CLEAN WATER

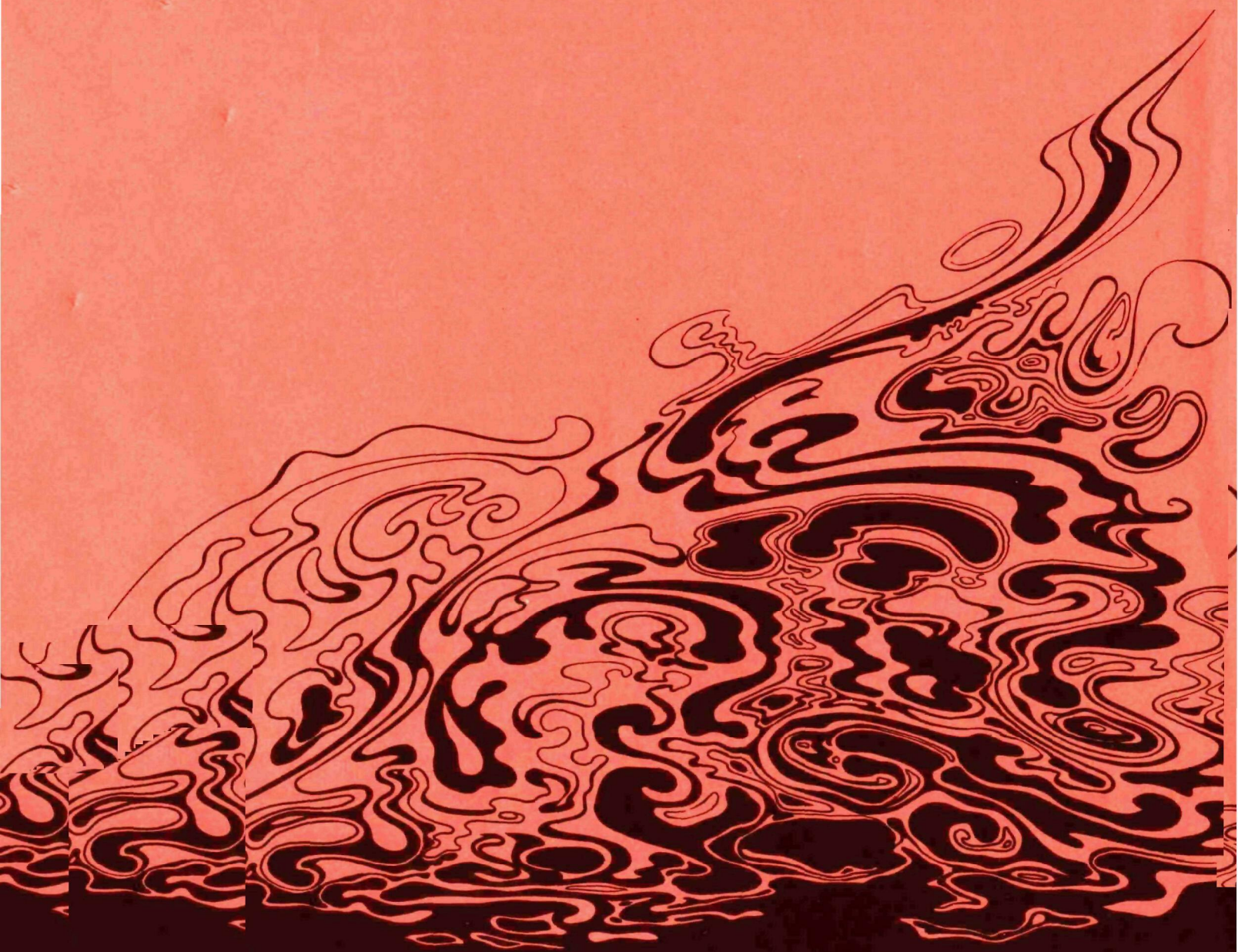# GELLING CRUDE OILS TO
REDUCE MARINE POLLUTION
FROM TANKER OIL SPILLS

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GELLING CRUDE OILS TO REDUCE MARINE
POLLUTION FROM TANKER OIL SPILLS

By

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for the

WATER QUALITY OFFICE

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ABSTRACT

It was expected that techniques similar to those used in the oil well
service industry and certain petroleum end-product uses could produce
gelled crude oil in a damaged tanker, thereby precluding flow of free
oil into the sea.

Laboratory evaluations of petroleum solidification, or gelling, techniques
and systems were conducted utilizing foreign and domestic crude oils
over a wide range of gravities and gelling agent proportions and concen-
trations. Methods for measuring gel strength were evaluated and the
most pertinent utilized in the screening of candidate gels. Concepts for
dispensing and mixing the gel agents were devised and tests were
conducted to verify the ability to form laboratory-quality gels in up to
1,000-gallon volumes.

The testing identified an amine/isocyanate combination as producing the
strongest gels, over the widest range of crude oil types, and the ability
to form those gels in quantity with two application systems suitable for
shipboard use. The results suggest that the gels would stop flow through
a tank rupture under only a limited range of potential conditions, but
that the flow rate might be significantly less than that of free oil
resulting in less pollution over a given time span. The results also show
that the gelled oil tends to remain floating in lumps at the water surface
and will not permit a slick to be formed. The ability of the gels to be
removed from tanks using conventional pumping apparatus was also
demonstrated.

Economics of applying the gelling technique in operation situations were
explored and system performance was related to historic spill clean-up
costs indicating the economic feasibility of the concept.

This report was submitted in fulfillment of Contract 14-12-497 under
the sponsorship of the Federal Water Quality Administration.

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CONCLUSIONS

A system for gelling crude oil has been developed which can result in a reduction in the marine pollution caused by the accidental discharge of crude oil from a damaged tanker. Both the chemical and mechanical aspects of the concept are feasible. However, effectiveness of the system, in terms of pollution reduction, is a function of the time lapse to initiate gelling, rupture size and rupture location in relation to the waterline. Complete stoppage of cargo flow through the leak would be accomplished for only a limited range of expected shipboard distress conditions. Further reduction in flow of the gelled cargo, over a more realistic range of potential operational conditions, would require a significantly stronger gel.

When pressure and hole-size conditions exist sufficient to cause the gelled oil to flow, the gelled product will leave the ship at a slower rate and the total loss to the sea over a given time span would be less than for ungelled oil. The gelled oil that does flow into water floats, tends to remain in lumps and does not form a slick.

The range of domestic and foreign crude oils tested in this program can be gelled using a 0.75:1.00 to 1.50:1.00 equivalent weight ratio combination of amine and isocyanate in concentrations of 5 percent of the crude oil gelled. The chemicals are available in quantity and can be handled and stored without elaborate or unusual precautions.

The optimum gels produced with this system can be expected to exhibit static shear strengths in the range of 12,000 to 25,000 dynes per square centimeter, as determined by penetrometer, extrusion rheometer, and static head tests. The strength variation is due primarily to the variation in composition of crude oil. The gelled oils produced can be unloaded from the tanker by using conventional positive displacement pumps.

The gels produced are the strongest possible using five percent of a system which has only a physical bonding attraction for the crude oil. A gel produced by chemical bonding of the crude oil may be possible, but the state-of-the-art does not permit a speculation of the composition, characteristics or cost of such a system at the present time.

The program demonstrated that the gels can be produced in 1,000-gallon quantities and of a quality equal to those produced in the laboratory using two different dispensing and mixing concepts. Such large volume production can be achieved using a pumped recirculation system with or without air added, or with a system of multiple nozzle probes traversing the tank to be gelled.

The chemical storage and dispensing equipment can be designed for shipboard installations or in appropriate size and weight modules to permit helicopter or surface transport modes to the point of need.

The cost of having the chemicals and equipment for the gel system installed on a ship for immediate use is estimated at 1.13 mils per ton-mile. This represents an increase of four percent in average crude oil shipping cost. The cost of having a gel system capable of being transported by helicopter or surface vessel to the point of need, exclusive of the transport costs, is .002 mils per ton-mile of current United States coastal oil transport. This represents a 0.18-percent increase in average shipping cost.

To economically justify the cost of chemicals and equipment in relation to historic spill cleanup costs, the total transportable system assumed as an economic model must be capable of precluding 23,000 barrels of oil loss to the sea annually. Each shipboard-installed system must be capable of precluding 1,500 barrels of loss annually.

RECOMMENDATIONS

On the basis of the conclusions, the following recommendations are offered. The action and research of the nature herein proposed could materially reduce the marine pollution caused by accidental oil spills by tankers.

1. The gel system devised should not be implemented in the waterborne oil transport industry at this time.

2. Further work to develop a stronger or better gel should not be undertaken until a more precise definition is made of the gel strength and flow properties required by the operational environment. Additional research should be undertaken to determine the conditions under which any gel would be expected to perform. This should include an analysis of past disasters causing marine pollution, with particular emphasis on the ship condition, as well as the pollution aspects. The frequency and severity of the disaster and the nature of, and increase in, damage during the period following the disaster should be given primary consideration. A definition of the gel characteristics necessary to meet various limits within the range of these conditions, together with detailed cost-benefit analysis, should be made. The specific output of this work must be a determination of the operational conditions the gel must satisfy and the resulting gel strength necessary to make implementation of the concept feasible.

3. If a stronger gel is required to justify implementation, additional research should be performed to develop a gel which will meet the pre-identified requirements. A new approach directed toward chemical (rather than physical) bonding should be initiated as part of such work.

4. Large-scale tests should be made to fully develop the existing or improved gelling method and equipment necessary to implement the working concept. A full analysis of the flow and strength characteristics of the gel under modeled operational conditions must also be completed.

SECTION 1

INTRODUCTION

Scope

This program identified and evaluated the concept of gelling systems for crude oil as they related to the problem of accidental spills from tankers. The scope did not include other marine oil pollution problems, such as offshore production, sunken tankers, natural seepage, or the overboard discharge of tank washings and dirty ballast water.

Purpose

The program was designed to establish and develop the basis for a working system which will cause crude oil to be thickened, or gelled, sufficiently to prevent its escape from a damaged tanker. The gelling materials, when introduced into leaking tanks, were to cause gelling of the oil sufficient to stop its flow from the tanker. System development required the identification and evaluation of gelling agents, methods to introduce the agents into the oil, testing of the system on volumes of oil significantly larger than laboratory scale to verify the design basis of a large-scale working system, and cost or cost estimates of the concept.

Background

Accidental oil discharges into the seas and waterways are a source of pollution which is a hazard to marine and bird life. This pollution also may be an actual, or potential, health hazard to man as well as a threat to the natural environment that augments his recreation and aesthetic enjoyment. Appendix A, Shipping Characteristics, gives more details on pollution possibilities.

Petroleum and petroleum products accounted for 37 percent of the 1,272,900 tons of United States waterborne commerce in 1965.[1] Crude oil imports are being received in tankers at the rate of 1,380,000 barrels per day at United States docks.[2]

Recent oil spills from waterborne transport of crude oil have demonstrated a need for prevention of these pollution sources. The Torrey Canyon grounding off Lands End, England in 1967, and the breakup of the Ocean Eagle near San Juan, Puerto Rico in 1968 are but two examples of many such oil spills from tankers. These accidental crude oil spills may be caused by collision, strandings, structural failure, fire and explosion.

After considering several alternate approaches directed at solving or reducing oil spill pollution, it was concluded that the optimum point in

the chain of events at which to attack the problem is when the oil is still in the tanker. At this point, it is possible to eliminate the pollution problem and also deal with the oil most readily. The wave and current action has not yet spread and dispersed the oil; thus, treating, gathering or disposing of the oil would be greatly reduced when accomplished in the tanker.

The oil field service companies routinely gel large volumes of crude oil in their field servicing operations. These companies own mobile gelling units which mix chemical agents to create the gels, often in large tanks of crude oil.

Based on this experience, it was proposed that the spillage of oil from a distressed tanker could be prevented by rapidly gelling the oil in a compartment in the ship. The formed gel would block the flow of oil from, and the flow of water into, the compartment. It was postulated that such a gel could be made using a relatively small gelling agent concentration. Since only the ruptured compartment (or those in imminent danger of rupture) must be treated, the gelling agent and effort required could be small when compared to materials and effort required to treat the oil after it had been spilled.

Program Description and Approach

The program reported herein was performed in two consecutive phases. The objectives of the first phase, or Basic Contract, was to identify and develop in the laboratory, a process or chemical agent that would produce a suitable gel utilizing the largest number of crude oil types. The second phase, or Option I, objective was to devise the mechanical system necessary to accomplish gellation and to demonstrate the ability of the system to gel a selected crude oil in larger-than-laboratory volumes (1,000 gallons).

Prior to actual development of gelling materials, it was necessary to conduct a literature search and a survey of in-house experience with materials and methods used. This investigation insured that all potential processes were considered and that the best materials could be selected for screening.

It was also necessary to search the literature concerning the shipping of oil and ship disasters involving spillage of oil. Once the nature and occurrence of the problem and its limits were determined, the operational criteria which the gelled crude oil must meet was described. The experimental procedure to be used in the laboratory for measuring the various processes' performance against the criteria was then defined.

The laboratory evaluation and development of the gelling materials proceeded with the wide screening of candidate materials in a single crude oil. After the candidate gelling materials were screened, the most promising materials were further tested in various typical crude oils shipped in ocean-going tankers.

Once the best gelling materials were determined in the laboratory, tests were conducted to demonstrate their ability to be formed in significantly larger volumes of oil. As part of these 1,000-gallon tests, evaluations were made of various dispensing and mixing methods devised for applying the gel constituents to the larger volumes of oil.

SECTION 2

GELLATION TECHNOLOGY

Gellation Systems

The literature survey revealed that none of the reports contained information directly pertaining to the gellation or solidification of crude oils; however, several detailed reports were obtained containing data concerning the solidification of fuel oils, particularly jet fuel. A comprehensive listing of reports of this type is given in the Bibliography. Related reports and information are found under listings such as hydrocarbons, solid fuels, aircraft fires, frac-oils, oil spillage/recovery, gels, and jet engine fuels. A few indirect listings are urea, polymers, urethanes, amides, metal stearates and soaps.

Gel Definition

The solid products derived from the action of various agents on liquids have been described in various ways. The term "gel" is entirely appropriate, but the diverse macroproperties of a "gel" make the description a broad one. A more limiting description is that the liquid has been "solidified." In any instance, the product desired is one that no longer flows under low to medium forces.

The phenomena which instigate properties of a gel claim an equally wide variety of descriptions. But in all instances, the material which is added to a liquid (in this case, crude oil),in some manner limits the movement or flow of the liquid. An agent which produces a gel also produces a colloid; i.e., finely divided particles of one material suspended in another material. The suspended particles may be insoluble liquid particles or solid particles but, in order to produce a gel, the particles must be attracted to one another or held together in order to form an immobile network. With the concept of a colloid in mind, we may define a few categories in which the many materials tested for gelling ability may be placed. These categories are distinguished by the method by which the gelling agent is introduced into the medium to be gelled.

Gel Categories

All the materials selected for gelling crude oils may be fitted into two categories; those which produce gels in situ by the reaction of two reagents and those which are dispersed physically into the crude oils, swell and cause a thickening of the oil.

In situ gels are formed when two or more materials which are dispersible in a medium to be gelled are added to that medium. These materials react

to form a product which has limited solubility. If the colloidal particles formed, because of the limited solubility of the reaction product, have sufficient attraction for one another, then a gel is produced. The soap gel is one example. This is a popular and well explored system used to gel many refined aliphatic hydrocarbons such as jet fuel. The mechanism involves reacting a fatty acid with about 50-percent caustic soda to produce a soap. The insoluble soap particles, in turn, become suspended to form a colloid. These colloidal particles become attracted to one another because of the polar properties of the soap, thus producing a network and a gel. The soap is also capable of acting as an emulsifying agent between the water (from the caustic soda) and the hydrocarbon, yielding an emulsion gel in which the suspended particles are water, and attraction is again gained through polarity.

Another type of in situ gel is the amine/isocyanate gel. Both the soluble amine and isocyanate are added to the medium and the following reaction yields a urea with limited solubility. A colloid is again produced but the attractive forces needed to form an immobile network are acquired through hydrogen bonding which we shall see has significant affects on the strength of the gelled system.

A cooling gel is produced by dissolving the gelling agent in the heated medium. Upon cooling, the dissolved gelling agent becomes more insoluble and tends to precipitate, producing suspended particles needed for a gel. Obviously, this type of gel is more difficult to produce, due to the necessity of heating and cooling the gelled medium. An example of a cooling gel is the metal salts such as aluminum stearate or sodium stearate. These materials are essentially soaps and produce the same gels as the soaps that are reacted in situ.

A swelling gel is produced simply by dissolving the gelling agent into the medium. Some metal salts such as aluminum napthenate will produce a gel by this technique, but the process is slow, 24 to 72 hours, and better results are usually obtained by heating.

Polymeric gel is obtained by the polar attraction or hydrogen bonding between smaller molecules, or by chemical bonding, resulting in a polymer. Usually, the gels produced by polymers are viscoelastic due to the high molecular weights and long chain configurations. Also, a good compatibility with a gelled medium is difficult to obtain. Either the polymer precipitates from the medium or the medium is insufficiently bound, resulting in a weak gel. A polymeric gel may be produced either in situ or by cooling or swelling.

Constituents

The literature search revealed several materials with a history of gelling hydrocarbons, such as jet fuels and some materials which were used for "thickening" crude oil, but it could only be speculated that these materials could "solidify" crude oils. Some of these materials include:

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Gel In Situ

1. Caustic + fatty acid $\longrightarrow$ soap + water
    $$NaOH + RCOOH \longrightarrow RCOO^- \; Na^+ + HOH$$

2. Amine + isocyanate $\longrightarrow$ urea
    $$RNH_2 + R'NCO \longrightarrow R\text{-}NHCONH\text{-}R'$$

3. Acid chloride + amine $\longrightarrow$ amide + hydrochloric acid
    $$RCOCl + R'NH_2 \longrightarrow RCONHR' + HCl$$

Gel By Other Methods

1. Metal soaps
2. Polyamides
3. Polar inorganic materials
4. Various proprietary reagents

Gel Requirements

A survey of ship failures and associated situations which arise revealed that, in order for the oil aboard a tanker to be advantageously solidified, the gelled oil should:

1. Have a specific gravity less than that of seawater
    (to offer the tanker additional buoyancy in the event
    it should begin to sink; also, should any gelled oil
    escape, it will remain on the surface for easy recovery).

2. Be oil insoluble (otherwise, the solubilizing effect
    of the ungelled crude oil will reduce the structural
    strength).

3. Be water insoluble (should any seawater penetrate
    into the tanker, the structural strength of the gelled
    oil will again be protected).

4. Have low percentage of gelling agent (to reduce the
    cost, storage area needed for the gelling agent and
    time needed to disperse the agent into the oil).

5. Be obtained by fast-acting gelling agents (the quicker
    the oil is gelled, the less will be spilled).

6. Be produced from easy-to-handle gelling agents.

7. Have high structural strength (the gelled oil should
    exhibit sufficient strength to seal the rupture).

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8. Have low toxicity to handling personnel and possibly be nonpoisonous to marine life.

9. Use gelling agents that remain stable after long storage periods (it is possible that the gelling agent will be incorporated into a permanent fixture for all tankers).

10. Be noncorrosive to the tanker.

11. Be removable from the tanker after docking.

Measuring Gel Strength

All of the gel requirements may be easily defined by standard test methods except for the structural strength of the gelled crude oil.

