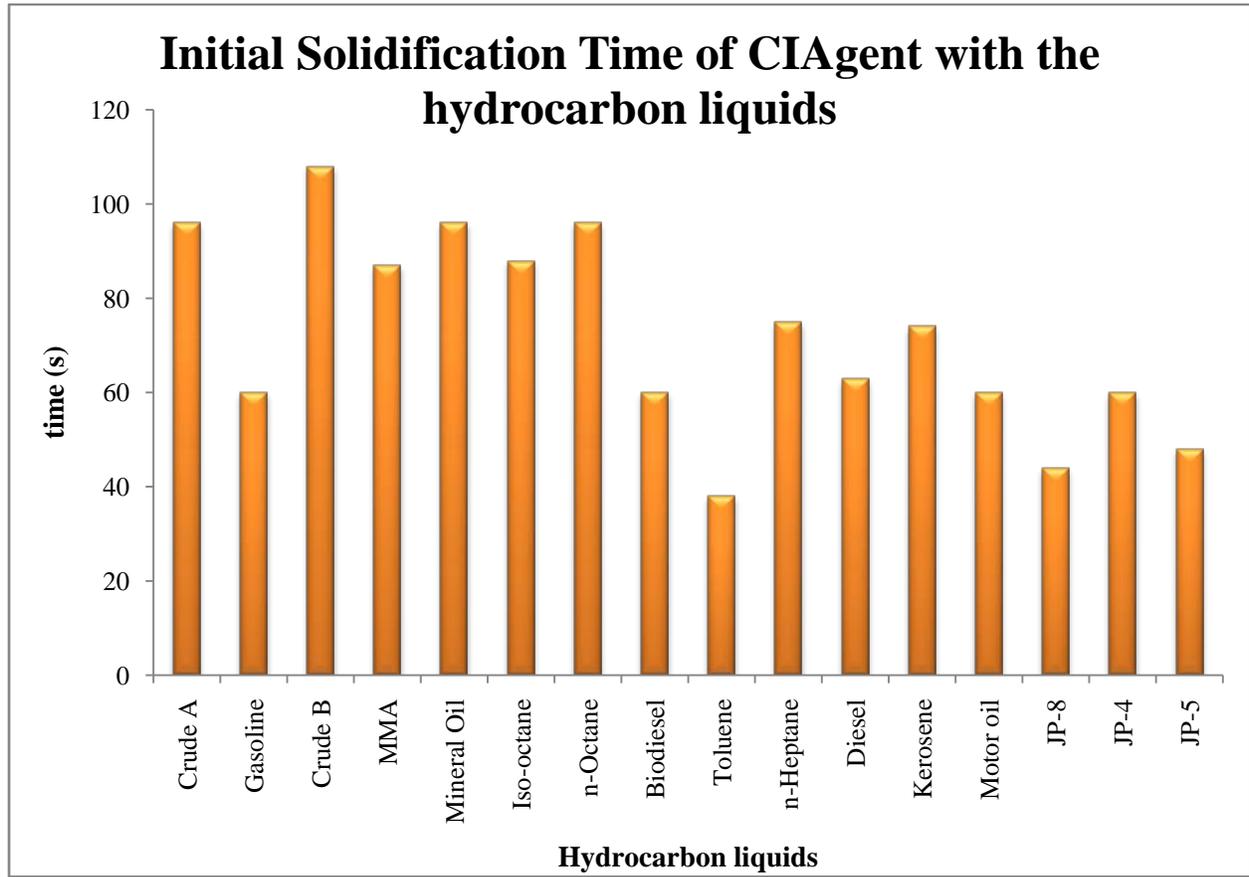


Figure 4. 8: Initial Solidification time of CIAgent with the Hydrocarbon liquids

The effectiveness of CIAgent© depends on the solidification time. Figure 4.8 shows the time taken for the initial solidification of the hydrocarbon liquids with CIAgent. The average solidification time was 72 seconds. CIAgent was an efficient solidifier solidifying most of the hydrocarbons in less than two minutes. Complete solidification occurs in about an hour to form a firmer and more consistent product.

Application Ratio of CIAgent©

CIAgent© was tested with the hydrocarbon liquids to determine its application rate. This ratio represents the amount of solidifier applied to the oil until no visible oil remained on the water surface. In all the cases tested, the solidification was completed within an hour. The final consistency of the solidified material ranged from a firm, solidified mass to a gel-like product.