In fact, the most perplexing issue raised in the conduct of the oil gel program has been that surrounding the measurement of gel strength. In attempting to answer the questions raised; i.e., how should a gel's strength be measured and which possible measures are meaningful, it was discovered that no standard or available method existed which could be directly correlated to actual flow, such as that resulting from a rupture in an oil tanker.

In reviewing available standard methods of measuring viscosities and physical strengths, grease technology contained the most useful information pertaining to a gel or a near solid material. From this technology, several basic methods were considered for measurement of the physical properties of the gels.

The rotary viscosimeter is suitable for fast relative measurements of lower viscosity materials, but gives little insight into yield points or stresses, or varying shear rates.

Measurement by penetrometer is a method by which a cone is allowed, through free fall, to penetrate a solid gel until it comes to rest. The strength of the gel is the weight of the cone divided by the total wetted area of the cone. A correction is made for buoyancy. These strengths obtained from penetrometer readings should be a good indication of a gel's resistance to initial flow (the shear rate approaches zero) but have limited usefulness as the shear rate increases. Appendix B, Penetrometer Use, describes this method.

A rheogram is a graph relating stress and viscosity to shear rate by extruding the material under pressure from a capillary tube using a Burrell-Severs or Ruska apparatus. The process satisfies the formula:

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$$T_w = K\left(\Gamma\right)^n + T_0$$

T_w = shear stress

K = apparent viscosity

Γ = shear rate

n = exponent varying with type of fluid involved

T_0 = intercept at zero shear rate

Where $\left(\Gamma\right)$ = 0, the strength of the gel is the yield shear stress. This figure is obtained by extrapolating data from the rheogram back to zero. Theoretically, this number should equal the penetrometer reading. Useful data concerning pumping resistance is obtained by considering higher shear rates.

Many other methods exist but are only variations of one of the basic methods described. For example, the "strand break-off" method, whereby grease or gel is extruded from a capillary until the strand breaks off, is similar to the rheometer test and produces a tensile stress yield figure. In each of these tests, the magnitude and exact meaning of the results vary considerably.

Investigation of these methods reveals that each method is making one of two types of measurements - static (yield strength, tensile strength), or dynamic (viscosity).

For a gel that will flow within the range of operational conditions to which it is subjected, both the static and dynamic properties are important. Since it is probable that the gelled oil creeps under low pressures before the yield point, the relationship and distinction between static and dynamic is not precise.

An excellent paper presented by Dr. D. W. Criddle and J. L. Dreher[3] at the NLGI 26th Annual Meeting, entitled "Yield Points of Lubricating Grease, " provides valuable insight into this relationship. In this paper, several methods of measuring yield points were studied. From this study, it was concluded that the yield point of a grease is dependent on three variables:

1.   Rate of deformation.

2.   Type of deformation.

3.   Work history of the grease.

It was concluded that the yield point is highly variable with the method of measurement; value differed from 40 to 100 percent. Criddle and Dreher also state that "Because the Bingham yield point depends upon the range

of shear rates chosen to obtain a best fit of the equation with experimental data, we do not consider the yield point to be fundamentally significant. Therefore, we are omitting Bingham yield points in this comparison." (In reference to the Buckingham Equation.) They also conclude that "... greases have many yield points, depending upon the type and rate of deformation. Therefore, the conditions under which yield points are obtained should be reported with the yield values."

The Bingham yield point plays an important part in the resistance to flow of gelled oil. Thus, a method is needed to identify the yield point-flow relationship under the operational conditions of flow through an orifice (hole) and any correlation which may exist with yield points derived from static and other dynamic techniques.

As mentioned above, the correlation between the various existing methods of measuring yield points is not good but, at least, the methods of measuring do exist. In relation to outflow of gelled oil through a hole, the link between the rate of overflow and strength is also currently undefined.

From the equation

$$T_w = K(\Gamma)^n + T_0$$

T_w should be relatable to the conditions existing under a pressure differential produced by a hole in a vessel. If $\Gamma = 0$ (zero shear rate), then the stress under consideration is T_0, or less. Also, Γ vary considerably with the method of measurement. For example, the Burrell-Severs apparatus uses a long, narrow capillary tube with a high length/diameter ratio, which is a considerable extreme from a hole in a tank which will have a low length (hull thickness)/diameter ratio. Also, the shape of the hole affects Γ. Although a correlation may exist without empirical data from a device simulating operational conditions to show the correlation, values obtained through existing techniques have little meaning in relation to operational conditions and resulting flow characteristics.

To best fit the requirements of this program, it was decided that the penetrometer method would be used to test the relative strengths of the gels produced. If strength in relation to large-scale or shipboard conditions is required, it will be necessary to develop a method for simulating the flow of oil from a rupture. The experimental data from the test method should result in an empirical relationship which may permit extrapolation to larger orders of magnitude.

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SECTION 3

LABORATORY EVALUATION OF GELS

All possible gelling materials resulting from the literature survey were
screened initially by application to a single crude oil. The strength, as
measured by the penetrometer, was the sole criteria for continued testing.
Any material selected as a result of the initial screening was subjected to
testing on all of the requirements. Table I, Measurement Methods for Gel
Criteria, lists the measurement methods used on the gels produced during
this program.

TABLE I. MEASUREMENT METHODS FOR GEL CRITERIA

Criteria	Method of Measure
Specific gravity	Not measured. Crude oil plus gelling agents in percentages considered will in no way be greater than sea water.
Oil insoluble	Gelled oil will be submerged in ungelled oil and tested after one month.
Water insoluble	Material will be floated in water for one month.
Percentage gelling agent	Plots of gel strength versus percent will be obtained.
Structural strength	Penetrometer ASTM D-217.
Gel time	Time to reach two thirds maximum strength as measured by penetrometer.

Initial Screening

All candidates for gelling were tested in 100-gram quantities of crude oil.
Any material showing possibility was examined at a higher or lower con-
centration and/or at varying part weight ratios in the case of multicom-
ponent systems. Appendix C, Chemicals and Suppliers, lists the source
of materials tested.

Soap gels at 10 percent prepared from fatty acids ranging from C_{12} to C_{20}
and sodium hydroxide were reacted in situ in Clearfork crude oil. These
materials were known for their ability to gel jet fuels, but failed to perform

satisfactorily in crude oil. Dispersants were added to enhance the reaction and resulted in some improvement but, still there was insufficient gel strength. It was felt that the proper solubility range was obtained at about C_{16}. Dicarboxylic acids produced similar results. These materials were difficult to work with because they were solids at room temperature. Appendix D, Soap Gel Screening Data, lists the data obtained from these screening tests.

Amides from octanoyl chloride and several of the fatty amines were produced in situ and a good increase in viscosity occurred, but still with unsuitable strength. The by-product, hydrochloric acid, made this reaction undesirable because of the corrosion to the ship.

Metal soaps such as aluminum stearate, calcium stearate and aluminum octoate were hard to mix into the oils and heating was used. Stringy viscoelastic gels formed but, due to the nature of the viscoelastic effect, these gels had no structural strength. See Appendix E, Swelling Gel Screening Data, for data on these tests.

Initial testing with the isocyanates and amines proved to be encouraging. Many of the commercially available isocyanates and diisocyanates were reacted with fatty amines and diamines. Those contained in the remainder of this report and hexamethylene diisocyanate ($NCO(CH_2)_6NCO$) showed good results. Hexamethylene diisocyanate was discontinued because of its high toxicity. Of the diamines tested, only those with long chain lengths, such as Jeffamine 400, produced ureas soluble enough in the crude oils. Thus, the combination of aromatic diisocyanates and fatty amines produced more solid gels than any other combination of materials. Appendix F, Isocyanate/Amine Gel Screening Data, lists the results of these screening tests.

Fumed silicas were incorporated into the crude oil and then various polar additives (isopropanol, glycerine, etc.) were incorporated to complete the gel network. Low strength gels were obtained at 10-percent levels. Because of high cost and difficult gelling technique, these systems were not feasible.

The fact that the gelling agents must react fast and be easily maneuvered, placed more emphasis on the in situ type of gel due to the relatively complicated aspects of obtaining a gel by the cooling or swelling methods. A gel should be obtainable with a minimum amount of mixing and at ambient temperatures. Although some initial testing was performed on gels of the swelling or cooling types, this information was considered as a secondary interest, since no strong gels or fast gels were obtained by these methods.

With emphasis placed on the in situ gel, the urea gelling system proved to be far superior. Many good gels were obtained with this system. Only fair to poor gels were obtained with the other in situ reactions.

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The following conclusions may be deduced from the data gathered during initial screening:

1. Many materials tested resulted in an increase in viscosity, but no materials (except those participating in the amine/isocyanate reaction to yield a urea) produced "solid" gels.

2. There is a relationship between the chemical constitution of the gelling agent and the type of gels produced. Molecules containing alkyl groups in the chain length ranges of C_6 to C_{18} demonstrated the proper solubilities necessary for the gel condition in both the soap and urea type gels.

3. Of all the isocyanates tested, toluene diisocyanate proved to be the most promising candidate because of low cost, ready availability and performance as a gelling component.

4. Of the amines tested, the fatty amines were the most promising and were readily available in the chain lengths from C_6 to C_{18}.

The following combinations of amines and isocyanates produced gels worthy of continued testing:

Armeen L-11 and TDI 80/20

Armeen C and MT-40

Jeffamine 400 and Octadecyl Isocyanate

Armeen L-15 and TDI 80/20

Armeen O and TDI 80/20

Armeen C and TDI 80/20

Detail Screening Parameters

The materials selected from the initial screening were subjected to the following test scheme to develop necessary comparative data:

1. The ratio of the two components of the gelling agents were varied and plotted against the gel strength to determine an optimum ratio.

2. The percentage of total gelling agent (both parts) was varied from one to five percent and plotted against gel strength.

3. Gelled oil was submerged in salt water and in ungelled oil to test gel retention.

4. Oil was gelled and tested at 32^0F and 100^0F to determine strength and speed of reaction.

5. Various methods of mixing the gelling agents into the crude oils were explored to identify characteristics and requirements.

6. Literature search and/or laboratory tests were conducted to obtain more detailed physical and chemical properties of each gelling agent.

7. Costs in terms of cents (of gelling agents) per gallon (of crude oil) were derived.

8. Strength tests relative to agent storage time were developed and conducted.

Classification of Crude Oils

Crude oils to be tested were received from various parts of the world. Each crude proved to have its own reaction toward the gelling agents. Gels produced ranged from pseudoplastic gels to viscoelastic.

Due to the wide variety of combinations of materials composing a crude oil (paraffinic and asphaltic materials as well as various inorganic compounds), an exact description was impractical. The description used here is the Bureau of Mines system by which crude oils are classified according to the API gravity of two key distillation fractions. First, the crude oil was distilled at atmospheric pressure, collecting fractions at regular intervals, usually 25^0C. A key fraction was collected from 250^0C to 275^0C (kerosene range). Then the distillation was continued (after cooling) at 40 mm mercury (vacuum). Fractions were again collected and key fraction two was collected from 275^0C to 300^0C. From the API gravity of these two fractions, the crude was classified as follows:

	Key Fraction 1	Key Fraction 2
Paraffin	40^0 or lighter	30^0 or lighter
Paraffin - intermediate	40^0 or lighter	20^0 to 30^0
Intermediate - paraffin	33^0 to 40^0	30^0 or lighter

	Key Fraction 1	Key Fraction 2
Intermediate	33^0 to 40^0	20^0 to 30^0
Intermediate - naphthene	33^0 to 40^0	20^0 or heavier
Naphthene - intermediate	33^0 or heavier	20^0 or heavier
Naphthene	33^0 or heavier	20^0 or heavier
Paraffin naphthene	40^0 or lighter	20^0 or heavier
Naphthene - paraffin	33^0 or heavier	30^0 or lighter

The API gravities were measured with standard API Baume hydrometers. These values were converted to specific gravity by the equation:

$$API = \frac{141.5}{sp\ gr\ 60^0/60^0\ F} - 131.5$$

Viscosities were measured from a Fann Model 35 Viscosimeter and recorded in centipoises. These values were converted by use of a suitable chart to Saybolt University Seconds (SSU) for reader convenience. This information is contained in Table II, Crude Oil Classification.

Gel Properties and Mechanics

Table III, Physical Properties of Gelling Materials, lists most of the common properties of the prime gelling agents.

All of the isocyanates are liquid at reasonable temperatures and could be used without heating in most instances. Some of the amines, Armeen O in particular, have rather high melting points and would require heating to the liquid state before application to the crude oil in cold climates. The isocyanates are slightly toxic as a result of the NCO group attached. However, adequate protection to operating personnel can be assured with reasonable care and standard chemical handling equipment.

The amines are not particularly toxic, their principal hazard being the slight caustic nature of the chemical. The flammability of all of these chemicals is less than the crude oils and add no additional fire hazard in transporting or storage; therefore, the shipboard storage and use of any of these chemicals can be safely accomplished, using the reasonable care required of any chemical agents.

TABLE II. CRUDE OIL CLASSIFICATION

| Crudes	Source	Viscosity Fan cps	Viscosity SSU	API Gravity	Initial Boiling Point - °C	Volume (ml) to 100°C	Volume (ml) 100°C	Volume (ml) 150°C	Volume (ml) 200°C	Volume (ml) 250°C	API Gravity 250°C	Volume (ml) to 275°C 40 mm Vacuum	Volume of Fraction 275°C	API Gravity 275°C - 300°C	Volume (ml) of Residue	Bureau of Mines Classification
Clearfork	Rankin, Texas	17.0	90	34.0	43	50	125	75	65	50	37.0	175	70	26.0	350	Intermediate
Westbrook	Snyder, Texas	15.0	80	24.5	34	50	130	95	90	70	35.0	150	100	17.0	300	Intermediate Napthene
Howard Glasscock	Snyder, Texas	13.0	68	32.0	43	50	120	95	105	60	36.5	200	80	23.5	290	Intermediate
Sweden Crude	Sun Oil Co.	2.3	14	47.0	38	95	180	170	215	75	37.0	170	40	20.5	55	Intermediate
Sun B Mix	Sun Oil Co.	4.0	43	39.0	43	40	120	150	150	115	37.0	250	60	23.5	115	Intermediate
Mirando-RHC Mix	Sun Oil Co.	20.0	100	23.0	115	--	--	30	200	130	27.5	425	30	15.6	185	Naphene Intermediate
Grade A, 469 Mix	Sun Oil Co.	57.0	300	23.5	54	--	40	40	70	85	30.5	375	60	21.0	33	Napthene Intermediate
Solvent Mix	Sun Oil Co.	--	--	48.0	43	125	170	130	100	60	41.0	190	50	28.5	175	Paraffin Intermediate
Lybian	Standard Oil of California	47.0	250	28.5												
Arabian Heavy	Standard Oil of California	25.5	166	28.5												
Arabian Light	Standard Oil of California	8.0	60	33.5												
Devonian	Atlantic-Richfield	2.5	35	46.0												
Cairo	Phillips Petroleum Co.	10.0	62	35.0												
Alaskan	Atlantic-Richfield	4.5	45	38.0												
Bachaquero	Atlantic-Richfield	300.0	200	17.0												

TABLE III. PHYSICAL PROPERTIES OF GELLING MATERIALS

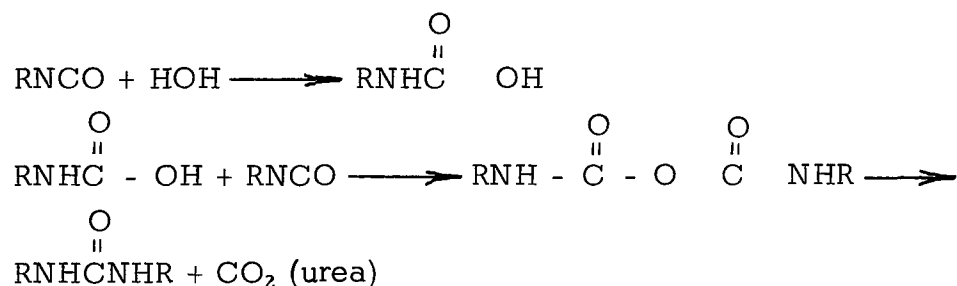| Material (Manufacturer)	Chemical Composition	Molecular Weight	Melting Point	Boiling Point	Flash Point	Single Oral Lethal Dose (Rats)(g/kg)	Cost/ lb
TDI 80/20	80% 2.4 Toluene 20% 2.6 Toluene	177	11.5- 13.5^{0}C	120/ 10 mm	132^{0}C open cup	4.9 - 6.7	$ .45
Tonco 90 (Upjohn)	Octadecyl Isocyanate $CH_3(CH_2)_{17}NCO$	295	10 - 20^{0}C	170/ 2 mm	185^{0}C open cup	30.0	2.25
MT-40 (Mobay)	Aromatic Isocyanate				295^{0}F		.31
Armeen C (Armour)	50% C_{12} 18% C_{14} 8% C_{16} } diamine 8% C_8 16% Other	223	24^{0}C		240^{0}F open cup		.49
Armeen O (Armour)	76% C_{18} 5% C_{16} } diamine 5% C_{18} 14% Other	267	+74^{0}F		320^{0}F open cup		.38
Armeen L-11 (Armour)	Primarily $CH_3(CH_2)_{10}NH_2$	170	-20^{0}F				.58
Armeen L-15 (Armour)	Primarily $CH_3(CH_2)_{14}NH_2$	226	+50^{0}F				.52
Jeffamine 400 (Jefferson)	$NH_2CH(CH_3)CH_2-$ $[OCH_2CH(CH_3)]_{5.6} -$ NH_2	400	-40^{0}F		347^{0}F open cup	0.75	.65

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Storage and Chemical Strength

It is anticipated that large quantities of gelling agents may be stored either aboard tankers or at some convenient location for rapid access in the event a rupture in a tanker occurs. Since large quantities of materials may be stored, economical use of these materials is essential.

The first step to preservation is prevention from contact with reactive materials. The amines react as a base. The most common deterioration is their reaction with carbonic acid (carbon dioxide and water vapor found in the air) to form carbonates:

$$RNH_2 + H_2CO_3 \longrightarrow RNH_3^+ \; HCO_3$$
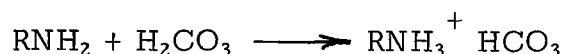
This reaction is usually reversible with heat. Also, the amines should be stored in containers coated with an inert lining as recommended by the manufacturer.

The isocyanates are more reactive, particularly toward water.

$$RNCO + HOH \longrightarrow RNH\overset{\overset{O}{\|}}{C} \; OH$$

$$RNH\overset{\overset{O}{\|}}{C} - OH + RNCO \longrightarrow RNH - \overset{\overset{O}{\|}}{C} - O \; \overset{\overset{O}{\|}}{C} \; NHR \longrightarrow$$

$$RNH\overset{\overset{O}{\|}}{C}NHR + CO_2 \; (urea)$$

The urea is easily detected in the isocyanate by cloudiness. This is not to be confused with the crystallization of some isocyanates, which can be removed by heating, and does not interfere with its chemical reactivity. The production of the urea is not reversible.

The isocyanate should also be stored in a lined container. In the event the containers are opened and exposed to the atmosphere, purging with an inert gas such as nitrogen is recommended, depending on the exposure. Storage in a cool area is always recommended. These materials are not harmed by freezing but, if frozen, must be melted before using.

If sampling is to be undertaken periodically, then it is advisable to design storage facilities for minimum exposure during sampling. Direction for testing these chemicals are included in Appendic G, Stability in Storage Tests for Gel Constituents. The manufacturer will supply information for testing specific materials.

Gel Mechanics

During laboratory testing of the various classes of gelling agents, the amine/isocyanate in situ reaction produces far superior gels than any

other system tested. Since the most promising reagents are of insufficient functionality to produce polymers (both reagents must have a functionality of two or greater), there are other forces holding the molecules together. These other forces are intermolecular forces of which hydrogen bonding is the most significant.

Ordinary chemical bonds have a strength of 50 to 100 kcal, compared to about 5 kcal, for electrostatic bonds such as hydrogen bonds. This explains the thixotropic effects of an electrostatically bonded network. Shear or mixing supplies sufficient energy to disorder these weaker bonds, due to the characteristics of the hydrogen bond. After mixing is stopped, the bonds recover and the gel is restored. If this is true, then we would expect that the greater a molecule's ability to form hydrogen bonds, the greater its ability to form gel networks. This is found to be true with certain limitations.
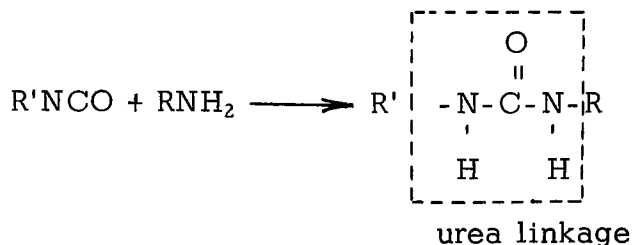
Which molecules are capable of forming hydrogen bonds? Only the elements O, N, and F are electronegative enough to produce hydrogen bonds of any significant strength. The hydrogen atom must be both chemically bonded and electrostatically bonded to these elements. Therefore, molecules which contain these elements may participate in hydrogen bonding if the geometric arrangement of the molecule permits. The "molar cohesive energy"[4] (intermolecular forces) of the many chemical groupings which were found to be of interest in the gellation of crude oil. These include:

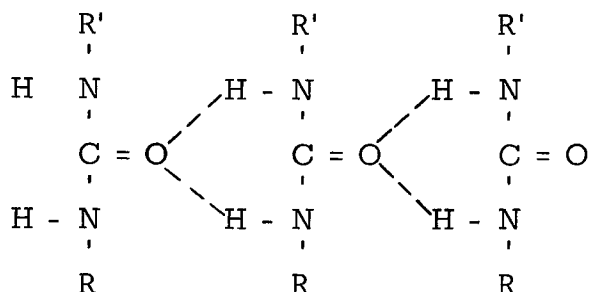| Group	Cohesive Energy kcal/molecules
$-CH_2$ (hydrocarbon)	0.68
$-COO$ (ester)	2.90
$-C_6H_4$ (aromatic)	3.90
$-CONH$ (amide)	8.50
$-OCONH$ (urethane)	8.74
$-NHCONH$ (urea)	higher

The higher the cohesive energy, the higher are the intermolecular forces. Then we expect the urea to have the highest potential for forming intermolecular bonds, and this has been found to be true. The urea type gels are the chemical class producing the strongest gels. The urethane gels show promise, but none are satisfactory. The same is true for the amine materials.

The basic chemical reaction to produce a urea from an isocyanate and an amine is:

$$R'NCO + RNH_2 \longrightarrow R' \begin{array}{c} O \\ \parallel \\ -N-C-N-R \\ \mid \quad\quad \mid \\ H \quad\quad H \end{array}$$

<div align="center">urea linkage</div>

The hydrogens attached to the nitrogens are capable of hydrogen bonding with either the oxygen or nitrogen, probably with the oxygen since it is more geometrically available. A typical network would be (dotted lines indicate hydrogen bonding):

$$
\begin{array}{ccc}
R' & R' & R' \\
\mid & \mid & \mid \\
H \quad N & H - N & H - N \\
\mid & \mid & \mid \\
C = O & C = O & C = O \\
\mid & \mid & \mid \\
H - N & H - N & H - N \\
\mid & \mid & \mid \\
R & R & R
\end{array}
$$

With this in mind, it is noticeable that decreasing cohesive energy (see listing above) corresponds to decreasing available hydrogens, nitrogens, and/or oxygens for electrostatic bonding.

Now that the ability to form secondary chemical bonds (intermolecular bonds) has been established, other necessities of the molecular structure must be explored. Since the crude oils or other hydrocarbons have little or no ability to participate in electrostatic bonding, it seems likely that the gelling agent (urea, urethane, amide, etc.) becomes incompatible (insoluble) and separate from the mixture. This occurs when the gelling agent is of low molecular weight and the active polar chemical groups make up a large percentage of the weight. If a group compatible with the nonpolar hydrocarbons is incorporated into the gelling agent molecule, partial solubility is gained and precipitation is avoided. Fatty amines were found to produce such an effect in the reactions with the isocyanates such as toluene diisocyanate. Chain lengths from C_7 to C_{18} yield a product of desired solubility. Solubility falls off as the chain length shortens, and the product becomes too soluble as the chain length lengthens. The proper solubility is important in forming the colloid which produces the gel.

Difficulty is encountered in obtaining a good solubility balance by using the urethane reaction. When octyl alcohol reacts with toluene diisocyanate, the product is a gummy liquid, which, in turn, proves to be soluble in crude oil. Viscosity is increased but no gel formed. Due to the lower cohesive energy of the urethane grouping, the addition of an eight carbon length hydrocarbon contributes significantly to the solubility of the urethane in the crude oil. If the chain length is shortened, then insufficient

compatibility is obtained to form a structural network with the oil. If this is thought of in terms of cohesive energy per unit weight, then the urethane grouping produces a less tightly bound system which is more easily solubilized and as the chain length of the alcohol increased (to gain compatibility), the cohesive energy concentration decreases.

All of the chemical classes discussed produce gels of varying physical characteristics with no class being limited in the type of gel they produce. The physical properties of the gels may be more closely correlated to the physical dimensions of the gelling molecule than with the chemical class.

Viscoelastic gels are those which resist deformation to an applied stress in a rubbery fashion. These gels are stringy and will recoil if the gel is strong enough. Consequently, a continuous force, although not very strong, will slowly displace the gel and cause it to run.

Pseudoplastic gels are those which exhibit a decrease in viscosity as the shear rate is increased.

A Bingham Body has a finite yield stress which must be exceeded before flow will occur. This type of gel holds its shape until sufficient stress is applied. Then it yields suddenly, perhaps breaking into parts if the gel is strong.

Besides exhibiting the above characteristics, the gel may also be thixo-tropic; i.e., viscosity decreases with time under a constant shear stress. Usually, the gel regains most of its viscosity when shear is removed.

The urea-type gels tested under this study produced gels classified as pseudoplastic and Bingham Bodies and are thixotropic, which would be an aid in the removal of the gelled oil from the tanker.

Testing of Gelled Crude Oils

Preparation

Several methods of incorporating the gelling agents into the crude oils in laboratory testing were evaluated:

1. Both amine and isocyanate were injected simultaneously through syringes into the oil with no other agitation. This resulted in fair gels with some localizing of the gelling agents producing lumps.

2. One ingredient was added and mixed into the oil then the other was injected by syringe with no other agitation. This decreased some of the localization but did not produce as smooth a gel as Method 3.

3.   Mixing one ingredient thoroughly then adding the
other ingredient by syringe and further agitating
with a laboratory stirrer for 15 seconds after addition
of the second ingredient was most effective and
was adopted for comparing gelling agents.

Methods 2 and 3 were utilized to determine the optimum sequence of the
agents. Equivalent gels were obtained if there was no delay (less than
15 minutes) between addition of the two ingredients; however, if there
was a delay, addition of the amine first proved far superior.

The more reactive isocyanate material deteriorates through its reaction
with water and other impurities in the crude oil. Table IV, Delayed
Gelling of Crude Oil, shows the variation obtained by varying the agent
addition sequence.

TABLE IV.   DELAYED GELLING OF CRUDE OIL

Added 1st	Added 2nd	Penetrometer Reading (2nd Ingredient Added 24 Hours Later) Gel Stand 1 Hour
Armeen C	TDI 80/20	283 (Br)
TDI 80/20	Armeen C	Weak Gel
Armeen O	TDI 80/20	360 (Br)
TDI 80/20	Armeen O	Weak Gel
Armeen C	MT-40	251 (Br)
MT-40	Armeen C	Weak Gel
Armeen L-15	TDI 80/20	211 (Br)
TDI 80/20	Armeen L-15	Weak Gel
Armeen L-11	TDI 80/20	196 (Br)

To conclude, the gels were prepared for laboratory testing by preparing
300 grams of gelled crude oil in a 600 milliliter beaker. The crude oils
were weighed into the beaker (285 grams in the case of a 5-percent gel),
the selected amine was added with agitation from a laboratory stirrer,
then the selected isocyanate was added under the same agitation. The
gels began to form immediately and were stirred for an additional 15

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seconds. Then the gelled crude oil was allowed to stand for one hour before testing on the penetrometer.

Optimum Amine and Isocyanate Ratio

During initial screening, the amines were mixed with the isocyanates in varying proportions to determine if a better gel could be obtained by deviation from the stoichiometric ratio. The results of this would determine if 1) any of the reagents were reacting with the crude, 2) any of the reagents were of a different strength than that posted in the literature, 3) steric effects were hindering the mobility of any reagent, or 4) any unknown factors were impairing the reagents' gelling ability which would be reflected in the mixing ratio. The mixing ratio (F) describes these ratios and is defined in the following equation:

$$\frac{EW_A \ F}{EW_I} = \frac{W_A}{W_I}$$

EW_A = equivalent weight of amine

EW_I = equivalent weight of isocyanate

W_A = weight of amine added

W_I = weight of isocyanate added

F = stoichiometric ratio factor

The ordinate of these graphs is the penetrometer reading in tenths of millimeters. It should be remembered that a lower penetrometer reading corresponds to a stronger gel.

From this data (see Appendix H, Optimum Ratio Studies), the optimum ratio of the amine to the isocyanate for the various systems is seen to be between 0.75:1.00 to 1.50:1.00 equivalent weight ratio.

Gel Strength Versus Percent Gelling Agent

Once the optimum weight ratios were established, these ratios were held constant and the percentage of total gelling agent was varied. Gels were formed at 5, 4, 3, 2 percent (and intervening half percentages) until the gel formed was too weak to record a penetrometer reading. Appendix I, Gels Strength Versus Percent Gelling Agent, contains a display of the data obtained from these tests. Data on the graphs was not extrapolated. The lowest percentage indicated by the curve drawn was the lowest which could be read on the penetrometer with each respective gelling system and crude oil. The wide variety of constituents of crude oils was equally

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reflected in the variety of responses of the crude oils to the gelling agents. If data can be gained during larger scale testing concerning gel strength needed to seal a prescribed rupture, these graphs would point out the least and most economical percentages which would produce the desired gel. A consolidation of the penetrometer readings are given in Table V, Penetrometer Reading of Gels for Five-Percent Agent Concentrations.

Weighed portions of gelled Clearfork crude were placed in weighed portions of synthetic seawater (ASTM D-1141) and ungelled Clearfork crude and allowed to stand 30 days. Then these gelled lumps were strained out of the respective liquid medium and the medium was reweighed and percentage weight loss (-) or weight gain (+) of the medium was recorded (Table VI, Solubilities of Five-Percent Clearfork Gels).

Gelling Under Temperature Variations

The six selected systems were tested for gelling ability at 100°F and 32°F in Clearfork crude and Solvent Mix crude. To accomplish this, all ingredients (crude, amine and isocyanate) were adjusted to the specified temperature. In the event the gelling agents were solid at 32°F, they were warmed until they first became liquids (the melting points of gelling ingredients are given in Table III, Physical Properties of Gelling Materials). The amine was then added and mixed into the oil. Next the isocyanate was added to gel the oil. These gels were aged one hour (still at specified temperature) and the penetrometer reading was recorded. The results are in Table VII, Gelling Under Various Temperatures.

Gelling Cost

Table VIII, Cost to Gel One Gallon of Crude Oil, was prepared to outline the raw material costs of the gelling agent. The costs of the raw materials were average, medium quantity figures. Bulk quantities would be less expensive.

Effects of Salt Water and Ungelled Oil

In the event the oil gelled aboard a tanker is spilled into the ocean, the gel must remain intact to form lumps which may be harvested. Also, in the event it is not necessary to gel all the oil contained in a tanker, then the gelled oil must retain its strength while in contact with ungelled oil.

Since none of the ingredients producing the urea gel are soluble in water (fatty amines become water soluble if the alkyl portion is shortened to C_6 or lower), and the oil itself is not soluble, then it is expected that no effects will be observed.

Since the fatty acid/caustic gel is of an ionic nature (acting as an emulsifier), oil gelled by this method turns cloudy upon contact with water.

TABLE V. PENETROMETER READING OF GELS FOR FIVE-PERCENT AGENT CONCENTRATIONS

Gel Agents	Gel Agents					
	Armeen C TDI 80/20	Armeen O TDI 80/20	Armeen L-15 TDI 80/20	Armeen C MT-40	POPDA 400 Tonco 90	Armeen L-11 TDI 80/20
Alaskan (Nikiski)	294	348	357	435	403	201
Arabian (Heavy)	241	380	430	276	217	358
Arabian (Light)	243	255	failed	258	284	220
Bachaquero	409	failed	362	367	349	269
Cairo (Egypt)	261	270	242	250	218	236
Clearfork	280	235	204	257	212	195
Devonian	268	323	300	275	257	225
Grade A 469 Mix	281	222	310	250	262	206
Howard Glasscock	237	286	275	276	219	221
Lybian	258	failed	293	270	260	390
Mirando	262	338	failed	260	222	211
Solvent Mix	311	327	failed	237	255	228
Sun B Mix	283	305	297	239	208	220
Sweden	280	327	351	232	288	241
Westbrook	230	326	304	285	195	255

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TABLE VI. SOLUBILITIES OF FIVE-PERCENT
CLEARFORK GELS

Gelling Agents		Water[+] (%)	Oil[+] (%)
Jeffamine 400	Octadecyl Isocyanate	-1.0	-.88
Armeen C	TDI 80/20	-1.3	0
Armeen L-15	TDI 80/20	-0.96	-0.83
Armeen C	MT 40		-1.17
Armeen O	TDI 80/20	-0.85	-3.33
Armeen L-11	TDI	-0.89	-3.4
[+] Soaking gel for 30 days caused this weight change on respective solvent (water or oil)			

TABLE VII. GELLING UNDER VARIOUS TEMPERATURES

Gelling System	Clearfork Crude Penetrometer Reading (Br)		Solvent Mix Penetrometer Reading (Br)	
	100°F	32°F	100°F	32°F
Armeen C and TDI 80/20	407	Gel too thin	330	386
Armeen O and TDI 80/20	324	247	372	322
Armeen L-15 and TDI 80/20	217	267	---	No gel formed
Armeen C and MT 40	377	---	390	258
POPDA 400 and Tonco 90	Gel too thin	325	219	Gel too thin
Armeen L-11 and TDI 80/20	192	216	259	206

TABLE VIII.   COST TO GEL ONE GALLON OF CRUDE OIL

System	Gelling Ingredients Cost/lb	Stoichiometric Ratio Factor	Percentage of Gelling Agent	
			1%	5%
Armeen O TDI 80/20	$.378 $.45	1.0	$.0309	$.156
Jeffamine 400 Octadocyl Isocyanate	$.65 $2.20	1.0	$.119	$.59
Armeen C TDI 80/20	$.488 $.45	.75	$.036	$.180
Armeen L-11 TDI 80/20	$.57 $.45	1.25	$.039	$.197
Armeen L-15 TDI 80/20	$.52 $.45	1.50	$.038	$.191
Armeen C MT-40	$.487 $.31	1.0	$.033	$.263

It could be expected that ungelled oil would present the most problems since it could possibly act as a solvent for the gelled oil. This was found to be true if the gelled oils and ungelled oils were blended with agitation but, if the gel was allowed to stand unagitated in the oil for 30 days, only slight swelling effects were observed. Only urea gels were strong enough to test in this manner.

Ten-Percent Gels

Preliminary calculations had indicated that for reason of cost for materials, the upper limit of amine/isocyanate used to get the crude oil would be held at five percent. For the purposes of gaining an insight into the results of applying a much higher concentration of gel constituents, a limited test was run at 10-percent concentration.

Two crude oils were selected, a high gravity Sweden crude of API 47, and a low gravity Bachaquero crude of API 17. Two gel constituent systems were selected, the lowest and highest cost of the systems selected for further testing. Table IX, Ten-Percent Gels, shows the results of this testing, indicating that the increase in strength gained would not seem to offset the doubling in cost of materials, or the increased storage space required for the additional chemicals.

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TABLE IX. TEN-PERCENT GELS

System	Weight Ratio (gm)	Crude Used And Amount (270 gm)	Penetrometer Reading (Br)
Armeen L-11 TDI 80/20	21.26 8.74	Sweden	240
Jeffamine 400 Octadecyl Isocyanate	12.12 17.88	Sweden	205
Armeen L-11 TDI 80/20	21.26 8.74	Bachaquero	185
Jeffamine 400 Octadecyl Isocyanate	12.12 17.88	Bachaquero	125 75 after standing 24 hours

Other Materials Gelled

As an auxiliary interest, some common solvents and fuels were gelled with the urea systems. Most aliphatic materials can be gelled with these materials. Aromatics tend to be weaker, stringy gels. Polar solvents produce weak particulate gels due to the limited solubility of the alkyl portions of urea gelling molecule. See Table X, Various Materials Gelled.

Flow Properties

A high gravity crude oil (API 38°) was gelled using 5-percent Armeen C-MT40 gelling agents. This gel was tested in a Burrell-Severs extrusion rheometer. Two graphs (Figure 1, Rheogram, Gelled Crude Oil) were obtained relating shear stress and viscosity to shear rate. From the rheogram, it was concluded that the gel was shear thinning and had a finite yield point. The yield shear stress of 11,000 dynes per square centimeter obtained corresponds closely to the 12,000 dynes per square centimeter obtained with the penetrometer. The difference in curves obtained from the worked and unworked gel shows the thixotropic nature of the gelled oil.

Summary

The laboratory evaluation of gelling systems resulted in gels which were far superior to any found in previous work or identified in the literature

TABLE X. VARIOUS MATERIALS GELLED

| Gelled Material	Gelling Agent	% Gelling Agent	Penetrometer Reading	Remarks
JP-5	Armeen O TDI 80/20	5	331 (Br)	Good gel was formed.
JP-5	Armeen L-11	5	244(Br) (8/15/69) 170(Br) (8/18/69)	Good gel formed with increase in strength after several days.
Toluene	Armeen O TDI 80/20	5	Failed (Br)	Very weak gel. Failed the penetrometer.
Toluene	Armeen L-11 TDI 80/20	5	No gel after 1 hr. 251 penetrometer reading after 4 hrs.	Good gel after 4 hours.
Regular Gasoline	Armeen L-11 TDI 80/20	5	292 (Al)	Viscoelastic gel. Forms a gellatinous blanket on surface.
Regular Gasoline	Armeen O TDI 80/20	5	379 (Al)	Viscoelastic gel. Stringy and thin.
Motor Oil SAE 30	Armeen O TDI 80/20	5	Failed Al	Thin and stringy gel.
Motor Oil SAE 30	Armeen L-11 TDI 80/20	5	350 (Br)	Weak stringy gel.
Isopropanol	Armeen L-11 TDI 80/20	5	377 (Al)	Weak particulate gel. Gelling agent formed suspended particles.