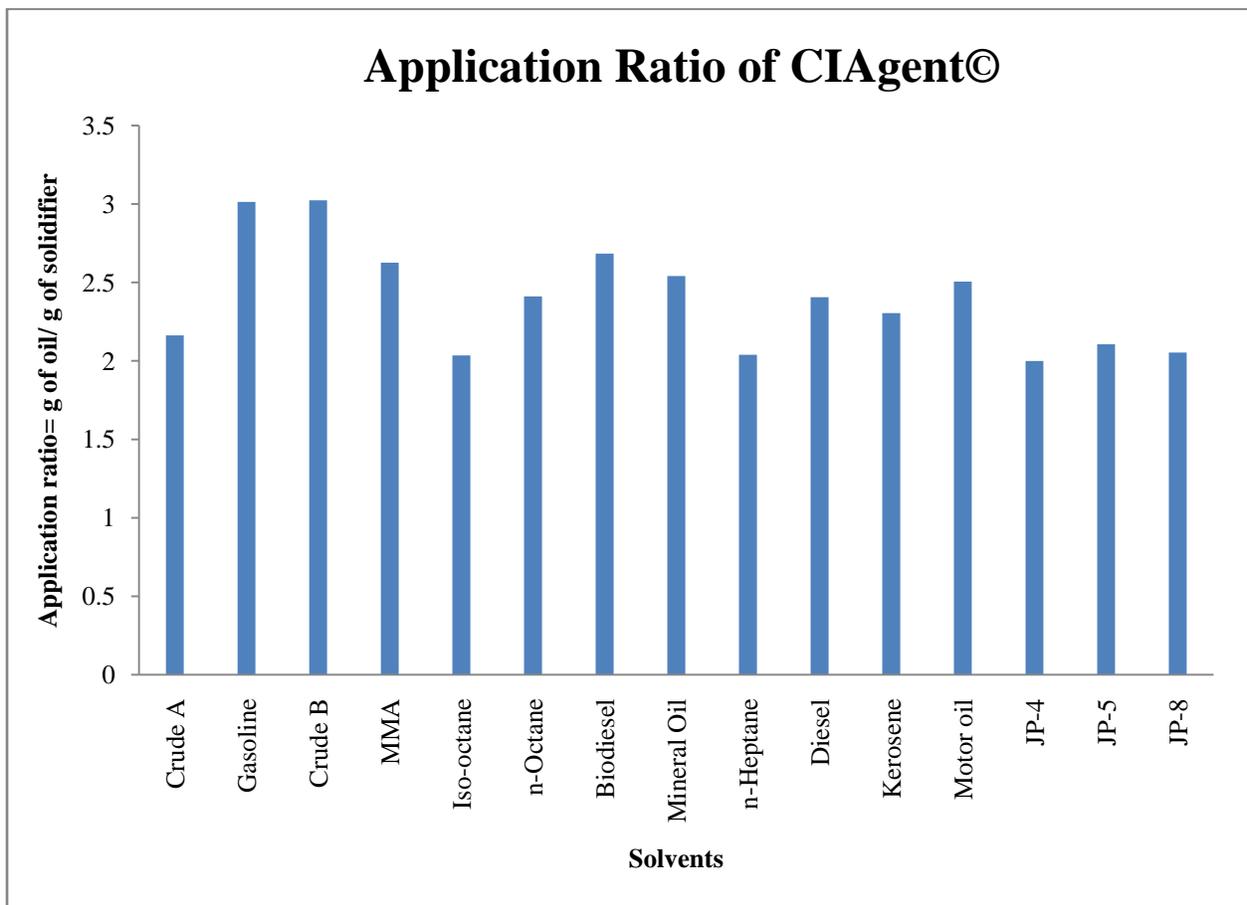


Figure 4.9 - Application Ratio of CIAgent©

The average application ratio of the CIAgent was **2.39 - 2.5 grams of oil per gram of CIAgent**. It was also noticed that gasoline and crude had an application ratio of 3:1 hydrocarbon to solidifier ratio. The application ratio again has implications on the amount of solidifier that has to be applied in case of an oil spill scenario. The application ratio is also affected by the viscosity of the hydrocarbon, temperature and the amount of volatiles in the hydrocarbon

4.4.4 - Determination of the Solubility Parameter of CIAgent

For polymer solutions, the heat of mixing is the energy change involved in forming one contact between the solvent and solute units at the expense of breaking a solute-solute and a solvent-solvent contact. This value is calculated using Hildebrand's regular solution theory, which gives

$$\frac{\Delta H_m}{V} = \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2 \quad (4.4)$$

where φ 's are the volume fractions of solvent and polymer and δ_1 is the solubility parameter of the solvent and δ_2 is the solubility parameter of the polymer. The dimension used widely is the Hildebrand. The polymer CIAgent© was weighed and was placed in a series of solvents of known solubility parameters. The polymer was allowed to reach thermal equilibrium and the temperature difference is calculated from which the heat of solution is determined. Each test had three trials. These values were used in the Equation 4.4 and the solubility parameter of the polymer is found. As shown in Table 4.2, the solubility parameter of the polymer was found to be **6.706 ± 0.386 hildebrand** with a 95 per cent confidence interval. The coefficient of variation was 0.0576 indicating that the data is consistent. Hence CIAgent© should be able to solidify

hydrocarbon liquids whose solubility parameters are in the range of 5 to 10 hildebrand or 10 to 20 MPa^{1/2}.

Solvents	ΔHm (cal/g)	φA	φB	Molar volume of Solvent, V (cm³/mol)	Molecular weight (g/mol)	δ1 (cal/cm³)^{1/2}	δ2 (cal/cm³)^{1/2}
Crude A	6.973	0.321	0.679	743.00	682	7.930	7.700
Gasoline	5.836	0.296	0.703	146.14	108	7.592	7.037
Crude B	5.110	0.266	0.733	607.57	519.78	7.780	7.551
Mineral Oil	3.305	0.307	0.693	415.57	347	7.122	6.894
MMA	3.781	0.276	0.724	106.10	100.12	8.759	4.533
Iso octane	1.152	0.400	0.600	166.10	114.23	6.891	5.075
n-Octane	1.221	0.357	0.643	163.50	114.22	7.576	5.648
Biodiesel	1.088	0.284	0.715	368.18	324	8.287	8.152
n-Heptane	0.186	0.404	0.596	147.40	100.2	7.478	6.753

Solvents	ΔH_m (cal/g)	ϕ_A	ϕ_B	Molar volume of Solvent, V (cm³/mol)	Molecular weight (g/mol)	δ_1 (cal/cm³)^{1/2}	δ_2 (cal/cm³)^{1/2}
Toluene	0.355	0.343	0.657	106.80	92.14	8.878	7.713

Table 4. 2 - Determination of the Solubility Parameter of CIAgent©

Solubility parameter determination from the swelling measurements.

The molecular weights of the hydrocarbon liquids like gasoline, mineral oil, biodiesel, motor oil, kerosene, diesel fuel were determined by mass spectrometry (Chemistry Department, Auburn University). The molecular weights of the other hydrocarbon liquids were found from literature and from the API gravity calculations. The molar volume was determined from these values. The solubility parameters of the solvents are found from solubility parameter handbooks. (Barton 1991). The solubility parameter of the solvents whose δ 's are unknown was calculated from the enthalpy of vaporization and the molar volume values. Table 4.3 gives the values of solubility parameter of all the solvents used in hildebrands and SI unit.

Solvents	δ (hildebrands)	δ (MPa ^{1/2})
Crude A (Mutelet 2002)	7.930	16.145
Gasoline	7.592	15.458
Crude B (Mutelet 2002)	7.780	15.840
MMA	8.759	17.833
Mineral Oil	7.122	14.500
Iso-octane	6.891	14.030
n-Octane	7.576	15.425
Biodiesel	8.287	16.872
Toluene	8.878	18.076
n-Heptane	7.478	15.225
Diesel	6.833	13.913
Kerosene	7.015	14.283
Motor oil	7.225	14.711
JP-8 (Martel 1988)	7.342	14.948
JP-4 (Ross 1974)	5.418	11.030
JP-5 (Ross 1974)	5.520	11.239

Table 4. 3 - Solubility Parameters of the Solvents

The CIAgent© is allowed to swell in a series of solvents of known solubility parameter. Table 4.3 gives the solubility parameter of the solvents. After the swelling was complete, each sample was reweighed and the weights, the specific volumes of polymer and solvent were used to calculate the swelling ratio, which is the ratio of the swollen volume to the dry volume. This is expressed by the following equation (Hamurcu 1993)

$$Q = 1 + \left(\frac{W_2}{W_1 - 1} \right) \frac{\rho_2}{\rho_1} \quad (4.5)$$

where Q = Equilibrium swelling ratio; W_1 = weight of the network before swelling; W_2 = weight of the network after swelling; ρ_1 = density of the solvent; ρ_2 = density of the polymer