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Figure 1. Rheogram, Gelled Crude Oil

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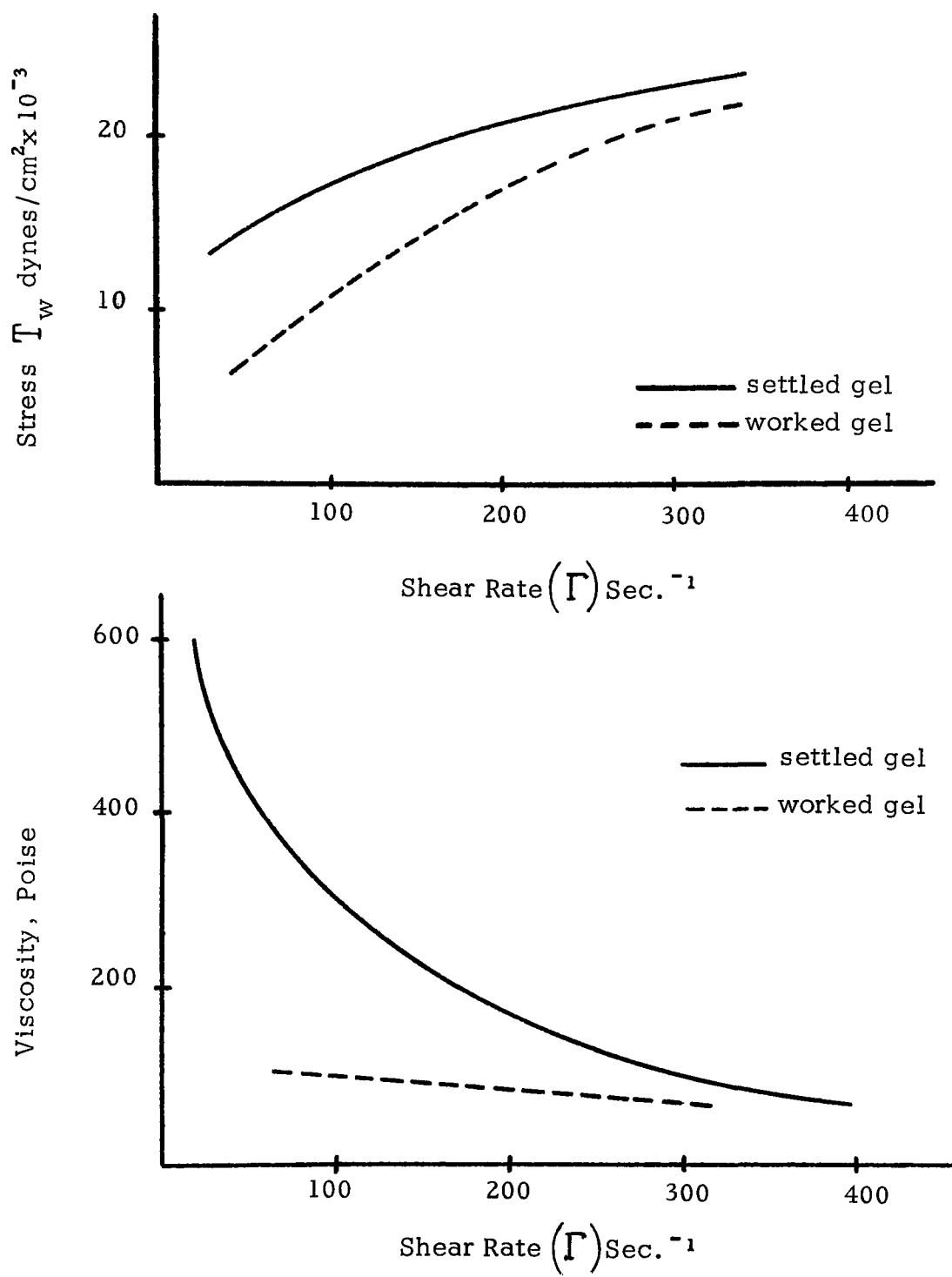
survey. All systems investigated resulted in a physical bond, such as hydrogen bonds or other electrostatic attraction, to form the gel. Therefore, from the physical bond standpoint, the urea-formed gel is the strongest gel possible at the percentages used.

It may be postulated that gels might be formed by chemical bonding, rather than physical bonding, using the unsaturation of the crude oil components or the naturally occurring impurities as one component with a catalyst or crosslinking agent as the additive. As far as can be determined, little, if any, work has ever been conducted in this area which might offer an entirely different approach to the problem. Any such investigation would require a major basic research effort. Whether a gel could be produced through this approach, or if such results could be routinely reproduced, or if such a system could be universal in its ability to gel all classes of crude, and what the character and strength of such a gel might be, is unknown and subject to only speculation at this time.

The laboratory evaluation of the amine/isocyanate gel systems shows that it is possible to produce gels in all domestic and foreign oils tested which are unaffected by salt water or crude oil. Gelling of crude oil is possible at the extremes of cold or hot climates which may be encountered. Many other finished petroleum products which may be transported can also be gelled by this same system.

The best overall system from all standpoints was Armeen L-11 and TDI 80/20. It was found, however, that the manufacturer, Armour Chemical, was not producing the chemical in larger than laboratory quantities. It was, therefore, eliminated from consideration in larger volume tests. The Jeffamine 400 and octadecyl isocyanate system produced the next strongest gel at room temperature but encountered some difficulty at climatic extremes. The cost was the highest of any system and large-scale production of the isocyanate, as would be required by wide usage, was questionable. This system was also eliminated from large-scale tests. The Armeen C and MT 40 system produced gels in all oils tested, performed well at climatic extremes and was moderate in cost and available in large quantities. This system was, therefore, selected to be used in the large-scale tests.

SECTION 4

LARGE TANK TESTS OF THE GELLING SYSTEM

Program Design

The 1,000-gallon tests were designed to verify that the chemical agents selected as a result of laboratory evaluation could produce gels of comparable characteristics in significantly larger volumes. The key to successful performance of these tests was the proper functioning of the dispensing and mixing concepts.

Dispersion Concepts

The best gelling agent combinations resulting from the laboratory study all require thorough, uniform and rapid distribution throughout the oil to be gelled. The initial task in dealing with volumes significantly larger-than-laboratory quantities was to devise means of introducing and dispersing the gel agents into the oil.

A total of 16 dispersing concepts were formulated, including preliminary assessments of their advantages and disadvantages. Each of these are detailed in Appendix J, Gel Agent Dispensing Concepts.

A relative evaluation of each of the 16 concepts was made, based on the preliminary assessments. This resulted in the immediate elimination of Concepts 8 through 16. The remaining concepts were then considered in more detail and the preliminary assessments extended.

The submersible pump concept (Concept 6) consists of lowering a pump into the oil to be gelled through which the chemical agents, oil and air can be pumped for gelling. The gelled oil containing air floats to the surface and suction and discharge of the submersible pump may be kept relatively free of the gelled oil. On the other hand, maneuvering the pumps and suction is cumbersome. It is difficult to keep the suction free of gelled, or partially gelled, oil. As viscosity increases, horsepower requirements are excessive and overall pump effectiveness is low for a large tank. This concept was not recommended to be included in the test program.

The propeller mixer concept (Concept 7) consists of a portable or permanent propeller mixer being positioned in the tank. The gelling agents are dispersed into the vortex formed by the propeller. This concept is similar to the use of a laboratory propeller stirrer in a beaker. In this case, it has been determined that horsepower requirements become excessive with increasing viscosity as the oil thickens. Poor mixing also results in portions of the tank due to maneuvering constraints. This concept was not recommended to be included in the test program.

The following concepts were recommended to be included in the test program. On a relative basis, they are the most practical in meeting overall system requirements.

Rotating Nozzles (Concept 1)

The rotating nozzle concept consists of using multiple openings in a tool in such a manner that when the fluids are pumped from the nozzle openings the tool rotates. The gelling chemicals are dispersed through the same nozzle openings. By varying the pressure and sequence of injection, the differing amounts of agents can be injected. The nozzle is raised and lowered through the oil to assure the dispersion of the chemicals throughout the oil to be gelled. Turbulence caused by the injection creates mixing.

There are some shipboard operating difficulties which seem solvable, providing the dispersion concept is successful. Some of these are: multiple baffles, web stiffeners and other obstructions in the tank; means of traversing the nozzles vertically through the tank, and methods of flushing the lines between agent application.

Recirculation (Concept 2)

The recirculation concept consists of pumping the oil from the tank through a manifold, where the two gelling chemicals are proportionally added and then returning the mixture to the original tank. The pump suction can be from the top or the bottom of the tank. The discharge of the oil-chemical mixture can also be on the top or bottom of the tank. Two proportioning pumps are required, one for each of the chemicals injected. The varying pump suction requirement aboard ship can be overcome by using a turbine pump (deep well type) immersed in the oil with a flexible suction attached with a floating intake port.

Recirculation With Air (Concept 3)

It was postulated that through the addition of a gas or air into the oil-chemical mixture at the time the gelling is occurring, the density of the gelled oil can be reduced. The lighter gelled oil floats on the ungelled oil and thus simplifies the possible problem of the gelled oil getting into the suction of the circulation pump and plugging it. In addition, it is believed this technique can assist in obtaining a uniform gel throughout the tank. This is a variation of Concept 2, requiring minimum equipment changes.

Vertical Sparger (Concept 4)

Locating sparger pipes adjacent and parallel to the outer hull might allow oil in the immediate area of likely damage or rupture to be gelled first. Turbulence caused by nozzle injection creates mixing, particularly near the

hull. Localized gelling might also be accomplished with Concepts 1 and 5; therefore, it is recognized that Concept 4 might be deferred until the others have been tested.

Horizontal Sparger (Concept 5)

The horizontal sparger concept is similar to the vertical sparger, except that this installation is appropriately located across the bottom of the compartment or tank. The attempt here is to gel the total volume of the tank. It is postulated that air is required to assist in the dispersion and mixing of the chemicals into the oil. The air also permits the gelled oil to rise to the top such that the ungelled oil would be in proximity to the sparger pipes for better mixing.

The list of concepts generated and the analysis and recommendations were submitted to the Contracting Office for approval. Concepts 1, 2 and 3 were approved for testing.

Facilities Design

Test Tank

The tank for the first scale-up from laboratory gelling tests was designed with a square cross section. This was done to start bridging the gap between laboratory container and actual ship tank shape. The fabricated steel tank dimensions were 4.5 feet wide, 4.5 feet long and 8 feet high. This allowed a 2.25-foot freeboard above the 1,000- gallon oil level. A steel ladder allowed test progress to be observed from above. A vertical sliding gate was placed on the bottom of one side of the tank. This gate was 4 feet long by 1 foot high and provided a variable opening to test the ability of the gelled oil to resist flow from the tank. A two-inch diameter valve opening at tank-bottom was also installed. No provisions were made at this time to measure flow properties against differential heads of sea-water.

Recirculation Dispersion System

Figure 2, Schematic of Recirculation System, is a schematic drawing of this dispensing method. The recirculation of the crude oil is accomplished using a centrifugal pump so that experimental recirculation rates can be varied by throttling the pump discharge. The gel agents are metered into the circu-lating crude oil by a duplex piston pump. The recirculation system (Concept 2) takes suction from the top of the oil and discharge the mixture of crude and gelling agents at the bottom of the tank. The recirculation system with air (Concept 3) takes suction from the bottom of the tank and discharges the gelling mixture on top of the ungelled oil. Air or gas injection can easily be provided in the recirculation line.
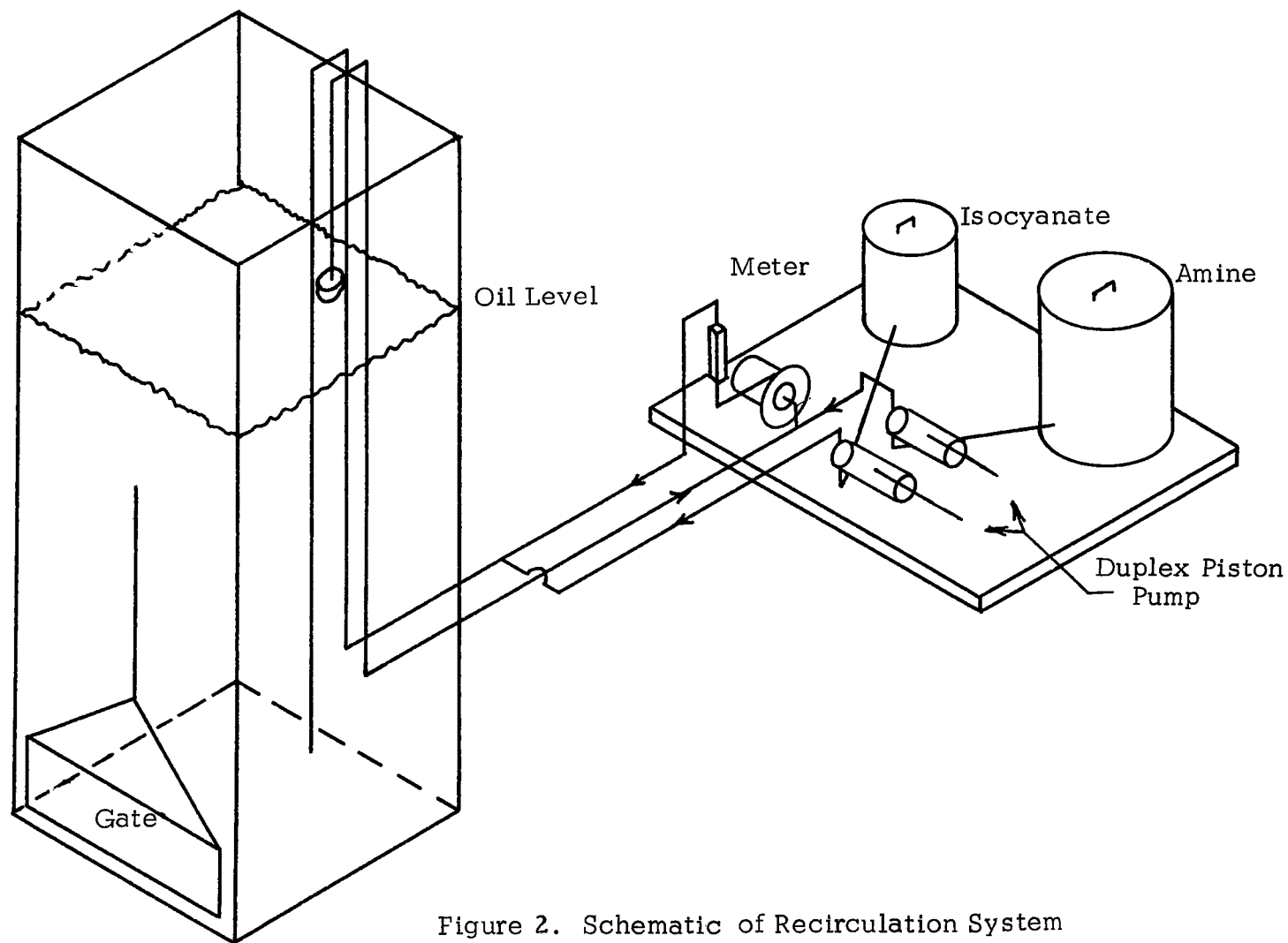
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Figure 2. Schematic of Recirculation System

Nozzle Dispersion System

The rotating nozzle dispensing system was designed to operate with a single line and a single pump to move both gelling agents with a crude oil flush between agents. The nozzle selected is a NCR-15, 1 1/2-inch revolving cellar nozzle, as sold by the Fyr-Fyter Company. The six nozzle holes are threaded for installing the 1/8-inch solid stream nozzles required by the gel agent volumes and rate of discharge. A cable and winch, attached to an "A" frame, is used to move the nozzle vertically through the crude oil. Figure 3, Schematic of Nozzle Dispensing System, is a schematic drawing of the rorating nozzle system.

Large-Scale Testing

A single chemical agent combination and a single crude oil were used in all tests to provide consistent data and to keep the number of tests and cost at a reasonable level. The agents were Armeen C and MT 40. The oil was a Wise County (Texas) conglomerate from the L. A. Henry Lease having an API gravity of 38.

Recirculation System (Concept 2)

Four tests were conducted using this concept at 5-percent agent concentration. The oil was recirculated with a Marlow-type HAIEC self-priming, centrifugal petroleum pump. The suction was taken just below the top of the oil level in the tank, and the mixed oil and gelling agents were discharged on the bottom of the tank. The gelling agents were applied to the recirculated oil, using a Neptune duplex chemical feed pump. The amine was injected in the pump suction and the isocyanate in the pump discharge. In theory, the mixture of oil and gelling agents was to be just ready to gel when discharged from the pipe in the bottom of the tank, gel on discharge with little or no dilution from the crude oil in the tank and gradually displace the ungelled oil toward the top of the tank. In practice, the gelled oil had such a neutral buoyancy in the crude oil that it moved with any currents in the tank rather than stay on the bottom. Therefore, instead of getting a uniform homogeneous gel throughout the tank, a mixture of gelled lumps in ungelled crude always resulted.

During these tests it was learned that the gel agent pumps and piping, particularly the isocyanate system, must be clean and dry before using to pump the agent. Particulars on this series of tests are included in Table XI, Recirculation Tests (Concept 2).