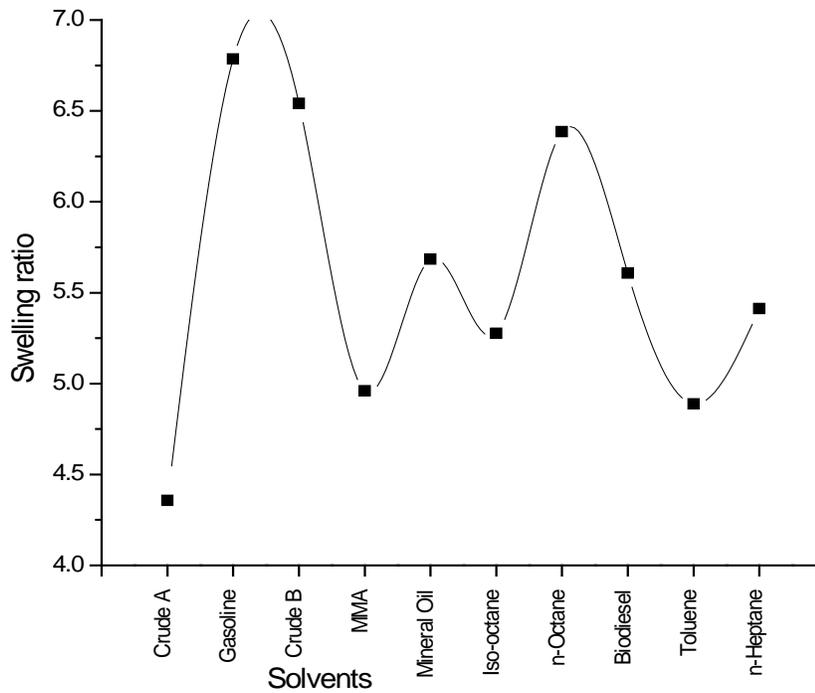


Figure 4.10 - Swelling Ratio of Solvents with a Positive Heat of Solidification

The largest value of the ratio or the highest degree of swelling was obtained by using the best solvent for the polymer. From Figure 4.10, it was estimated that the highest degree of swelling is obtained for gasoline which has a heat of solidification value of 5.836 cal/g or 630.29 cal/mol and a swelling ratio of 6.785 in the solidifier CIAgent©. This value is taken as Q_{max} and used to calculate the solubility parameter.

The solubility parameter δ is proportional to the cohesion of the material or the strength of attraction between molecules making up the material. A method based on the evaluation of maximum swelling in a series of solvents of known solubility parameters was used. The solubility of a polymer in any solvent depends on the square of the difference between their solubility parameter values. This value should be as small as possible for good solubility of a polymer in any solvent. The following relation was used for this purpose (Gee, 1943 and 1946)

$$\frac{Q}{Q_{max}} = \exp(-\alpha Q (\delta_{solvent} - \delta_{polymer})^2) \quad (4.6)$$

This equation is rearranged as

$$\left(Q^{-1} \ln\left(\frac{Q}{Q_{max}}\right)\right)^{1/2} = \alpha^{0.5} (\delta_{solvent} - \delta_{polymer}) \quad (4.7)$$

A plot of $\left(Q^{-1} \ln\left(\frac{Q}{Q_{max}}\right)\right)^{1/2}$ versus the solubility parameters of a series of solvents will give $\alpha^{1/2}$ and the $\delta_{polymer}$ values from the slope and intersection of the horizontal axis of the obtained line. Figure 4.10 illustrates the plot of left hand side of Equation 4.7 versus the solubility parameter of the various solvents used. From the plot the solubility parameter was found to be **7.251 hildebrands or 14.76 MPa^{1/2}** and the value of $\alpha = 0.108 \text{ cm}^3/\text{cal}$ using least square regression method.

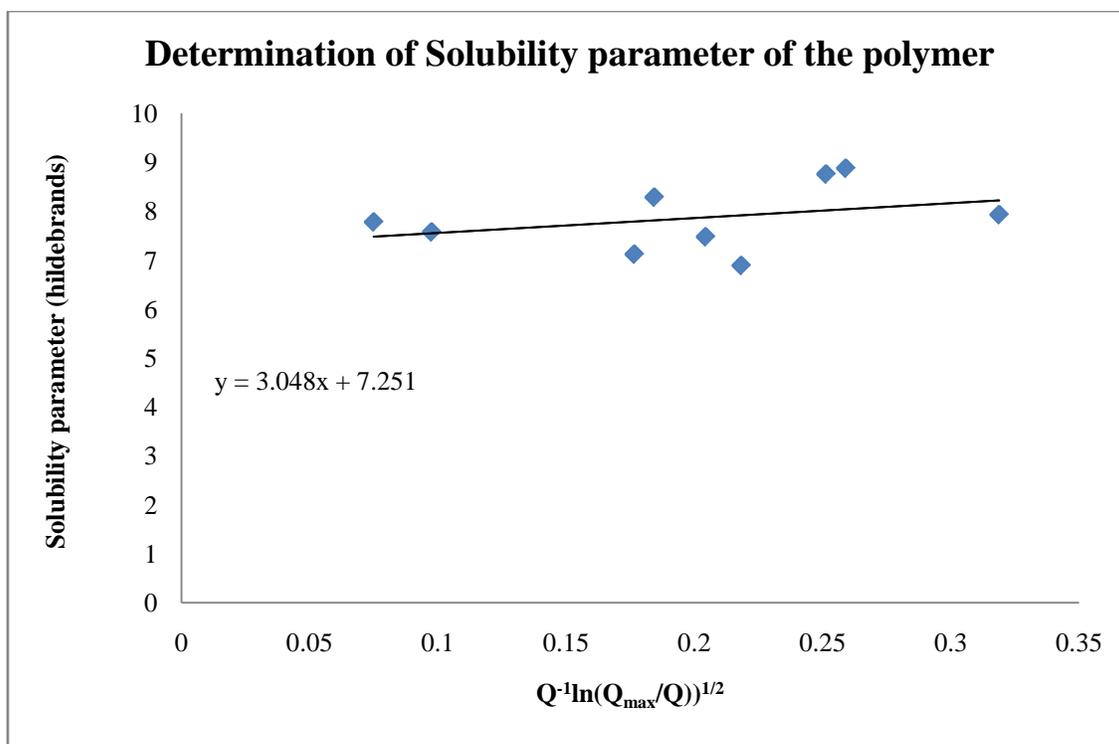


Figure 4. 11 - Determination of Solubility Parameter of the Polymer

Solubility parameter determination of polymer from solvents that showed an exothermic response

When the heat of solidification (ΔH_s) is negative, the Hildebrand solubility parameter cannot be calculated. The difficulty arises from the fact that the square root of the solubility parameter should be estimated to obtain the Hildebrand parameter of the material of interest. The solubility parameter theory does allow for exothermic enthalpies of solutions. The exothermic enthalpies (i.e., negative interaction parameters) are obtained when the intermolecular interaction between the molecules within a mixture is dominated by the directional interactions. Since there is no available method to accurately determine the solubility

parameter of the polymer, it could be estimated from a plot of the swelling ratio versus the ΔH_s as shown in Figure 4.11.

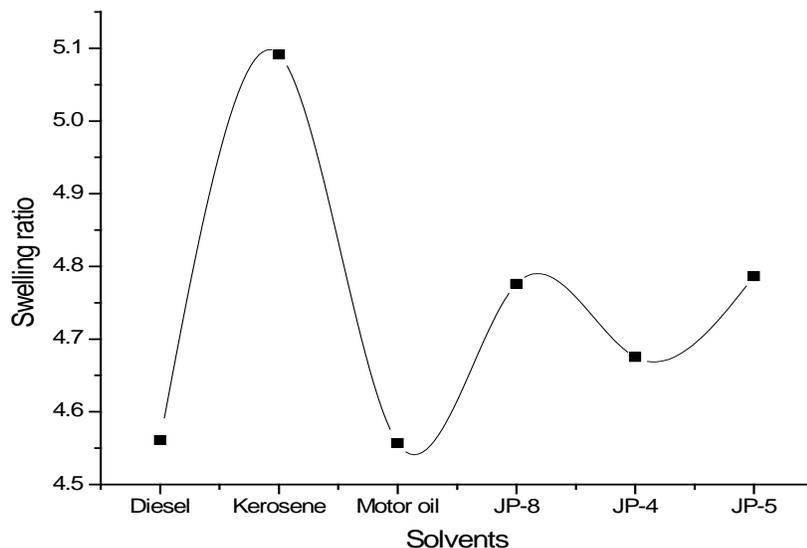


Figure 4.12 - Swelling Ratio vs. Solvents with Negative Heats of Solidification

From the plot it was observed that the swelling was the maximum for kerosene. From Table 4.2 the solubility parameter of kerosene was found to be 7.015. Hence the solubility parameter of the polymer must be similar to that of kerosene, as the solubility parameter of the polymer can be estimated from the solubility parameter of the solvent with a largest swelling ratio or the highest degree of swelling.

4.4.5 - Determining the range of solvents that works for the solidifier

The objective is to determine the differences in the affinity of the solidifier for the different hydrocarbon liquids. These differences are used to divide the solvents into two groups, one that is considered “good” and the other that is considered “bad”.

Teas Graph.

A Teas graph uses fractional parameter as shown in Equations 4.8 and 4.9. It is an empirical system with little theoretical justification. Solvent positions are located on the graph according to Hansen values. A Teas graph is the most convenient method by which the solubility information can be illustrated. Figure 4.13 shows the Teas graph of the solvents whose Hansen solubility parameters were known. It could be seen from the graph that for most of the solvents tested, the solubility parameter was mainly due to dispersive forces. The polar and hydrogen bonding forces are negligible. According to the graph it was safe to assume that the δ_p and δ_h of the solidifier are also negligible because of the principle “like seeds like”.

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \quad f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \quad f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \quad (4.8)$$

$$f_d + f_p + f_h = 100 \quad (4.9)$$

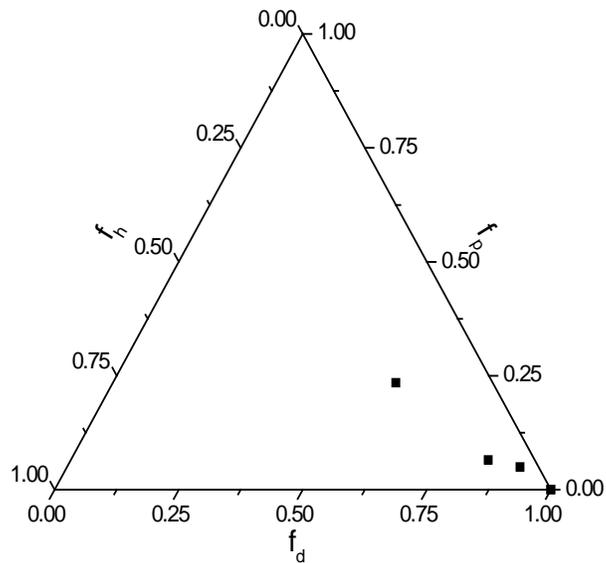


Figure 4.13: Teas Graph of Known Hansen Solubility Parameters

Polymer Solubility Window

Using the solvent positions, it was possible to indicate the polymer solubility with the help of the degree of swelling values. Accordingly, the solvents were divided as good and bad solvents for the particular polymer. The edges of the area or the polymer solubility window can be determined by solvating the polymer in a series of solvents and determining their solubility as shown in Figure 4.14

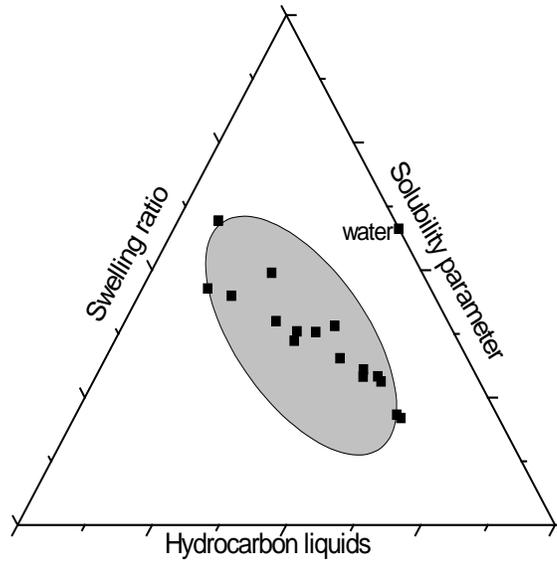


Figure 4. 14: Solidifier Solubility Window

The polymer solubility graph gives an approximate range of solvents for which the CIAgent© will work as an effective solidifier. Any solvent that falls within the solubility circle would associate in CIAgent©. The range of the solubility parameter of the solvent for which the CIAgent© works is approximately 5 to 10 hildebrands. The smaller the difference of the δ 's of the solvent and the polymer, the higher their association. This is an approximate method as there were no available three dimensional solubility parameter data for some of the solvents that were used in the test.

4.5 - Conclusions

CIAgent© was solvated in a series of hydrocarbon liquids of known solubility parameters. From the heats of solidification values obtained using a solution calorimeter, the solubility parameter of CIAgent© was calculated to be **6.706 ± 0.386 hildebrand** with a 95 per cent confidence interval.

CIAgent© had the maximum swelling with gasoline. From the swelling ratios of the solvents in CIAgent©, the solubility parameter of the solidifier was approximately found to be **7.251 hildebrands (14.76 MPa^{1/2})** with a regression value of 0.46. Since a negative heat of solidification was also observed for some solvents, a separate swelling plot was constructed for these solvents. Kerosene had the maximum swelling and the approximate value of the solubility parameter was found to be around 7.015 hildebrands. According to the polymer solubility window plot, it was found that CIAgent© should be able to solidify hydrocarbon liquids whose solubility parameter lies in the range of 5 to 10 hildebrands. This conclusion is tempered by the fact that most of the solvents used were mixtures making it difficult to estimate the three-dimensional solubility parameters of these solvents.

The laboratory application ratio of the CIAgent© to the hydrocarbon liquids was **2.39 to 2.5** grams of oil to grams of CIAgent©. The general observation was that the lighter the oil, the greater was the tendency to solidify. These calculations proved to be very useful in determining the extent and procedure for the application of CIAgent© in oil spill scenarios.