Recirculation With Air System (Concept 3)

Four tests were conducted using this concept. Experimental observations are included in Table XII, Recirculation Tests (Concept 3). The equipment for this test series was the same as that for Concept 2 with the addition
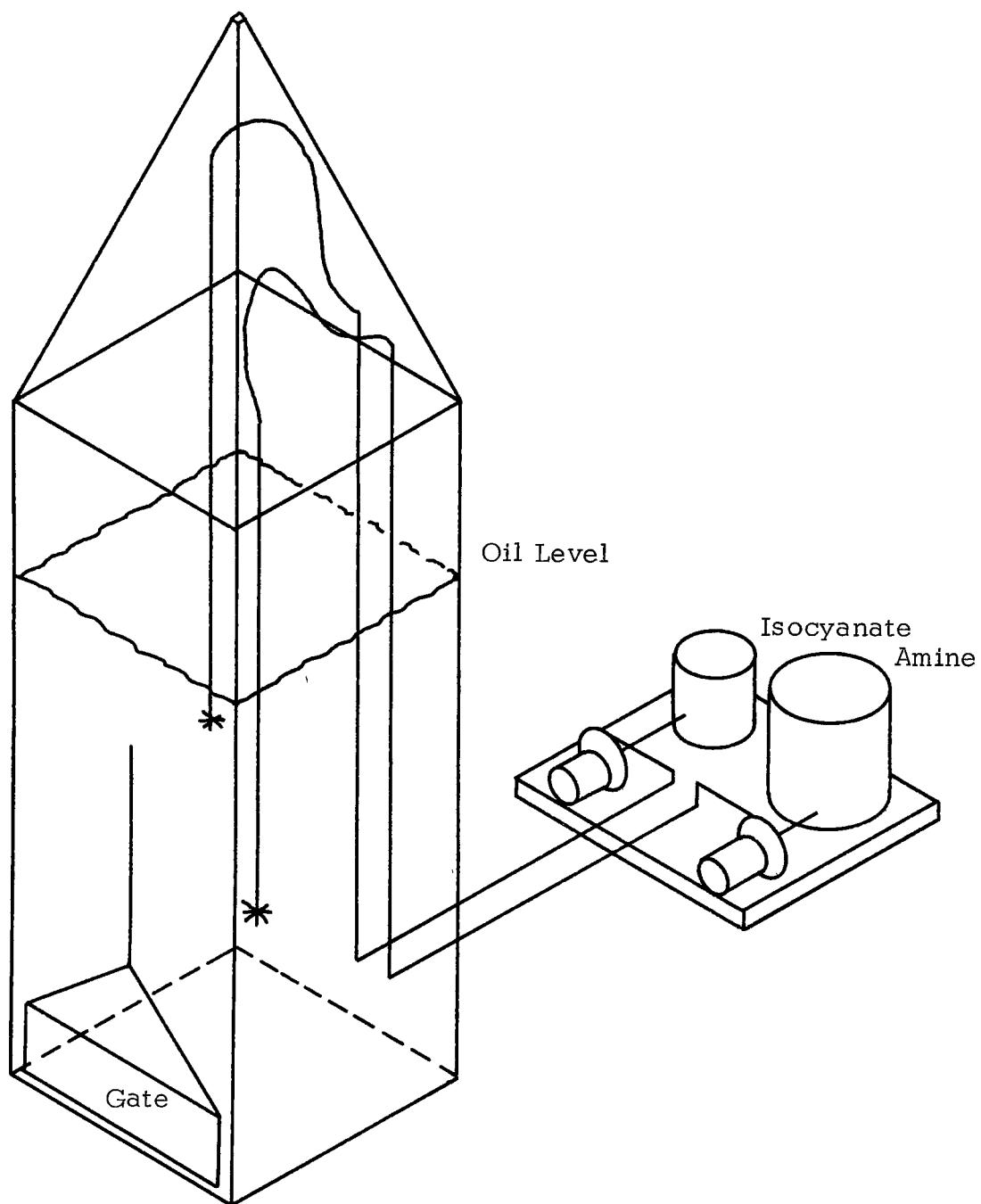
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Figure 3. Schematic of Nozzle Dispensing System

TABLE XI. RECIRCULATION TESTS (CONCEPT 2)

Test	1	2	3	4
Date	1/25/70	1/29/70	4/9/70	4/15/70
Oil (gal.)	450	1,000	500	1,000
Recirculation Rate, Oil (gpm)	8.2	8.2	8.0	8.0
Amine Rate (gph)	17.9	17.9	17.9	13.5
Isocyanate Rate (gph)	6.6	6.6	6.6	5.0
Percent Gel Agents by Weight	5.0	5.0	5.0	3.0
Penetrometer Reading	Floating Lump 285	255	313	300

Remarks:

Test 1   Lumps of gelled oil suspended in ungelled crude. Flowed freely from 2-inch opening in bottom of tank.

Test 2   Same as Test 1.

Test 3 - Extreme difficulty in keeping isocyanate pump lines open. Frequent cleaning necessary. Resultant gel poorer than previous tests.

Test 4 - Changed discharge to reduce mixing of gelled and ungelled oil. Results same as Test 1.

of an eductor placed in the discharge line. The suction line was changed from the top of the oil level to the bottom of the tank, and the discharge line placed at the top level of the oil. The discharge line included an elbow which made the mixture discharge parallel to the oil surface. The eductor was placed about three feet ahead of the discharge point and was fitted with a low pressure nitrogen line into the throat. The nitrogen was used in lieu of a compressed air source for convenience.

The first test in this series (Test 5) used too much nitrogen. An agent concentration of 3.5 percent was used. The gelled oil increased in volume by

TABLE XII. RECIRCULATION TESTS (CONCEPT 3)

Test	5	6	7	8
Date	4/22/70	5/4/70	5/11/70	6/2/70
Oil (gal.)	1,000	950	1,000	1,000
Recirculation Rate (gpm)	7.8	7.8	6.5	6.3
Amine Rate (gph)	13.5	13.5	13.5	13.5
Isocyanate Rate (gph)	5.0	5.0	5.0	5.0
Nitrogen Rate (cfh)	100	30	10	0
Percent Gel Agents by Weight	3.5	3.5	5.0	5.0
Penetrometer Reading	313	392	246	209

Remarks:

Test 5 - Trouble with isocyanate pump lines clogging. Resultant gel very foamy. Volume increased 20 percent. Lumps of gelled oil and ungelled oil flowed freely out of 2-inch opening for about 100 gallons, then flow slowed as ungelled oil decreased.

Test 6 - Gel somewhat thinner than Test 5, but much less foamy. Oil appears to be uniformly gelled except for bottom part of tank. Oil flowed freely until all poorly gelled oil exhausted. Flow then slowed.

Test 7 - Uniform gel except for bottom amount in tank. Oil flowed freely out of 2-inch valve on bottom of tank until mixture of gelled and ungelled oil exhausted. Gelled oil then flowed slowly out of valve.

Test 8 - Uniform gel except for about 100 gallons on bottom of tank. Gelled oil exuded out of 2-inch valve until 4.75 head of gelled oil reached. Gate opened one inch, gelled oil exuded until one foot head reached.

20 percent which was assumed to be intolerable aboard ship. Also, the increased foaming of the gel reduced its strength to resist flowing.

As in all tests in this series, the centrifugal pump used in recirculation lacked sufficient lift to remove the bottom few inches of crude oil which had been thickened slightly by dilution of the gel mixture first returned to the tank prior to complete gelling. In an actual shipboard situation, this pump would be a positive displacement pump, eliminating the difficulty.

The next test (Test 6) was a repeat of the previous test, using less nitrogen. The resulting gelled oil was less foamy but still lacked strength to resist flowing out of the 2-inch valve at the bottom of the tank with 6.75 feet of gelled oil above the valve.

Test 7 increased the gel agent/oil ratio to 5 percent and reduced the flotation nitrogen. The gel formed well about five seconds after discharge, floated on top of crude in the tank and, as the test progressed, gradually lowered the ungelled oil level. The resulting gelled oil flowed out of the 2-inch valve opening under 6.75 feet of gelled oil head. No attempt was made to determine the limits on this extrusion.

Tests made during the recirculation of oil alone showed that sufficient air would be introduced by the normal vacuum produced by the eductor. The next test (Test 8) was performed in this manner. The gelled oil floated as before with the resulting gel the stiffest of any test and fully equal to any produced in the laboratory. After the gelling was completed, the 2-inch valve on the bottom of the tank was opened, allowing the gelled oil to flow. The extruded oil was continually removed to keep the external resistance to flow uniform. The gelled oil flowed until the head inside the tank was reduced from 6.75 feet to 4.75 feet, measured from the top of the opening. The sliding gate was then opened one inch, providing a .33-square-foot opening. The gelled oil slowly extruded until a 1-foot head was reached as measured from the top of the opening. The gate was then opened to two inches and the remainder of the gelled oil flowed out.

Nozzle Systems (Concept 1)

The concept being tested in this series originally included a series of nozzles which would revolve around a central shaft, distributing the gelling agents. It was found in practice, however, that for small-scale tests there are no commercial devices suitable. One such device which was investigated was a fire fighting cellar nozzle. The six nozzle openings were much too large and were modified to suit the volumes of agents to be used on these tests. The 5/16-inch and 1/4-inch nozzle openings were tapped and fitted with 1/8-inch nozzles. It was found that the discharge from the nozzles produced insufficient torque to provide much rotational movement when submerged in a liquid. Also, the close clearances of the bearing surfaces were easily fouled by small particles, stopping the rotation.

In search for suitable nozzles, a tank cleaning nozzle manufactured by Spraying Systems Company was found which had a 360 degrees coverage approximately normal to the delivery pipe. The deflector cap was machined so as to make the spray normal to the supply pipe instead of the upward deflection.

Liquid-in-liquid spray patterns were observed prior to gelling tests in an open top water tank with colored particles to indicate flows. It was found that the mixing zone of each nozzle hole included a sector of about 25 degrees. The practical radius of the mixing zone appeared to be about 250 nozzle diameters. Some mixing was observed beyond that point but appeared to be very minor. In view of this, the nozzle was modified to have eight holes .093 inch in diameter. This would result in almost complete mixing coverage to the nearest tank wall.

The first test of the series (Test 9) was made delivering both the amine and isocyanate through the same pipe and nozzle with a crude oil flush of the lines between deliveries. The crude oil flush did not remove all of the amines. The reaction between the full strength isocyanate and residual amine was sufficient to partly clog the nozzles and reduce the mixing effectiveness. Subsequent tests were performed using separate pumps, lines and nozzles for each gelling agent.

The next three tests in the series were essentially the same in procedure and end results. Nozzle size changes were made to attempt to improve mixing, and filters were installed later to protect the nozzle openings. These tests all appeared to mix the amine satisfactorily into the crude oil, but very shortly (15 to 30 seconds) after starting the isocyanate injection, the crude oil began to thicken rapidly, reducing the radius of the mixing zone and eventually allowing mixing only in the immediate vicinity of the nozzles. Table XIII, Nozzle Tests (Concept 1), lists particulars on this series.

Nozzle With Gas Agitation System

The mixing of the gelling agents into the crude oil appeared to need improving. The nozzle test setup was changed to include an inert gas sparger placed on the bottom of the tank. A series of 16 nozzles placed one foot apart and three inches from the outer wall of the tank were installed in the tank. A nitrogen bottle with regulator and rotameter were connected by hose to the sparger. It was believed that the gas bubbles rising along the walls of the tank would improve the mixing by increasing the circulation within the tank. Table XIV, Nozzle Tests, Gas Agitation, details these tests.

The first test in this series (Test 13) resulted in a gel only slightly thicker than the crude oil. The low pressure of the isocyanate injection was thought to be responsible for the poor gel. The isocyanate injection pressure was increased for the next test (Test 14) by reducing the nozzle size. The injection pressure increased and the gel consistency thickened

TABLE XIII. NOZZLE TESTS (CONCEPT 1)

Test	9	10	11	12
Date	6/16/70	6/22/70	6/24/70	6/25/70
Oil (gal.)	500	500	500	500
Amine (gal.)	23	23	23	23
Isocyanate (gal.)	9	9	9	9
Percent Gel Agent by Weight	6.5	6.5	6.5	6.5
Number and Size Nozzles (in.)	8-.093	6-.081 8-.106	6-.093 8-.125	6-.093 8-.125
Injection Pressure (psi)	80	50	80 Isocyanate 40 Amine	48 Isocyanate 40 Amine
Injection Time (min)	4.0	3.0	4.5	2.25

Remarks:

Test 9 - Thin, mushy gel. Localized gelling in center of tank.

Test 10 - Thin gel with localized heavier gelling in center of tank.

Test 11 - Thin gel with localized heavier gelling around center of tank. Isocyanate nozzles plugged.

Test 12 - Filters ahead of nozzles. Thin gel with localized heavier gelling in center.

considerably, but still thinner than desired. Since the limit of volume versus pressure available from the turbine injection pump had been reached, a pressure shooting tank was installed which would use nitrogen pressure to inject the isocyanate.

The nozzle arrangement for both amine and isocyanate were changed at this time. A 1-inch diameter pipe coupling was drilled and tapped to accept a commercial solid stream nozzle. The amine nozzle head contained 12 Spraying System Company nozzles (number T0010) with 0.086-inch openings. The isocyanate nozzle head contained 6 equally spaced nozzles (number TT0008) with 0.061-inch openings.

TABLE XIV. NOZZLE TESTS, GAS AGITATION

Test	13	14	15	16
Date	7/2/70	7/9/70	7/14/70	7/16/70
Oil (gal.)	500	500	500	500
Amine (gal.)	23	23	23	23
Isocyanate (gal.)	9	9	9	9
Percent Gel Agents by Weight	6.5	6.5	6.5	6.5
Size and Number Nozzles, Amine (in.)	8-.125	8-.125	12-.086	12-.086
Size and Number Nozzles, Isocyanate (in.)	6-.093	6-.086	6-.061	6-.125
Injection Pressure, Amine	26	35	34	33
Injection Pressure, Isocyanate	22	43	100	100
Gas Flow (cfh)	40	35	30	30

Remarks:

    Test 13   Oil only slightly thicker.

    Test 14   Uniform gel penetrometer 325.

    Test 15 - Uniform gel penetrometer 295.

    Test 16 - Uniform gel penetrometer 254.

The next test (Test 15) and the confirming test (Test 16) both resulted in gels which were equal to any of the laboratory gels.

Summary

Mechanical Systems

The recirculation system is a successful and simplified method to gel oil. All the oil in a tank was treated uniformly and gelled. The determination of the pump rate and proportioning of the chemicals into the circulation line were accomplished by conventional equipment and good engineering practices. The mixing of the chemicals in the circulation line was sufficient to result in a gel which was comparable to gels produced under laboraotry conditions.

The method, however, is relatively slow and would require approximately four hours to gel an average center tank using a 100 barrel/minute recirculation pump.

Based on program results at this point, the recirculation dispersion system required no further test to determine operating limitations. Actual equipment size and power requirements associated with particular ship installations, however, must be determined for each installation. This conclusion is applicable to both the shipboard installed and helicopter transported systems.

Non-rotating nozzles of proper size and application pressure will produce 360 degrees coverage with sufficient agitation to adequately mix and disperse the agents in a 1,000-gallon tank. A separate line and nozzle must be used for each agent and both chemicals could be dispersed simultaneously. The resulting gel is comparable to gels produced under laboratory conditions.

This method is relatively fast. It took 2 1/2 minutes to complete dispersion in the 1,000-gallon tank with a delay between agent injection injections. In fact, total dispersion must be rapid because of gel set-up time.

The program results provided the necessary information from which the parameters determining the operating limitations and equipment requirements for larger volume nozzle dispersion system tests can be identified and planned. The critical factors related to the nozzle dispersion radius as related to the dimensional volume to be gelled. The 1,000-gallon tests provided one limited volume related set of variables.

Gel Characteristics

Program tests have shown that gels comparable to those produced in the laboratory can be produced in large volumes with the mechanical systems devised.

The tests produced two data points for the gel relative to its ability to resist flow through a rupture with differential pressure. These two points indicate that the best gel developed will not keep the cargo from flowing through the rupture under all conditions.

In all of the 1,000-gallon tests the gelled oil would flow out of a two-inch valve opening under a head of 6.75 feet of gelled oil. This translates to a differential pressure of 2.5 psi. An attempt was made to define the upper limit of the head of gelled oil under which no flow would occur. It was found that for a gel which was comparable to the best laboratory gel, a head of 4.75 feet of gelled oil produced no flow through the two-inch valve. This relates to a pressure differential of 1.75 psi and a shear stress of 12,000 dynes per square centimeter. Referring to the rheogram on the gelled oil Figure 1, this indicates an extremely high shear rate for the small opening.

Similarly, the gate tests defined a no flow pressure differential for the best gel of .35 psi or a shear stress of 24,000 dynes per square centimeter with gap dimensions of 4 feet wide by 1 inch high. The penetrometer reading on this gel was 209 which translates to a yield shear stress of 25,000 dynes per square centimeter.

The tank tests indicated that the gel, as produced in the laboratory and reproduced in the tests, lacks the strength to withstand differential pressures greater than 1.75 psi (heads of 4.75 feet), when bridging a 2-inch round hole or pressures of .35 psi (heads of one foot), when bridging holes 4 feet long by 1 inch high.

In the normal fully loaded shipboard containment configuration (plotted on Figure 4, Pressure Differentials Cargo Versus Seawater), differential pressures at the bottom of a tank will range from .7 psi to 1.0 psi outward. At the waterline, this range becomes 3.4 psi to 6.0 psi. When a rupture occurs below the waterline, oil will flow through the rupture until the pressure is equalized or to the lowest point of the rupture if above the waterline. When the rupture passes through the waterline, water will enter the tank and eventually displace all the oil. In summary, the deeper the rupture is located the more favorable the situation.

Under the worst conditions, (a rupture above, at, or through the waterline) the gel might be effective in holding cargo a minimum of one foot above the waterline (Figure 4, Pressure Differentials Cargo Versus Seawater). For a rupture completely below the waterline oil loss prior to the gel becoming effective would be less than the above and a function of the maximum dimension rupture area and its depth below the waterline. The minimum loss would be experienced with the rupture at the bottom.

It can readily be seen that the limits of effectiveness of the best gel produced, in terms of cargo loss to be avoided, is a complicated
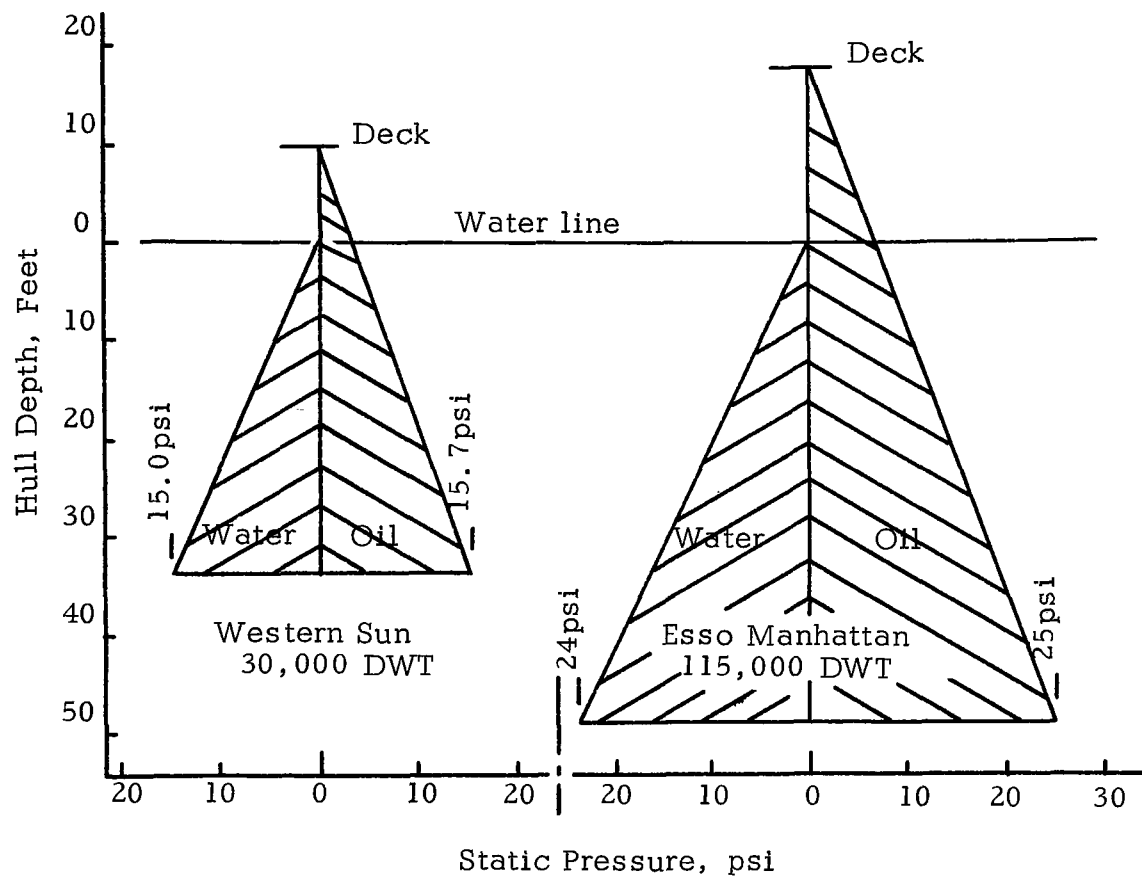
Figure 4.   Pressure Differentials Cargo Versus Seawater

function of the rupture dimensions, its location in relation to the water-line, the size of the tank and the time lapse between rupture and gelling. Furthermore, the performance criteria becomes more severe if the water-line is lowered as a result of the ship running aground.