CHAPTER 5

Effectiveness of CIAgent© as a Hydrocarbon Solidifier for SPCC Secondary Containment in Electric Utility Industry

Abstract:

Utility industries have to develop extensive contingency plans to handle accidental spills and leaks of transformer fluid. CIAgent© Barrier Boom is an ideal solution for providing secondary containment as required by Spill Prevention Control and Countermeasure Plan (SPCC). CIAgent© Barrier Boom is designed to prevent the flow of hydrocarbons from a containment site while allowing the unimpeded flow of water. CIAgent© polymers have a molecular structure that associates strongly with liquid hydrocarbons (e. g., oils, gasoline and mineral oil), solidifying the hydrocarbon liquid upon contact into an inert, solid rubber-like mass.

The research characterized the effectiveness of CIAgent© for hydrocarbons that could be encountered in an electric utility spill. Experiments were conducted using a solution calorimeter (Parr Instruments, Model No. 6755). A temperature versus time plot was obtained for each hydrocarbon liquid tested and the temperature change upon solidification was determined. This temperature change was then correlated to the heat of solidification values. The results show that solidification is a viable method for controlling and remediating oil spills. The characterization method helps in evaluating the rate and extent of CIAgent© application for oil spill cleanup.

5.1- Introduction

Electric utility substations are used for transmission (high voltage), distribution (low voltage), transformation of power from one voltage level to another, interconnection of alternate sources of power and controlling system voltage and power flow. A typical substation facility consists of a small building with a fenced-in yard containing transformers, switches, voltage regulators, and metering equipment used to adjust voltages and monitor circuits. Various electrical instruments installed in the substations use oil that provides the necessary insulation characteristics. Power transformers, oil-filled reactors, large regulators and circuit breakers are the greatest potential source of major oil spills in substations. Hence the containment and control of oil spills at electric utility substations is a great concern for most electric utilities. The environmental impact of oil spills and their cleanup is highly regulated at the local, state and federal levels. The quantity of oil on site, topography and soil characteristics, rate of flow of discharged oil have to be evaluated to necessitate the need for secondary oil containment. The cleanup costs, in the event of a spill, are very high. The costs associated with the clean up, in the event of a spill, are very high (Sahazizian and Kertesz 2007).

CIAgent© Barrier Boom is one of the easiest and cost effective spill containment solutions used in substations and other facilities to meet SPCC (Spill Prevention Control and Countermeasure) requirements. It is designed to prevent the flow of hydrocarbon liquid without impeding the flow of water. CIAgent© Barrier Booms are made from a non-woven geotextile material (GEOTEX 1201) filled with CIAgent© granules, a solidifier with a proprietary blend of USDA food-grade polymers. CIAgent© is a dry granular powder and can encapsulate transformer oils, through a rapid transformation into a cohesive rubber-like mass upon contact. CIAgent© “solidifies the

oil” into a solid mass with minimal volumetric increases. The reaction that takes place is a physical reaction rather than a chemical reaction. The boom wall is backed with Agent-X, a non-woven geotextile material with CIAgent© embedded within the fabric (CIAgent© Solutions). The objective of the research was to determine the heat of solidification values using a solution calorimeter and its implications as to how the CIAgent© applications should be conducted.

CIAgent© Barrier Booms are used in substations and other facilities for oil spill containment. The dimensions of the barrier booms will vary by facility dimensions and by the depth of rock. The subsurface of a facility needs to be impervious or made impervious with a proper liner.

5.2 Literature Review

5.2.1 Use of CIAgent as a Secondary Containment for EU Industry

CIAgent Barrier Boom

CIAgent Barrier Booms are used in electric utility substations for oil spill containment to meet SPCC requirements. The barrier boom installed will allow the water to pass but prevents the oil from migrating off the substations. The dimensions of the boom will vary with the facility dimensions and by the depth of rock. The subsurface of a facility needs to be impervious or made impervious with a proper liner. Once placed vertically in the ground, the CIAgent Barrier boom will be completely covered with clean washed aggregate. CIAgent encapsulates the oil upon contact turning it into a cohesive rubber-like mass.

The inter wall protective covering is made from the polypropylene fibers called Geotex 1201. This nonwoven geo-textile is needle punched to form a strong fabric that retains its dimensional stability capable of withstanding the construction installation stresses. Barrier

booms are used in subsurface drainage, separation, stabilization, erosion control and cushioning applications. The geo-textile is resistant to ultraviolet degradation and to biological and chemical environments normally found in soils and provides a low rate of 75 g/min/sqft.

The back wall of the CIAgent Barrier Boom is a double sided, 12 oz. per square yard, per side, geo-textile (Agent X) that is embedded with 100-450 grams of CIAgent, a co-polymer block blend (per square yard). The Agent X material has a flow rate greater than 10 gallons per square foot/minute. The fibers are hydrophobic and oleophilic. They are able to remove more than 90% of a 30,000 PPM hydrocarbon contamination per 10 liters of water, per square foot. These inner polymers must be able to solidify transformer oil in less than two minutes and must become impervious upon contact with that hydrocarbon. The amount of solidification is approximately ½ gallon per square foot or 4 to 5 pounds of oil, depending on the viscosity of oil.

Figure 5.1 shows the schematic of a typical CIAgent© Barrier Boom.

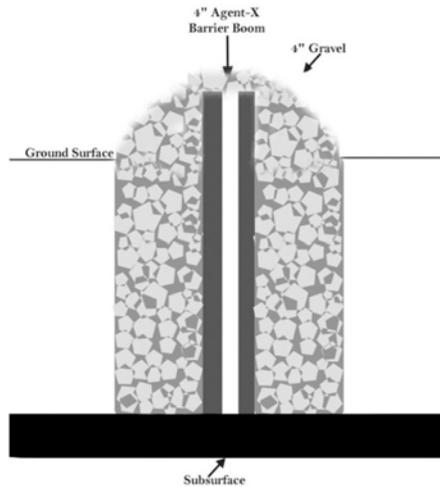


Figure 5.1: CIAgent Barrier Boom (CIAgent Solutions)

Installation Method

A trench is dug down slightly into the subsurface's inside or outside fence. The CIAgent Barrier Boom is placed in the ground vertically on edge into subsurface. All loose rock and dirt should be removed from the trench and a small bed of Bentonite powder should be poured on each side of the boom at the subsurface and that clean washed stones should be added until the trench is brought back to grade and the Barrier Boom is covered. Other methods include retrofitting a substation requiring a dike on an impervious subsurface and retrofitting a substation requiring a dike in conjunction with a clay liner, where a clay liner is placed over the flap of the CIAgent Barrier Boom.

CIAgent products are chosen as a solidifier in an EU industry because they are long lasting and they allow water to pass through them, but would capture and lock any transformer oil.

5.3 Materials and Methods

The effectiveness of a solidifier is given by the solidification temperature change, solidification time and weight ratio of the solidifier and the solvents (Fingas 1992). The heat of solidification is used to estimate the ease of solidification between the solidifier and the hydrocarbon liquid (Ghalambor 1996). A solution calorimeter is an instrument used to measure the heat evolved or absorbed by chemical reactions. A Parr Solution Calorimeter (Model No.6755) was used in this experiment. All the measurements were made at room temperature and atmospheric pressure. A bench scale study was used to calculate the optimum ratio of CIAgent© to transformer oil. The same ratio was used with the same test conditions in the solution calorimeter to find the heat of solidification.

The CIAgent was taken in the glass Dewar and the transformer oil was taken in the rotating glass cell. Both the reactants are allowed to reach an initial pre-period equilibrium. The reaction is started by depressing the push rod and dropping the contents of the cell into the Dewar flask. The system was then allowed to reach a post period equilibrium. A Temperature – Time plot was obtained from the calorimeter for solidifier and the transformer oil and the readings were plotted to obtain the reaction heat by the equations 3.1, 3.5 and 3.6. The excess solidifier was weighed to determine the required solidifier mass, m

5.4 Results and Discussions

The effectiveness of a solidifier is defined as the amount of solidifier that is required to solidify oil under standard conditions. Some of the application or monitoring issues associated with the use of solidifiers and addressed in this paper are temperature change during solidification; application rate and solidification time.

Solidification Temperature change

CIAgent consists of cross-linking agents and in order for the reactions to take place, the cross link between the agents must be broken. The experiments showed that CIAgent tends to absorb energy from the surrounding atmosphere (endothermic reaction) in its solidification with transformer oil. This process can be envisioned from the drop in oil temperature after CIAgent is introduced. The drop in temperature is calibrated from the difference in the temperature of the pre-period (T_i) and post-period solidification (T_f) as follows $\Delta T = T_f - T_i$

Figure 5.2 shows the drop in temperature of the transformer oil when CIAgent is introduced. The heat solidification was calculated from the temperature change using equation

3.5 and 3.6. Three trials were conducted for each test. From the heat values, the ease with which the CIAgent reacts with the transformer oil was determined. The greater the heat value, faster was the reaction and higher the integrity of the product.

The change in temperature when CIAgent is introduced is mixed with the transformer oil was 0.18 ± 0.02 . The heat of solidification of transformer oil calculated from the temperature change is about 3.305-cal/gram, which is relatively high. Hence the by-product of transformer oil solidification has a better integrity and the disposal is easily done using simple mechanical equipments.

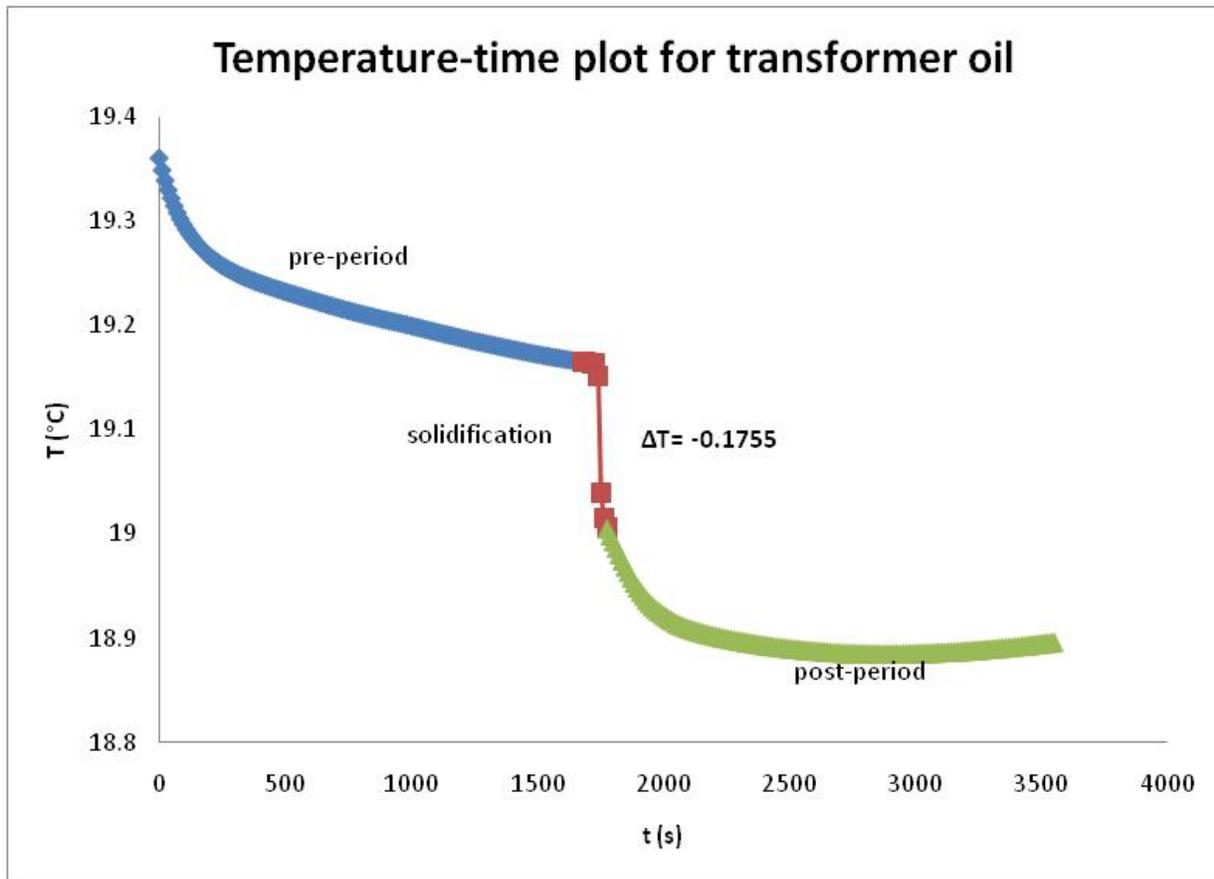


Figure 5. 2: Temperature – Time plot for Transformer Oil

The procedure helps in determining how CIAgent applications should be conducted in oil spill scenarios in electric utility industries. The heat of solidification values also help in determining the integrity of the by-product, which is particularly useful during pick-up and disposal.

Application Ratio

The application ratio is the amount of solidifier applied to the oil until no visible oil remained on the water surface.

$$\textit{Application ratio} = \textit{grams of oil} / \textit{grams of solidifier} \quad (5.3)$$

The solidification of transformer oil was completed within an hour. The final product had a firm, gel-like consistency. The application ratio was also affected by the viscosity of the oil, temperature and the amount of volatiles present. The average application ratio of CIAgent© to the transformer oil was 2.5 grams of hydrocarbon liquid per gram of CIAgent© . The figure 3 shows a comparative plot of the application ratio of transformer oil and the other solvents that were tested. The application ratio of CIAgent© to the transformer oil was relatively higher than the other solvents that were tested. The consumption level of the solidifier or the quantity of agent needed to solidify the transformer oil was between 35- 40 percent.