While the observations of gel performance in the tank tests were limited, it seems apparent that the strength range of the gels produced was insufficient to preclude flow from a rupture of significant size over all but a limited range of pressure differentials. The value of the gellation system developed would seem to rest primarily on the reduced flow rate of the gelled cargo and decreased pollution in any given time span. The strength ranges for the gels produced, derived from various test data is quite consistent. Based on this consistency, some generalizations from the rheogram can be made. Analysis of the rheogram indicates that the flow rate of the gelled cargo will decrease as flow occurs and terminate at some positive pressure differential (critical shear stress). Because of this, the gel would also be expected to resist flushing and intrusion of water resulting in even smaller rates of loss from the tanker than ungelled oil. Establishing these performance characteristics precisely for the gellation system developed requires extensive testing under more varied and controlled conditions than those required for the development of the system to this point.

In addition to strength, the handling characteristics of the gel were observed. Following each test, the gelled oil was transferred by a positive displacement pump to a larger waste pit where it was subjected to local climatic extremes for several months. The pumped material reformed into large globs of gelled oil, which floated on the water in the pit. At no time was there an oil slick or loose oil observed on the surface of the water.

SECTION 5

SYSTEM APPLICATION

Most United States tankers built prior to the 1960s have relatively short cargo tanks usually 40 feet or less in length. The cargo section is divided by two longitudinal bulkheads into port, center and starboard tanks. The center tanks are usually approximately square and the wing tank width usually about half the length. The majority of the ships in United States waters are of this configuration. Two classes of ships now in service were selected as application examples.

Requirements

The 30,000 DWT class tanker represents the most frequently used ship in United States service. The dimensions of an average wing tank in such ships (The Western Sun, Sun Oil Company owner) are 40 feet long, 24 feet wide and 45 feet deep. The nominal capacity, loaded to 4-foot ullage, is 7,500 barrels of crude oil.

If the nozzle method was to be used to gel the oil, extrapolation from the 1,000-gallon test would indicate the need for 2-nozzle probes in this tank, each to gel half the tank or a plan area of 20 feet by 24 feet. To achieve this, each nozzle probe would require the following:

Isocyanate nozzles	10
Amine nozzles	20
Nozzles size	0.75 in.
Isocyanate pump size	55 bbl per min
Amine pump size	100 bbl per min
Quantity isocyanate	2,325 gal.
Quantity amine	7,250 gal.

If the recirculation method were used to gel the oil in the tank, the following would be required:

Recirculation pump	200 bbl per min
Isocyanate pump	55 gal.per min
Amine pump	150 gal. per min
Quantity isocyanate	5,560 gal.
Quantity amine	14,500 gal.

The 250,000 DWT class ship represents one of the largest ships now in worldwide service. The dimensions of a forward wing tank on the Esso Scotia, a 249,952 DWT tanker launched in 1969, are 200 feet long, 47 feet wide and 84 feet deep. The nominal capacity of this tank (98% full) is 144,000 barrels of crude oil.

If the nozzle method were used to gel the oil, extrapolation from the 1,000-gallon test would indicate the need for 5 nozzle probes in this tank, each to gel the oil over a planned area of 40 feet by 47 feet. To achieve this, each nozzle probe would require the following:

Isocyanate nozzles	20
Amine nozzles	36
Nozzle size	1.5 in.
Isocyanate pump	350 bbl per min
Amine pump	750 bbl per min
Quantity isocyanate	375 bbl
Quantity amine	1,075 bbl

If the recirculation method were used on this ship to gel the oil in one tank, the following would be required:

Recirculation pump	2,000 bbl per min
Isocyanate pump	550 gal. per min
Amine pump	1,500 gal. per min
Quantity isocyanate	2,000 bbl
Quantity amine	5,500 bbl

Previous experience with gelled hydrocarbons has shown that they can be pumped satisfactorily with a positive displacement pump. Experience gained in removing the gelled oil from the 1,000-gallon tank has verified this. After each test, the gelled oil was pumped out of the tank using a Worthington gear pump, 7 GAUM, through a 2-inch suction hose and a 2 1/2-inch discharge hose. Extremely stiff or well set gels can be thinned if necessary with heat using steam or by applying fresh crude. In almost every case unloading would be accomplished in port where a variety of accessable pumps and other equipment would be available.

System Economic Analysis

In most cases, the availability of an oil gelling system should be considered an insurance policy against certain sources of water pollution. The response capability of the system, in time, is the critical factor determining the pollution risk assumed. Lower risk indicates a high system cost resulting from a more expensive and immediately employable system.

Two types of systems can be considered, one protecting each ship plying United States contiguous water, another protecting geographic areas available to any ship in extremities or with a probability of being placed in extremities.

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The shipboard installed system will have the capability to commence gelling the tank in jeopardy in the shortest possible time, thus reducing the free oil lost before gelling starts. If it is assumed that the ship is the Sun Oil Company's Texas Sun with 51,700 DWT capacity, the shipboard installed system will cost $150,000 as listed in Table XV, Equipment List, Concept 1 Gel System, Shipboard Installed. If it is further assumed that four tanks on the ship will need protection and that the chemical life is three years, the chemical cost will be $135,666 per year. The equipment cost, amortized over 20 years, will be $7,500 per year, making a chemical and equipment cost of $143,166 per year. A routine trip for this ship is from the Texas Gulf to Marcus Hook, Pennsylvania, a distance of 1,825 miles. Thirty trips a year carrying 51,700 tons per trip will amount to 2,830 million ton-miles per year. This will result in a ton-mile cost of 0.051 mils. Compared with a 1.13 mils/ton-mile cost for a 2,000-mile haul in a 48,000 DWT tanker, this represents an increased shipping cost of approximately four percent for this protection.

For ships in United States territorial waters which do not have the shipboard installed system, a helicopter transportable system complete with pumps, hoses, and chemicals can be devised which will provide assistance in times of distress. These helicopter systems, if placed every 150 miles along the United States coast, could be in convenient reach of any ship in jeopardy in a relatively short time. At each base, there could be stored sufficient chemicals to gel one 25,000-barrel tank, equivalent to a center tank on the Esso Manhattan. Additional chemicals and equipment, if needed, could be transported from the adjacent helicopter bases. Assuming the dispensing equipment cost is the same as that for a shipboard installed system, equipment stored at the bases with a 20-year expected life would result in a yearly charge of $185,000. The cost of chemicals stored at these sites will total $6,300,000. A three-year chemical life would result in a yearly charge of of $2,100,000 for chemicals. Approximately 100 billion ton-miles of United States waterborne oil transport are traveled each year. This would result in a ton-mile cost of .002 mils and, when compared to the average 1.08 mils per ton-mile cost for a 3,000-mile haul in a 48,000 DWT tanker, represents a shipping cost increase of only 0.18 percent for this protection.

While at first glance the helicopter transported system appears to be a much less costly system, it must be remembered that the time lag between the disaster and the arrival of the equipment and chemicals has allowed oil to freely flow from any rupture. An additional cost will be incurred in the capital costs for the helicopters and the expenses incurred in manning and maintaining the systems.

While some comprehensive studies of the occurrence, nature, and characteristics of tanker spills have recently been made available, most published information tends to dwell heavily on the pollution aspects and results. Important details concerning the location, size

TABLE XV. EQUIPMENT LIST CONCEPT 1 GEL SYSTEM,
SHIPBOARD INSTALLED

Item	Estimated Cost
Isocyanate tank, 30,000-gallon capacity	$ 9,000
Amine tank, 100,000-gallon capacity	20,000
Isocyanate pump, 400 gpm at 100 psi	2,500
Amine pump, 1,000 gpm at 100 psi	5,000
Motor generator, 100 kw diesel driven	12,000
Distributor piping and hose	3,500
Mixing nozzles	2,000
Flexible hose, 100 feet	1,000
Hoist and derrick, portable, extendable	15,000
Electric control panel, starters, etc.	5,000
Electric wiring and cables	3,000
Nitrogen blanket system	2,000
SUB TOTAL	$80,000
Marine engineering	20,000
Installation	50,000
TOTAL ONE TIME COST TO INSTALL	$150,000

and history of the actual leakage for the documented occurrences seem to be generally unavailable.

Likewise, information concerning the historical costs of eliminating the spills and their environmental effects is sketchy and not very precise. Many costs are not included in the published figures, and in fact are not known. Similarly, the volumes of oil spilled and removed are often not known, or appear as very rough estimates. Regardless of the precision of the data, however, there is a need to establish an economic framework in which to evaluate the cost-benefit relationship of a proposed oil spill control system.

Available information indicates that the identified cost to remove spills has ranged from $10 to $50 per barrel of oil spilled. This range does not include many important costs, such as wildlife care and beach rehabilitation, gratis labor and many other costs currently classified as intangibles, necessary to completely restore the environment. It is possible that a more realistic total cost might approach $150 to $200 per barrel.

While the reduction in flow rate under large pressure differentials and rupture sizes, and resistance to water displacement has not yet been accurately defined for the oil gel, it is possible, within the above cost framework, to identify the reduction in pollution required for the system to be economically appealing. The annual cost in chemicals and equipment should be offset by an expected reduction in oil exiting to the general environment, thereby eliminating the clean-up costs for that increment.

Based on an estimated total clean-up cost of $100 per barrel, the shipboard installed and transportable systems should be capable of eliminating the flow of approximately 1,500 and 23,000 barrels per year respectively into the sea to justify the chemical and equipment costs.

Observation of the waste pit during tests indicated that the gelled oil which does leave the ship will tend to remain in lumps and will not form slicks. These characteristics provide other intangible savings in reducing the costs associated with wildlife, marinelife and shoreline damage.

SECTION 6

ACKNOWLEDGEMENTS

SECTION 7

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SECTION 8

GLOSSARY

<u>API</u> - American Petroleum Institute

<u>ABS</u> - American Bureau of Shipping

<u>DWT</u> - Dead Weight Tons, the carrying capacity of a ship

<u>Wing tank</u> - Tanks along the sides of a ship divided into port (left) and starboard (right) tanks

<u>Center tank</u> - A line of tanks in the center of the ship between port and starboard wing tanks

<u>Ullage</u> - The void above the liquid in a tank to allow for expansion, etc.

<u>Stoichiometric ratio</u> - The theoretical chemical combining ratio

<u>The Bingham yield point</u> - The point at which a solid begins to flow when subjected to constantly increasing stress

<u>Penetrometer reading</u> - A measure of gel strength outlined in ASTM-217.

SECTION 9

APPENDICES

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APPENDIX A

SHIPPING CHARACTERISTICS

APPENDIX A

SHIPPING CHARACTERISTICS

There are approximately 3,500 tankers in use worldwide in transporting crude oil and other petroleum products. Of this number, 352 are American flag ships over 10,000 DWT. The United States coastal fleet consists of about 250 tankers with an average carrying capacity of 22,500 DWT or 190,000 barrels of crude oil. Table A-1, Typical United States Built Tankers, is a listing of the tankers which regularly visit United States ports. The tankers unloading at United States ports, whether foreign or domestic, are limited to 100,000 DWT or less by the generally shallow Western hemisphere harbors. The large ships, 150,000 DWT to 350,000 DWT, are mainly used in the Persian Gulf-Western Europe or Persian Gulf-Japan runs.

Prior to 1956, and subsequent to the closing of the Suez Canal, tankers were generally limited to 100,000 DWT, or less, the maximum size which can travel the canal. As a direct result of the canal closing, very large tankers were developed which could operate from the Persian Gulf to Western Europe at less cost than smaller ships using the canal. Now under contract to class in 33 different countries, according to the American Bureau of Shipping Standards, are 1,795 merchant ships of all types with a gross total of 15,700,000 tons or an average of 8,700 DWT per ship. In 1969, orders were placed for 88 tankers in the 20,000 to 30,000 DWT range. As of the end of 1969, the ABS had classed only 46 tankers over 100,000 DWT. While the trend toward larger ships is apparent (estimated at approximately 110 plus ships in service or on order) for both the Persian Gulf-Japan and Persian Gulf-Western Europe runs, the major portion of world tanker fleet additions are small ships.

Only American built, manned and registered ships can be used in United States coastal traffic, i.e., both load and unload from United States ports. Foreign registered ships can either load or unload at United States ports, not both. This factor coupled with shallow port restrictions promotes the use of relatively smaller United States built ships in United States commerce. In the future, larger tankers may be unloaded offshore into pipelines or smaller shuttle tankers, or use harbors deepened extensively by dredging.

The 1965 waterborne commerce of petroleum products in the United States amounted to 97 billion ton miles, with an estimated 68.8 million tons of crude oil imported via tanker during 1969. The 1969 imports were 40-percent from Canada, 26-percent from Latin America, 15-percent from Africa, 12-percent from the Middle East, and the remainder from the Far East. This indicates that two-thirds of the imports are transported in the same coastal vessels as used in domestic trade. Table A-II, Tanker Fleet of Leading Countries, lists the tankers registered in the top nine countries in 1969.

TABLE A-I.   TYPICAL UNITED STATES BUILT TANKERS

	T2-SE-A1	Olympic Games	Esso Dallas	Western Sun	Esso Gettysburg	Sinclair Texas	Texas Sun	Esso New Orleans	Princess Sophie	Esso Manhattan
Nominal DWT	16,700	18,000	28,000	30,000	35,000	47,000	51,700	67,800	70,000	115,000
Draft (ft)	30	30	33	35	37	38	40	40	44	49
Cargo Capacity (bbl)	141,000	152,200	225,000	251,100	317,700	395,000	418,000	583,000	586,000	1,000,000
Number of Wing Tanks	18	18	20	20	20	14	22	12	28	32
Number of Center Tanks	8	9	10	10	10	11	11	5	14	16
Size of Wing Tanks (ft)	36x17x38	36x18x38	40x22x42	40x24x45	40x27x48	30x80x49	45x30x50	102x35x54	40x35x60	40x40x67
Size of Center Tanks (ft)	36x36x38	36x36x38	40x40x42	40x40x45	40x40x48	40x40x49	45x42x50	102x45x54	40x45x60	40x52x67
Cargo Capacity Wing Tanks (bbl)	4,000	4,200	6,500	7,666*	9,300	22,000	11,150*	34,500	15,000	19,300
Cargo Capacity Center Tanks (bbl)	8,500	8,500	10,000	11,250*	12,500	13,500	16,000*	44,200	19,200	25,000

* Loaded to 4' Ullage

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TABLE A-II. TANKER FLEET OF LEADING COUNTRIES

Country	Ships Under 10,000 DWT	Ships Over 10,000 DWT	Total Tonnage Over 10,000 DWT (Million)	Average DWT (Over 10,000)
Liberia		674	30.8	45,000
Great Britain		400	18.7	46,000
Norway		303	15.6	51,000
Japan	127	161	13.3	82,000
United States	59	352	8.9	25,000
Greece		172	5.7	33,000
Panama	30	140	4.8	34,000
France	41	135	4.2	31,000
Russia	158	167	3.9	23,000

The situations under which it will be necessary to employ the gelling system are varied and serve to identify the operating and employment characteristics which must be designed into the system.

Collision

The greatest potential for accidental oil spills is from collisions. The Liverpool Underwriters Association reported 196 collisions involving 238 tankers occurred during the period of June 1964 to April 1967. Oil spills resulted from 22 of these collisions. The spills resulting from a collision may be minor (a small amount of oil lost from one tank) to major (a large amount of oil lost from more than one tank). There is, however, little likelihood of additional leakage over that caused by the collision. Therefore, if the leaking oil is to be stopped by gelling the oil in the leaking tank, it must be done as soon as possible after the collision. This will require shipboard dispersing and mixing equipment and a supply of gelling chemicals on board. In this type failure, it is likely that only one or two tanks will be involved. Once these are gelled, no further tanks may need to be protected.

Strandings

While the frequency of strandings is considerably less than that of collisions, the percentage and severity of the oil spills is greater. The Liverpool Underwriters Association reported 91 stranding incidents occurred between June 1964 and April 1967, resulting in 17 cases of oil spillage. The oil spills resulting from strandings, like those from collisions, may be major spills or minor ones. The stranding-caused spills are very likely to increase with time stranded due to the instability of the ship partially out of water and at the mercy of wind and waves. The Torrey Canyon disaster, for instance, started with six of 18 tanks torn open on impact and the remainder of the tanks eventually broken by heavy seas. In another incident, the tanker, Arrow, ran aground on a Wednesday, northeast of Halifax, spilling some Bunker C grade oil. The leakage continued until it split in two the following Sunday, snapping as it balanced on the small reef. The stopping of the oil flow in this type accident will be a two-part operation. First, immediate gelling of the oil in the leaking tanks must be accomplished. The immediate response requirement will place a high priority on a shipboard-carried system. Gelling of the unruptured tanks of oil will prevent their loss in the event of further breakup. This may be done in a non-emergency made using additional chemicals supplied by barge, boat or helicopter.

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Structural Failures

The occurrence of Group I structural failures in United States ships since World War II is well documented. A Group I fracture is one that is at least 10 feet long and has weakened the main hull structure sufficiently to either sink the ship or place it in a dangerous condition until repaired. During the period of 1943 through 1963, there were 116 recorded Group I casualties of United States tankers, mostly World War II built tankers. Improper loading, poor structural details and notch sensitive steel were principal causes of failure. While this is a low probability type failure, there is clearly a potential source of oil spills. Often there is a total fracture of the hull, separating the power source and pumping equipment from part of the cargo. Once the casualty has occurred, there is little chance that other tanks will begin leaking oil.

Here again, a quick gelling operation must be done on the leaking tanks, along with any in jeopardy, with shipboard equipment and chemicals.

Explosion and Fire

Fire is probably the most common disaster which may confront a petroleum tanker. If a tank is ruptured as a result of the fire, the petroleum cargo probably will burn, thus preventing widespread water pollution. The gelling of the adjacent tanks, or any tank in jeopardy, with shipboard equipment and chemicals would result in a petroleum product with a reduced vapor pressure, thus reducing its flammability.

Summary

The holes in ships which will require the gelling technique to stop the outflow of oil are as varied as the types of accidents which may befall the ship. In the event of a collision, the hole will be expected to occur through the waterline, be fairly large, and may not get larger with the passage of time.

In the event of a stranding or grounding, the hole will be expected to occur below the waterline, principally on the bottom of the ship. The character and size of the hole will be dependent on the obstruction struck. Also, the hole will likely get worse with the passage of time, due to the instability of the ship and the unusual stresses produced. The differential pressures between the oil inside the tank and seawater outside at the rupture will not be great, with equilibrium being reached in short order, except when significant tidal action occurs.

The holes formed by structural failures are likely to be large and quickly formed. The crack will usually stop at some crack-arresting discontinuity, and not propogate unless additional stress is placed on the area.

Summarizing, the holes which will require plugging are likely to be large; i.e., several square feet, above, at or below the waterline and quickly formed.

In order to stop flow through such openings, both from an external tank rupture into the water or via an external tank from a subsequently ruptured interior tank, the gelled oil must have the ability to bridge the gap:

- over a potential maximum rupture dimension of several feet,

- under a variety of possible pressure differentials, and

- without losing its integrity by itself rupturing and flowing.

These requirements indicate the need for a gelled oil with high elasticity, shear, and tensile strength in bending.

While the potential pressure conditions under which the gel will be placed in practice can be readily reproduced in laboratory-scale tests, the physical dimensions of the rupture, or gap over which it must operate, cannot be readily reproduced. These dimensions can only be achieved in large-scale tests. The numbers and character of the variables involved make a theoretical approach impossible. Prior work in these phenomena were determined in the Basic Contract to be insufficient and inappropriate. Further work in this area was beyond the scope and intent of this program.

APPENDIX B

PENETROMETER USE

APPENDIX B

PENETROMETER USE

The test procedure given by ASTM-217 was followed to measure gel strength by use of a penetrometer. A summary of this method follows:

1. The unworked gel (or grease) was adjusted to 77°F and placed in position for test.

2. The tip of the cone was brought to the top (level surface) of the gel.

3. The cone was released and allowed to fall or reach equilibrium for five seconds.

4. The cone travel was measured in tenths of millimeters read direct from the dial.

Two cones were used during testing, a heavier brass cone (102.5 grams) and a lighter aluminum cone (35.0 grams). The holding movable attachment to the penetrometer weighed 47.5 grams. Thus, the total weight exacted by each cone was:

Brass	150.0 grams
Aluminum	82.5 grams

The cone used in each test is indicated by (Br) or (Al). All measurements are reported as tenths of millimeters of cone travel, with notation given as to which cone was used.

Cone travel may be converted to various pressure units due to the fact that the wetted surface area of the cone is constantly increasing during its fall; however, the general formula for the calculation of pressure is:

$$\text{Pressure} = \frac{\text{Weight cone - buoyancy}}{\text{Total wetted surface area}}$$

The buoyancy must be determined from volume displacement multiplied by the specific gravity of the medium. The volume of a cone is given by:

$$V = \pi/3 \; r^2 h$$

and the surface area by:

$$A = \pi r \sqrt{r^2 + h^2}$$

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For any cone drop greater than 15 mm (150 mm/10) the general formula for pressure may be resolved to:

$$\text{Dynes}\Big/\text{cm}^2 = \left[\frac{\text{wt cone in gms-sp gr }(1.047)(H-1.081)^3+.1987)}{(4.4429)(H-1.1081)^2 + 1.2714}\right]980.7$$

$$\text{Grams}\Big/\text{in}^2 = \frac{\text{wt cone in gms-sp gr }(1.047)(H-1.081)^3 + .1987}{(4.4429)(H-1.081)^2 + 1.2714/6.452}$$

where H is cone travel in centimeters (1 centimeter = 100 mm/10).
For conversion 69, 109 dynes/cm² = 453.6 gm/in² = 1 pound/in².

When using the Bingham Body and pseudoplastic type gels, a penetrometer cone drop greater than about 275 mm/10 (Br) is equivalent to a gel that will slump when erected in a column 3 inches high and 3 1/2 inches in diameter. A gel reading greater than 325 mm/10 will pour from a beaker. Due to the wide variety of physical properties of gels, these numbers can only be considered as a rule of thumb.

 WHAT IS WEIGHT ØF CØNE IN GRAMS
? 150.
WHAT IS SPECIFIC GRAVITY ØF MEASURED MEDIUM   BRASS
? .892

CHART ØF 10TH MM CØNE DROP VS. DYNES/SQ.CM. DIVIDED BY 100

	0	1	2	3	4	5	6	7	8	9
15	717.7	704.8	692.0	679.3	666.9	654.6	642.6	630.7	619.0	607.6
16	596.3	585.2	574.3	563.7	553.2	543.0	532.9	523.0	513.4	503.9
17	494.6	485.5	476.6	467.9	459.4	451.0	442.8	434.8	427.0	419.4
18	411.9	404.5	397.3	390.3	383.5	376.7	370.2	363.7	357.5	351.3
19	345.3	339.4	333.6	328.0	322.5	317.1	311.8	306.6	301.6	296.6
20	291.8	287.1	282.4	277.9	273.4	269.1	264.8	260.7	256.6	252.6
21	248.7	244.8	241.1	237.4	233.8	230.3	226.8	223.4	220.1	216.8
22	213.6	210.5	207.5	204.4	201.5	198.6	195.8	193.0	190.3	187.6
23	185.0	182.4	179.9	177.4	175.0	172.6	170.3	168.0	165.7	163.5
24	161.3	159.2	157.1	155.0	153.0	151.0	149.1	147.2	145.3	143.4
25	141.6	139.8	138.1	136.3	134.6	133.0	131.3	129.7	128.1	126.6
26	125.0	123.5	122.1	120.6	119.2	117.8	116.4	115.0	113.7	112.3
27	111.0	109.7	108.5	107.2	106.0	104.8	103.6	102.5	101.3	100.2
28	99.1	98.0	96.9	95.8	94.8	93.7	92.7	91.7	90.7	89.7
29	88.8	87.8	86.9	86.0	85.1	84.2	83.3	82.4	81.6	80.7
30	79.9	79.0	78.2	77.4	76.6	75.9	75.1	74.3	73.6	72.8
31	72.1	71.4	70.7	70.0	69.3	68.6	67.9	67.3	66.6	65.9
32	65.3	64.7	64.0	63.4	62.8	62.2	61.6	61.0	60.5	59.9
33	59.3	58.8	58.2	57.6	57.1	56.6	56.0	55.5	55.0	54.5
34	54.0	53.5	53.0	52.5	52.0	51.6	51.1	50.6	50.2	49.7
35	49.3	48.8	48.4	47.9	47.5	47.1	46.7	46.2	45.8	45.4
36	45.0	44.6	44.2	43.8	43.5	43.1	42.7	42.3	41.9	41.6
37	41.2	40.9	40.5	40.1	39.8	39.5	39.1	38.8	38.4	38.1
38	37.8	37.5	37.1	36.8	36.5	36.2	35.9	35.6	35.3	35.0
39	34.7	34.4	34.1	33.8	33.5	33.2	32.9	32.6	32.4	32.1
40	31.8	31.6	31.3	31.0	30.8	30.5	30.2	30.0	29.7	29.5
41	29.2	29.0	28.7	28.5	28.3	28.0	27.8	27.6	27.3	27.1
42	26.9	26.6	26.4	26.2	26.0	25.7	25.5	25.3	25.1	24.9
43	24.7	24.5	24.3	24.1	23.9	23.7	23.5	23.3	23.1	22.9
44	22.7	22.5	22.3	22.1	21.9	21.7	21.5	21.3	21.2	21.0

EXAMPLE: 246 MM/10 CØNE TRAVEL INDICATES 14,910 DYNES/SQ CM

WHAT IS WEIGHT ØF CØNE IN GRAMS
? 82.5
WHAT IS SPECIFIC GRAVITY ØF MEASURED MEDIUM   ALUMINUM
? .892

CHART ØF 10TH MM CØNE DRØP VS. DYNES/SQ.CM. DIVIDED BY 100

	0	1	2	3	4	5	6	7	8	9
15	395.0	387.9	380.8	373.9	367.0	360.3	353.6	347.1	340.6	334.3
16	328.1	322.0	316.0	310.1	304.3	298.7	293.1	287.7	282.3	277.1
17	272.0	267.0	262.1	257.3	252.6	248.0	243.4	239.0	234.7	230.5
18	226.3	222.3	218.3	214.5	210.7	207.0	203.3	199.8	196.3	192.9
19	189.6	186.3	183.1	180.0	177.0	174.0	171.1	168.2	165.4	162.7
20	160.0	157.4	154.8	152.3	149.9	147.5	145.1	142.8	140.5	138.3
21	136.2	134.1	132.0	129.9	127.9	126.0	124.1	122.2	120.4	118.6
22	116.8	115.1	113.4	111.7	110.1	108.5	106.9	105.3	103.8	102.4
23	100.9	99.5	98.1	96.7	95.4	94.0	92.7	91.5	90.2	89.0
24	87.8	86.6	85.4	84.3	83.2	82.1	81.0	79.9	78.9	77.8
25	76.8	75.8	74.8	73.9	72.9	72.0	71.1	70.2	69.3	68.5
26	67.6	66.8	65.9	65.1	64.3	63.5	62.8	62.0	61.2	60.5
27	59.8	59.1	58.4	57.7	57.0	56.3	55.6	55.0	54.3	53.7
28	53.1	52.5	51.9	51.3	50.7	50.1	49.5	49.0	48.4	47.9
29	47.3	46.8	46.3	45.8	45.2	44.7	44.2	43.8	43.3	42.8
30	42.3	41.9	41.4	41.0	40.5	40.1	39.6	39.2	38.8	38.4
31	38.0	37.5	37.1	36.8	36.4	36.0	35.6	35.2	34.8	34.5
32	34.1	33.8	33.4	33.0	32.7	32.4	32.0	31.7	31.4	31.0
33	30.7	30.4	30.1	29.8	29.5	29.2	28.9	28.6	28.3	28.0
34	27.7	27.4	27.1	26.8	26.6	26.3	26.0	25.8	25.5	25.2
35	25.0	24.7	24.5	24.2	24.0	23.7	23.5	23.3	23.0	22.8
36	22.6	22.3	22.1	21.9	21.7	21.4	21.2	21.0	20.8	20.6
37	20.4	20.2	20.0	19.7	19.5	19.3	19.1	19.0	18.8	18.6
38	18.4	18.2	18.0	17.8	17.6	17.4	17.3	17.1	16.9	16.7
39	16.6	16.4	16.2	16.1	15.9	15.7	15.6	15.4	15.2	15.1
40	14.9	14.7	14.6	14.4	14.3	14.1	14.0	13.8	13.7	13.5
41	13.4	13.2	13.1	13.0	12.8	12.7	12.5	12.4	12.3	12.1
42	12.0	11.8	11.7	11.6	11.5	11.3	11.2	11.1	10.9	10.8
43	10.7	10.6	10.4	10.3	10.2	10.1	10.0	9.8	9.7	9.6
44	9.5	9.4	9.3	9.1	9.0	8.9	8.8	8.7	8.6	8.5

EXAMPLE: 492 MM/10 CØNE TRAVEL INDICATES 440 DYNES/SQ CM

APPENDIX C

CHEMICALS AND SUPPLIERS

APPENDIX C

CHEMICALS AND SUPPLIERS

Name	Type	Supplier
N-3-APCHA	Primary amine	Abbott Chemicals
Alamine 3	Primary amine	General Mills
Alamine 4D	Primary amine	General Mills
Alamine 15D	Primary amine	General Mills
Actinol D29LR	Primary amine	Arizona Chemical
Actinol F.A. 2	Primary amine	Arizona Chemical
Actinol F.A. 3	Primary amine	Arizona Chemical
Armeen C	Primary amine	Armour Chemical
Armeen O	Primary amine	Armour Chemical
Armeen L-9	Primary amine	Armour Chemical
Armeen L-7	Primary amine	Armour Chemical
Armeen L-11	Primary amine	Armour Chemical
Armeen L-15	Primary amine	Armour Chemical
2-(2-Aminothalamine)	Diamine	Armour Chemical
Diam 26	Diamine	General Mills
DMAPA	Diamine	Generic
Duomeen C	Diamine	Armour Chemical
3,3-DADPA	Primary amine	Matheson & Coleman
Dicyclohexylamine	Cyclic amine	Matheson & Coleman
DETA	Triamine	Matheson & Coleman
EDA	Diamine	Eastman Organic Chem.
1,6-Hexanediamine	Diamine	Eastman Organic Chem.
N-Hexylamine	Cyclic amine	Eastman Organic Chem.
Neofat 140	Fatty acid	Armour Chemical
Pamak 1	Fatty acid	Hercules, Inc.
Pamak 4	Fatty acid	Hercules, Inc.
Pamak 6	Fatty acid	Hercules, Inc.
Pamak 10	Fatty acid	Hercules, Inc.
Pamak 546A	Fatty acid	Hercules, Inc.
Pamak S1418	Fatty acid	Hercules, Inc.
Pamak DLE	Fatty acid	Hercules, Inc.
P & G L-310	Fatty acid	Procter & Gamble
P & G S-210	Fatty acid	Procter & Gamble
POPDA[++] 190	Diamine	Jefferson Chemical Co.
POPDA[++] 230	Diamine	Jefferson Chemical Co.
POPDA[++] 400	Diamine	Jefferson Chemical Co.
POPDA[++] 1000	Diamine	Jefferson Chemical Co.
POPDA[++] 2000	Diamine	Jefferson Chemical Co.
POPTA[++] 403	Triamine	Jefferson Chemical Co.

[++]POPDA and POPTA are now Jeffamine

Name	Type	Supplier
Emersol 310	Fatty acid	Emery Industries, Inc.
Emersol 305	Fatty acid	Emery Industries, Inc.
Emersol 233	Fatty acid	Emery Industries, Inc.
Emery 3162	Fatty acid	Emery Industries, Inc.
Emersol 315	Fatty acid	Emery Industries, Inc.
RD-3826	Fatty acid	Armour Chemical
S-1598	Fatty acid	Hercules, Inc.
S-1597	Fatty acid	Hercules, Inc.
TC 1678		Hercules, Inc.
TC 1857		Hercules, Inc.
Versadyme 216		General Mills
G-17		General Mills
HMD	Hexylmethyl-diisocyanate	Mobay Chemical
Isonate 136T	Bitolylene diisocyanate	Upjohn
MRS	Polyisocyanate	Mobay Chemical
MT-40	Organic isocyanate	Mobay Chemical
MDI	Methane diisocyanate	Mobay Chemical
NCO-10	Polyisocyanate	Kaiser
TDI 65/35	Toluene diisocyanate 65/35	DuPont Chemical
TDI 80/20	Toluene diisocyanate 80/20	DuPont Chemical
TMD-1	Diisocyanate	Thorson Chemical Corp.
Tonco 90	Octadecyl isocyanate	Upjohn
T.P.M.T.	Triphenyl methane triisocyanate	
TP 2540		
TP 4040		
Mondur O	Octadecyl isocyanate	Mobay Chemical

APPENDIX D

SOAP GEL SCREENING DATA

TABLE D-I. SOAP GEL SCREENING DATA

Components	Gelling Components (% by volume)			Remarks (i.e., viscosity, penetrometer reading, etc.)
	Run 1	Run 2	Run 3	
Actinol D29LR ‡	10	5	2	Shear-sensitive gel.
NaOH	5	2	1	
Actinol F.A. 2	10	5	2	Weak gel formed in Run 1 with viscosity increase to
NaOH	5	2	1	186 cps.
Actinol F.A. 3	10	5	2	Weak and thin gel formed having a viscosity of 130cps
NaOH	5	2	1	(Run 1)
Emersol 305 ‡	10	5	2	Run 1 formed a thin gel of 148 cps. Others were not
NaOH	5	2	1	successful.
Emersol 310	10	5	2	First run yielded a weak dilatent gel. Viscosity
NaOH	5	2	1	increased to 200 cps. Other runs not important.
Emersol 315	10	5	2	Slight viscosity increase in first run, no gels were
NaOH	5	2	1	formed.

‡ Two component systems comprised of NaOH and a proprietary fatty acid.

Components	Gelling Components (% by volume)			Remarks (i.e., viscosity, penetrometer reading, etc.)
	Run 1	Run 2	Run3	
Emersol 233 ⧣	10	5	2	Weak thixotropic gel formed in first run. Others unimportant.
NaOH	5	2	1	
Emery 3162	10	5	2	Waxlike precipitate formed upon standing.
NaOH	5	2	1	
G-17	10	5	2	Forms a heavy precipitate.
NaOH	5	2	1	
Neofat 140	10	5	2	No gels were formed. Oil remained thin. A thin brown crust formed on top of the oil upon standing.
NaOH	5	2	1	
Pamak 1	10	5	2	Viscosity increases but no gels were formed.
NaOH	5	2	1	
Pamak 4 ⧣ ⧣	10	5	2	Thin gel in first run with 200 cps viscosity. Others not important.
NaOH	5	2	1	

⧣ Two component systems comprised of NaOH and a proprietary fatty acid.

⧣ ⧣ Gellation systems showed similar results using CR-280, an ethoxylated dehydroabietylamine as an additive to enhance gellation. Fatty acid was mixed with CR-280 in the ratio of 80 ml fatty acid to 20 ml CR-280.

Components	Gelling Components (% by volume)			Remarks (i.e., viscosity, penetrometer reading, etc.)
	Run 1	Run 2	Run 3	
Pamak 6 ‖	10	5	2	Thin gel formed in first run with 182 cps viscosity. No other runs successful.
NaOH	5	2	1	
Pamak 10	10	5	2	In first run a moderately thick gel was formed. Weaker gel formed in Run 2 and no gel in Run 3.
NaOH	5	2	1	
Pamak 546A	10	5	2	Weak, dilatent gels formed in first run, none in Run 3.
NaOH	5	2	1	
Pamak S1418	10	5	2	Very thin gel formed in first run. Other runs were unsuccessful.
NaOH	5	2	1	
Pamak DLE ‖ ‖	10	5	2	Medium thin gel with some viscosity increase.
NaOH	5	2	1	
P & G L-310	10	5	2	Thin gel with some viscosity increase.
NaOH	5	2	1	

‖ Gellation systems showed similar results using CR-280, an ethoxylated dehydroabietylamine as an additive to enhance gellation. Fatty acid was mixed with CR-280 in the ratio of 80 ml fatty acid to 20 ml CR-280.

Components	Gelling Components (% by volume)			Remarks (i.e., viscosity, penetrometer reading, etc.)
	Run 1	Run 2	Run 3	
P & G S-210 +	10	5	2	Thin gel was formed with some viscosity increase.
NaOH	5	2	1	
S-1597	10	5	2	Thin gel was formed with some viscosity increase.
NaOH	5	2	1	
S-1598 + +	10	5	2	Thin gel was formed with some viscosity increase.
NaOH	5	2	1	
TC 1678 + +	10	5	2	Thin gel was formed with some viscosity increase.
NaOH	5	2	1	
TC 1857	10	5	2	Thin gel was formed with some viscosity increase.
NaOH	5	2	1	
Versadyme 216	10	5	2	Precipitate formed, no gel.
NaOH	5	2	1	

+ Gellation systems showed similar results using CR-280, an ethoxylated dehydroabietylamine as an additive to enhance gellation. Fatty acid was mixed with CR-280 in the ratio of 80 ml fatty acid to 20 ml CR-280.