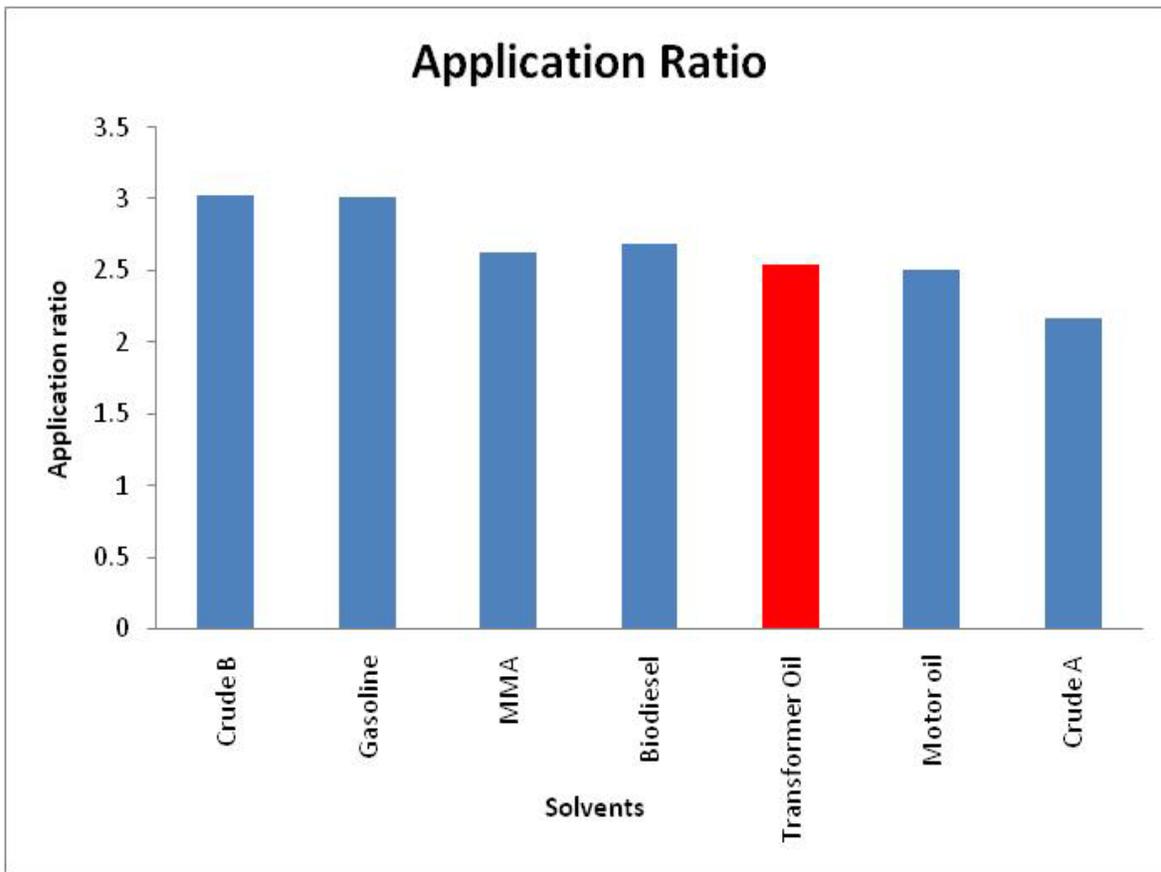


Figure 5.3: Comparative plot of the application ratio of the various solvents

Initial Solidification Time:

The effectiveness of CIAgent© depends on the solidification time. Figure 4 shows the time taken for the initial solidification of the hydrocarbon liquids with CIAgent©. The average solidification time for transformer oil was 96 seconds. The figure 4 shows that CIAgent© was an efficient solidifier solidifying most of the hydrocarbons in less than two minutes. Complete solidification occurs in about an hour to form a firmer and more consistent product. A higher integrity of the solidified material is preferred for easier removal and disposal.

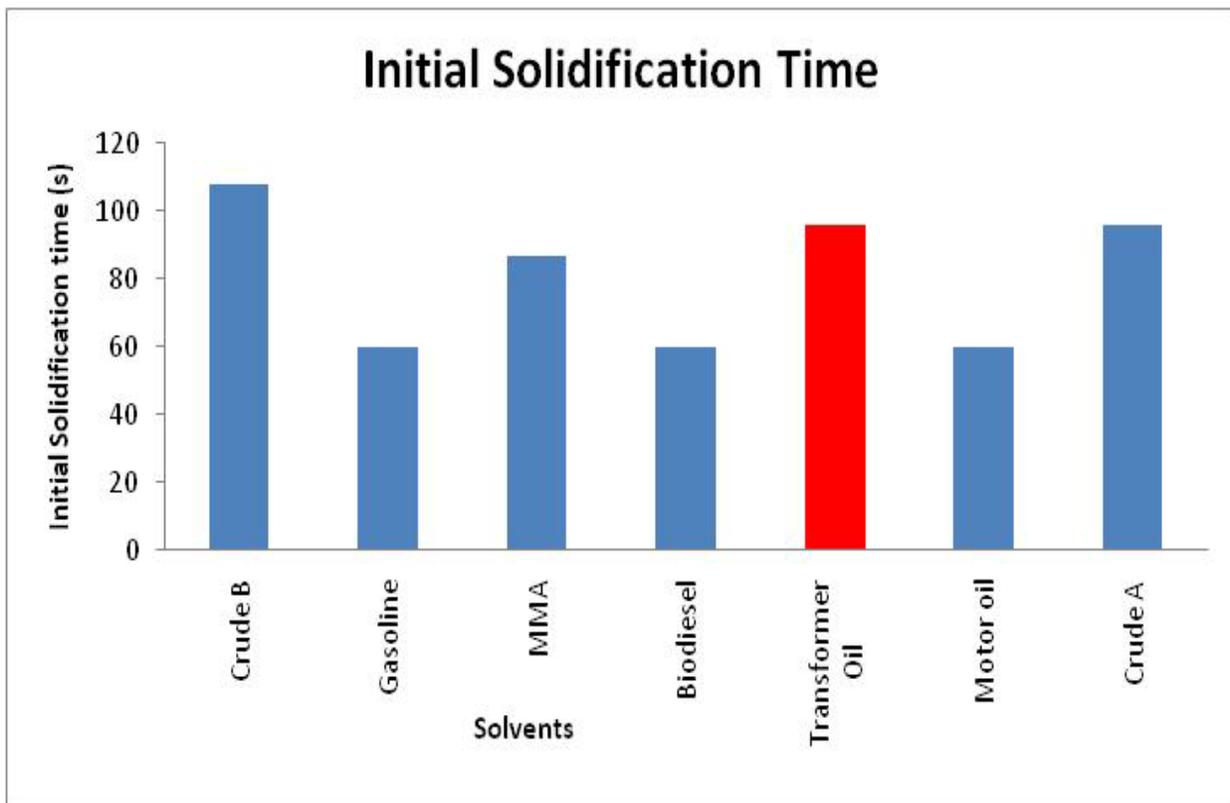


Figure 5.4: Initial solidification time of the various solvents tested

5.5 Conclusions

The effectiveness of a solidifier depends on various factors such as temperature change, amount of solidifier added and the solidification time. The heat of solidification plays a major role in determining the solidifier's effectiveness. The solution calorimeter was able to screen the oils based on energy absorption and determine the effectiveness based on the heat of solidification. The higher the heat of solidification values, the better the integrity of the by-product. For the transformer oil (highly refined mineral oil) with CIAgent®, the heat of solidification value was found to be 3.305-cal/g. This was a relatively high value compared to

the other hydrocarbon liquids that were tested. Higher integrity of the by-product is preferred for its pickup and disposal.

The application ratio of transformer oil to the CIAgent© was 2.5 grams of oil per grams of CIAgent©. The quantity of agent needed to solidify the transformer oil was 40 percent by weight of the oil to be recovered. The solidification time for the initial association of CIAgent© with the transformer oil (shown by the drop in temperature) was found to be 96 seconds. Fast acting products like CIAgent© are beneficial where it could be applied to the perimeter of the oil, forming a solidified barrier to prevent further spreading. Complete solidification occurs in less than an hour to form a more firm and consistent product. Hence these results show that CIAgent© is an efficient and quicker method of solidifying any transformer oil leaks and spills in the electric power substations. The installation of CIAgent© Barrier Boom is an efficient way of reducing the spread of oil in the electric power substations. While it is easier to measure the effectiveness in the laboratory than in the actual field conditions, laboratory tests may not be representative of the actual conditions. Hence the results obtained should only be viewed as representative only and not necessarily reflecting the actual conditions.

CHAPTER 6

Overall Conclusions

The concept of solubility parameter is that “Like seeds like”. Hence the highly cross-linked polymer is most likely to form a swollen gel when the solubility parameters are similar and the interaction parameter is at its minimum. The solidifier, which is a blend of polymers, was solvated in a hydrocarbon liquid of known solubility parameters. From the heats of solidification values obtained using a Solution calorimeter, the solubility parameter of CIAgent was calculated to be **6.706 ± 0.386 hildebrand** with a 95% confidence interval.

The solubility parameter was also calculated from the swelling measurements. It was found that CIAgent had the maximum swelling in Gasoline, indicating that their solubility parameters should be approximately equal. From the plots, the value of the solidifier that corresponds to the highest degree of swelling was found to be **7.251 hildebrands / 14.76 MPa^{1/2}**. Since negative heats of solidification were observed for some solvents, a separate swelling plot was constructed for these solvents. Kerosene had the maximum swelling and the approximate value of the solubility parameter was found to be 7.015 hildebrands.

The drop in temperature after the introduction of the solidifier to the oil was calculated from the pre-period and post period reaction as explained in Section 3.1. This procedure was used for the calculation of the reaction heat. From the heat of solidification, the ease with which the solidifier reacts with the hydrocarbon liquid was determined. The greater the heat value, the faster the reaction and better integrity was achieved. A high integrity by product is preferred as it is more stable and less likely to break down during pick up and disposal. Crudes and gasoline

were found to have the highest heat of reaction with the CIAgent© indicating that the reaction is faster with better by-product integrity.

The application ratio of CIAgent© to the hydrocarbon liquids was **2.4 - 2.5** (in laboratory). The application rate was within the recommended range for solidifiers about 35 - 40 percent. The initial association of CIAgent© with the hydrocarbon liquids was found to be less than 2 minutes for most of the solvents. Solidification of the hydrocarbon liquids increased with time. They tend to form a firm coherent mass over time. The solidification was considered complete within 1 hour. The general observation was that the lighter the oil the greater was the tendency to solidify. The application ratio in field conditions might be lower than the laboratory conditions due to overspray in field conditions.

A range of hydrocarbon liquids for which the CIAgent© works for is found out by using the fractional three dimensional solubility parameters of the solvents and plotting them on a Teas graph as it has a better clarity and was easy to use. A three dimensional graph is drawn so as to determine the polymer – hydrocarbon liquid solubility window. According to the polymer solubility window plot, it was found that CIAgent© should be able to solidify hydrocarbon liquids whose solubility parameter lies in the range of $\delta = 5 - 10$ hildebrand. The only drawback was that most of the solvents that were used were mixtures making it very difficult to estimate the three dimensional solubility parameters of these solvents. Calculations of these parameters by using group contribution methods were very tedious. There were also some limitations on the calculations because of the proprietary nature of the CIAgent.

These calculations proved to be very useful in determining the extent and procedure for the application of CIAgent in oil spill scenarios. The release and absorption of heat during the

solidification process has implications for how the solidifier application should be conducted. This graph can be easily read and accessed by the Regional Response Team (RRT) and the CIAgent© applications on oil spills can be easily understood using the solidification times, application ratio and the solubility data. This data would also be useful for conducting CIAgent© applications for secondary containment in the electric utility substations. Most of the hydrocarbon liquids tested is used in these substations and hence it was necessary that they had to be characterized with CIAgent© to provide an efficient system of containing the spills in EU substations.

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APPENDIX

CIAGENT Material Safety Data Sheet

SECTION I: Manufacturer Information

Product Name: **Cheap Insurance/CIAGENT**

Manufacturer: C.I.Agent Solutions, 11760 Commonwealth Drive, Louisville, KY 40299

Product Information: 800-255-6073

SECTION II: Physical Data

Specific Gravity: 0.94

Physical State: Solid

Solubility in Water: Negligible

Odor: Odorless

SECTION III: Fire and Explosion Hazards

Flash point: N/A

Flammable Limits /% Volume in Air: N/A

Extinguishing Media: Water Fog, Foam, Dry Chemical, CO₂

Special Fire Fighting Procedures and Precautions: Material will not burn unless preheated. Do not enter confined fire space without full bunker gear (helmet with face shield, bunker coats, gloves, and rubber boots), including a positive pressure NIOSH approved self contained breathing apparatus. Cool fire exposed containers with water.

SECTION IV: Reactivity

Stability: Stable

Conditions and Materials to Avoid:

Materials: Avoid contact with strong oxidizing agents.

Conditions: Product contains residual unsaturation, which can undergo exothermic oxidative degradation. Accumulation of product in areas exposed to elevated temperatures for extended periods in air may result in self-heating and autoignition. Guideline is five days at 200° F.

Hazardous Decomposition Products:

At processing temperatures, some degree of thermal degradation will occur, although highly dependent on temperature and environmental conditions, a variety of decomposition products may be present ranging from simple hydrocarbons (such as methane and propane) to toxic irritating gases (carbon monoxide/dioxide, acrolein, halogenated compounds, acids, ketones, aldehydes).

SECTION V Health Information

Eye Contact: Product may cause irritation to the eyes.

Skin Contact: Product may be minimally irritating to the skin.

Inhalation: Product may cause mild irritation to the nose and throat.

Ingestion: Product is generally considered to have a low order of acute oral toxicity.

Signs and Symptoms: Irritation as noted above.

Aggravated Medical Conditions: Preexisting eye, skin, and respiratory disorders may be aggravated by exposure to this product.