TABLE D-II. SOAP GEL SCREENING DATA

Components	Gelling Components (% by volume)			Remarks (i.e., viscosity, penetrometer reading, etc.)
	Run 1	Run 2	Run 3	
Actinol F. A. 2	10	5	2	Gel formed in Run 1. Other runs unsuccessful.
NaOH	5	2	1	
Actinol F.A. 3	10	5	2	Thin gel in all except Run 3.
NaOH	5	2	1	
Emersol 310	10	5	2	Waxlike precipitate formed upon standing.
NaOH	5	2	1	
Emery 3162	10	5	2	Thin gel with high viscosity in first run, others unsuccessful.
NaOH	5	2	1	
Neofat 140	10	5	2	Thin gel with high viscosity in first run, other unsuccessful.
NaOH	5	2	1	
Pamak 1	10	5	2	Weak gels formed in Runs 1 and 2. Noticeable viscosity increase.
NaOH	5	2	1	

Components	Gelling Components (% by volume)			Remarks (i.e., viscosity, penetrometer reading, etc.)
	Run 1	Run 2	Run 3	
Pamak 10	10	5	2	No gel formation. Only slight viscosity increase.
NaOH	5	2	1	
Pamak S1418	10	5	2	First run yielded a thick greaselike gel. Second run was a thin gel with slight viscosity increase.
NaOH	5	2	1	
Pamak 546A	10	5	2	First run yielded a thick greaselike gel. Second run was a thin gel with slight viscosity increase.
NaOH	5	2	1	
P & G L-310	10	5	2	First run yielded a thick greaselike gel. Second run was a thin gel with slight viscosity increase.
NaOH	5	2	1	
S-1597	10	5	2	First run showed thick visco-elastic gel. Other runs were unsuccessful.
NaOH	5	2	1	

APPENDIX E

SWELLING GEL SCREENING DATA

TABLE E-I.   SWELLING GEL SCREENING DATA

Gelling Agent	Percentage	Remarks
Aluminum Octoate	> 20	No gel
Special Lithium Isostearate	> 20	No gel
Alumagel	> 20	Weak gel
Aluminum Stearate	> 20	No gel
Zinc Soap	> 20	No gel
Calcium Stearate	> 20	No gel

APPENDIX F

ISOCYANATE/AMINE GEL SCREENING DATA

TABLE F-I.   AMINE TONCO 90 GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i. e. , viscosity, penetrometer reading, etc.)
Alamine 3 Tonco 90	1. 50 3. 50	No gel, slight viscosity increase.
Alamine 4D Tonco 90	1. 90 3. 10	No gel, slight viscosity increase.
Alamine 15D Tonco 90	2. 40 2. 60	No gel, slight viscosity increase.
Armeen L-7 Tonco 90	1. 40 3. 60	Shear-sensitive, thin gel.
Armeen L-9 Tonco 90	3. 02 1. 98	Shear-sensitive, thin gel.
Armeen L-9 Tonco 90	1. 65 3. 40	Thick & firm gel formed.
Armeen L-11 Tonco 90	1. 80 3. 20	No gel, no viscosity increase.
Armeen L-15 Tonco 90	2. 20 2. 80	No gel, no viscosity increase.
Armeen O Tonco 90	2. 35 2. 60	Thin, shear-sensitive gel.

Components	Gelling Components (% By Weight)	Remarks (i.e. viscosity, penetrometer reading, etc.)
Armeen C Tonco 90	1.95 3.10	Thin, shear-sensitive gel.
Diam 26 Tonco 90	1.80 3.20	Thin gel formed.
DMAPA Tonco 90	1.30 3.70	Firm, homogeneous gel formed.
Dicyclo hexylamine Tonco 90	1.90 3.10	No gel and no viscosity increase.
Duomeen C Tonco 90	1.40 3.60	No gel, slight viscosity increase.
N-Hexylamine Tonco 90	1.30 3.70	Shear-sensitive, thin gel.
POPDA 190 Tonco 90	1.20 3.70	Shear-sensitive, thin gel.
POPDA 190 Tonco 90	0.60 4.40	No gel, increase in viscosity.
POPDA 230 Tonco 90	1.40 3.60	No gel, increase in viscosity.
POPDA 1000 Tonco 90	3.15 1.85	Shear-sensitive, thin gel.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
POPDA 2000 Tonco 90	3.90 1.15	No gel, no viscosity increase.
POPTA 403 Tonco 90	1.55 3.40	No gel, slight viscosity increase.

Two component systems a proprietary amine and a proprietary isocyanate.

TABLE F-II. AMINE HMD GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Alamine 3 HMD	3.00 2.00	Spontaneous formation of good gel.
Alamine 4D HMD	3.40 1.60	Spontaneous formation of good gel.
Alamine 4D HMD	4.10 0.90	No gel, increase in viscosity.
Alamine 15D HMD	3.80 1.20	Spontaneous formation of good gel.
Alamine 15D HMD	4.60 0.40	Thin gel with viscosity increase.
Alamine 15D HMD	3.60 1.40	A shear-sensitive precipitate gel formed.
Diam 26 HMD	3.30 1.70	Formation of a grainy precipitate gel. Shear sensitive.
DMAPA HMD	2.60 2.40	Formation of a shear-sensitive, weak gel.
Armeen L-11 HMD	4.10 0.90	Firm, thixotropic gel.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Duomeen HMD	3.00 2.00	Formation of shear-sensitive, firm gel.
Ethylenediamine HMD	1.30 3.70	No gel, increase in viscosity.
1,6-Hexanediamine HMD	2.00 3.00	No gel, increase in viscosity.
Armeen L-11 HMD	3.40 1.60	Formation of a strong, firm gel.
Armeen L-11 HMD	3.10 1.90	No gel, increase in viscosity.
Armeen L-15 HMD	4.40 0.60	Good gel formation. Thick and homogeneous.
Armeen L-15 HMD	3.10 1.90	No gel, noticeable increase in viscosity.
Armeen L-15 HMD	3.70 1.30	Formation of strong, firm gel.
N-Hexylamine HMD	2.70 2.30	Spontaneous formation of tough gel.
N-Hexylamine HMD	1.10 0.90	Formation of non shear-sensitive gel. (2%)

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Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
N-Hexylamine HMD	3.20 1.80	Formed good, thick gel.
N-Hexylamine HMD	2.20 2.80	Good, firm gel. Highly thixotropic.
RD 3826 HMD	3.50 1.50	Formed good, firm gel. Not shear sensitive.
Two component systems a proprietary amine and a proprietary isocyanate.		

TABLE F-III. AMINE MT-40 GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Alamine 4D MT-40	3.10 1.85	Thin gel, shear sensitive.
Alamine 15D MT-40	3.60 1.45	Thin gel, shear sensitive.
Armeen C MT-40	3.20 1.80	Firm and thixotropic gel.
Armeen O MT-40	3.60 1.40	No gel. Thin liquid.
3,3-DADPA MT-40	1.55 3.45	Thin gel. Shear sensitive.
Diam 26 MT-40	3.10 1.95	Thin gel. Shear sensitive.
Dicyclohexylamine MT-40	3.00 2.00	No gel. Thin liquid.
DMAPA MT-40	2.45 2.50	No gel. Thin liquid.
Duomeen C MT-40	3.40 1.60	Thick, greaselike gel. Shear sensitive.

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Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading. etc.)
EDA MT-40	3.70 1.30	Thin liquid, no viscosity increase.
1,6-Hexylamine MT-40	1.80 3.20	No gel. Slight viscosity increase.
L-7 MT-40	2.60 2.40	Thin, shear-sensitive gel. Viscosity increase.
L-9 MT-40	2.90 2.10	Thin, shear sensitive gel. Viscosity increase.
L-11 MT-40	3.10 1.90	Thin, shear-sensitive gel. Viscosity increase.
L-15 MT-40	3.40 1.60	Thin liquid only slight viscosity increase.
N-3-APCHA MT-40	3.20 1.85	Very thin liquid. Granular precipitate was formed.
N-Hexylamine MT-40	2.45 2.55	Shear sensitive, thin gel formed.
POPDA 190 MT-40	2.40 2.65	Shear-sensitive, thin gel formed.
POPDA 230 MT-40	2.30 2.65	No gel. Some viscosity increase.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
POPDA 400 MT-40	3.00 2.00	Large mass of precipitate forms.
POPDA 1000 MT-40	3.95 1.05	Large mass of precipitate forms.
POPDA 2000 MT-40	4.36 0.60	Large mass of precipitate forms.
POPTA 403 MT-40	2.50 2.50	Globular percipitate forms. Increase in viscosity.

Two component systems a proprietary amine and a proprietary isocyanate.

TABLE F-IV. AMINE MRS GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Alamine 4D MRS	2.90 2.10	No gel, some viscosity increase.
Alamine 15D MRS	3.30 1.65	Very thin gel. Noticeable increase in viscosity.
Armeen C MRS	2.90 2.10	Shear-sensitive, weak gel, 100 cps.
Armeen O MRS	3.35 1.65	Shear-sensitive weak gel. Viscosity increase to 200 cps.
Diam 26 MRS	2.80 2.20	Grainy precipitate settled upon standing.
Dicyclohexylamine MRS	2.70 2.30	No gel, slight viscosity increase.
DMAPA MRS	2.20 2.80	Insoluable mass settles out as precipitate.
3,3-DADPA MRS	3.90 1.10	No gel, no viscosity increase.
Duomeen C MRS	3.15 1.85	No gel, some increase in viscosity.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
1,6-Hexanediamine MRS	1.50 3.45	Shear-sensitive, grainy gel. Some viscosity increase.
L-7 MRS	2.30 2.70	Increase in viscosity but no gel.
L-9 MRS	2.60 2.40	Increase in viscosity but no gel.
L-11 MRS	2.80 2.20	Increase in viscosity but no gel.
L-15 MRS	3.15 1.85	Increase in viscosity but no gel.
POPDA 190 MRS	2.10 2.90	Forms granular precipitate upon standing.
POPDA 230 MRS	2.30 2.65	No gel. Slight increase in viscosity.
POPDA 400 MRS	3.00 2.00	Forms large mass of spongy precipitate.
POPDA 1000 MRS	3.95 1.05	Forms large mass of spongy precipitate.
POPDA 2000 MRS	4.35 0.60	Forms large mass of spongy precipitate.

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Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
POPTA 403 MRS	2.50 2.50	Globular precipitate formed
N-Hexylamine MRS	2.15 2.85	Only slight increase in viscosity.
Two component systems a proprietary amine and a proprietary isocyanate.		

TABLE F-V. AMINE MDI GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity penetrometer reading, etc.)
Armeen C MDI	2.20 2.80	Thin, shear-sensitive gel.
Armeen C MDI	1.64 3.36	Thin, shear-sensitive gel.
L-7 MDI	1.50 3.50	Thin, shear-sensitive gel.
L-7 MDI	1.22 3.78	Large amount of precipitate settled out.
Armeen O MDI	2.65 2.30	Large amount of precipitate settled out.
Armeen O MDI	2.24 2.76	Large amount of precipitate settled out.
L-9 MDI	1.80 3.25	Large amount of precipitate settled out.
L-9 MDI	1.10 3.90	Waxlike precipitate formed upon standing.
Two component systems a proprietary amine and a proprietary isocyanate.		

TABLE F-VI. AMINE ISONATE 136-T GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Armeen C Isonate 136-T	2.05 2.95	Thin, shear-sensitive gel.
Armeen C Isonate 136-T	1.46 3.54	Thin, shear-sensitive gel.
L-7 Isonate 136-T	1.50 3.50	Thin, shear-sensitive gel.
L-7 Isonate 136-T	0.80 4.20	No gel, slight viscosity increase.
L-9 Isonate 136-T	1.80 3.20	Thin grainy gel. Shear sensitive.
L-9 Isonate 136-T	1.16 3.84	Weak, shear-sensitive gel.
Armeen O Isonate 136-T	2.50 2.50	Thin gel. Shear sensitive.
Armeen O Isonate 136-T	2.00 3.00	Thin gel. Shear sensitive.
Two component systems a proprietary amine and a proprietary isocyanate.		

TABLE F-VII. AMINE TDI 65/35 GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Duomeen C TDI 65/35	3.00 2.00	Spontaneous formation of shear-sensitive gel.
Duomeen C TDI 65/35	1.60 3.40	Spontaneous formation of non-globular type of slurry.
EDA TDI 65/35	1.30 3.70	No gel, only viscosity increase.
EDA TDI 65/35	0.50 4.50	No gel, only viscosity increase.
1,6-Hexanediamine TDI 65/35	2.00 3.00	No gel, only viscosity increase.
1,6-Hexanediamine TDI 65/35	1.00 4.00	No gel, only viscosity increase.

Two component systems a proprietary amine and a proprietary isocyanate.

TABLE F-VIII. AMINE NCO-10 GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Alamine 3 NCO-10	2.50 2.50	Formation of globular precipitate. Increase in viscosity.
Alamine 4D NCO-10	2.90 2.10	Heavy precipitate formed. Slight viscosity increase.
Alamine 15D NCO-10	3.30 1.70	Spontaneous formation of grainy gel.
Armeen C NCO-10	2.90 2.10	Shear-sensitive weak gel.
Armeen C NCO-10	3.48 1.52	Thin liquid, some increase in viscosity.
Armeen C NCO-10	2.48 2.52	No gel, only viscosity increase.
Armeen O NCO-10	1.65 3.30	Grainy gel. Thick and greaselike.
Armeen O NCO-10	1.98 3.00	Firm, thixotropic gel formed.
Armeen O NCO-10	3.30 1.65	Thick and firm gel formed.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
DADPA NCO-10	1.65 3.35	Thin, runny liquid.
DETA NCO-10	1.39 3.61	Grainy precipitate formed.
Diam 26 NCO-10	2.80 2.20	Slow formation of non-globular precipitate.
DMAPA NCO-10	2.00 3.00	No gel, some viscosity increase.
Duomeen C NCO-10	2.40 2.60	No gel, no viscosity increase.
Duomeen C NCO-10	2.40 2.60	No gel, no viscosity increase.
1,6-Hexanediamine NCO-10	1.50 3.50	Slow formation of a weak gel.
N-Hexylamine NCO-10	2.20 2.80	Formed a precipitate.
L-7 NCO-10	2.65 2.35	No gel only viscosity increase.
L-9 NCO-10	2.60 2.40	No gel only viscosity increase.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
L-9 NCO-10	2.12 2.88	Smooth, thin gel formed.
L-11 NCO-10	2.80 2.20	Weak gel formed.
L-11 NCO-10	5.60 4.40	No gel was formed, only large amount of precipitate.
L-11 NCO-10	3.40 1.60	Shear-sensitive, weak gel.
L-11 NCO-10	2.40 2.60	Shear-sensitive, weak gel.
L-15 NCO-10	1.90 3.10	Good gel formed.
L-15 NCO-10	2.30 2.70	Fairly good gel.
L-15 NCO-10	1.30 3.70	No gel, no viscosity increase.
POPDA 190 NCO-10	2.06 2.94	Increase in viscosity, no gel.
POPDA 230 NCO-10	2.30 2.70	Increase in viscosity, no gel.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
POPDA 230 NCO-10	1.80 3.20	Increase in viscosity, no gel.
POPDA 230 NCO-10	2.80 2.20	Large amount of precipitate. formed.
POPDA 400 NCO-10	3.00 2.00	Large amount of precipitate formed.
POPDA 400 NCO-10	2.6 2.4	Mushy gel with globular precipitate.
POPDA 400 NCO-10	3.60 1.40	Globular precipitate settled out.
POPDA NCO-10	4.00 1.00	Precipitate settled out on standing.
POPDA NCO-10	4.40 0.60	Precipitate settled out on standing.
POPTA 403 NCO-10	2.50 2.50	Grainy gel formed.
POPTA 403 NCO-10	2.00 3.00	Shear-sensitive, grainy gel.
POPTA 403 NCO-10	3.00 2.00	No gel. Some viscosity increase.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity penetrometer reading, etc.)
RD-3826 NCO-10	3.00 2.00	Shear-sensitive gel formed.
TETA NCO-10	1.77 3.23	No gel, slight viscosity increase.
EDA NCO-10	0.90 4.10	No gel, slight viscosity increase.
Two component systems a proprietary amine and a proprietary isocyanate.		

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Alamine 3 TDI 80/20	1.70 3.30	A weak, thixotropic gel formed.
Alamine 3 TDI 80/20	1.40 3.60	No gel, only viscosity increase.
Alamine 4D TDI 80/20	2.30 2.70	Spontaneous formation of good, thixotropic gel.
Alamine 4D TDI 80/20	2.80 2.20	Thin, shear-sensitive gel.
Alamine 4D TDI 80/20	1.70 3.30	Thin, shear-sensitive gel.
Alamine 15D TDI 80/20	2.70 2.30	Shear-sensitive gel formed.
2-2(Aminothalamine) TDI 80/20	2.50 2.50	No gel, very slight increase in viscosity.
Armeen L-7 TDI 80/20	2.80 2.15	Shear-sensitive gel. Gel thick, but not hard.
Armeen L-9 TDI 80/20	2.80 2.20	Shear-sensitive, thin gel.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading etc.)
DADPA TDI 80/20	1.90 3.10	No gel. Only slight viscosity increase.
DETA TDI 80/20	1.63 3.37	Precipitate formed upon standing.
Diam 26 TDI 80/20	2.20 2.80	Precipitate formed upon standing
DMAPA TDI 80/20	2.80 2.20	Weak gel formed.
Duomeen C TDI 80/20	2.50 2.50	Spontaneous formation of globular precipitate.
Duomeen C TDI 80/20	3.20 1.80	Spontaneous formation of grainy gel.
Duomeen C TDI 80/20	2.00 3.00	Precipitate is formed upon standing.
Duomeen C TDI 80/20	1.80 3.20	No gel. Only slight increase in viscosity.
EDA TDI 80/20	0.60 4.40	No gel. Only slight increase in viscosity.
EDA TDI 80/20	1.50 3.50	Precipitate present with only a slight increase in viscosity
Duomeen C TDI 80/20	3.00 2.00	A weak, precipitate gel formed.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
EDA TDI 80/20	1.30 3.70	Spontaneous formation of grainy gel.
1,6-Hexanediamine TDI 80/20	2.00 3.00	No gel. Only slight viscosity increase.
N-Hexylamine TDI 80/20	2.40 2.60	Spontaneous formation of shear-sensitive gel.
N-Hexylamine TDI 80/20	6.60 5.40	Spontaneous formation of firm gel.
POPDA 190 TDI 80/20	2.30 2.70	Only slight viscosity increase.
POPDA 230 TDI 80/20	2.50 2.50	Only slight viscosity increase.
POPDA 400 TDI 80/20	3.20 1.80	Globular precipitate formed.
POPDA 400 TDI 80/20	2.80 2.20	Only slight viscosity increase.
POPDA 400 TDI 80/20	1.20 0.67	Weak semi-solid gel formed.
POPDA TDI 80/20	4.10 0.90	Formation of globular precipitate.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
POPDA 2000 TDI 80/20	4.50 0.50	Formation of globular precipitate.
POPTA 403 TDI 80/20	2.70 2.25	Formation of a thin gel.
POPTA 403 TDI 80/20	3.30 1.70	Only slight increase in viscosity.
RD-3826 TDI 80/20	2.40 2.60	No gel. Precipitate formed.
TEPA TDI 80/20	2.40 2.60	No gel. Precipitate formed.
TETA TDI 80/20	2.03 2.97	No gel, only slight viscosity increase.
Two component systems a proprietary amine and a proprietary isocyanate.		

TABLE F-X. AMINE T.P.M.T. GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
EDA T.P.M.T.	1.00 4.00	Spontaneous formation of a precipitate.
1,6-Hexanediamine T.P.M.T.	1.60 3.40	Spontaneous formation of a precipitate.
Duomeen C T.P.M.T.	2.50 2.50	Spontaneous formation of a precipitate.
Armeen L-11 TP 2540 and TDI	0.70 4.30	No gel and no viscosity increase.
1,6-Hexanediamine TP 2540 and TDI	0.30 4.70	Formed a precipitate.
Armeen L-11 TP 4040 and TDI	0.50 4.50	No gel, no viscosity increase.
1,6-Hexanediamine TP 4040 and TDI	0.20 4.80	Formed a precipitate.

Two component systems a proprietary amine and a proprietary isocyanate.

TABLE F-XI. AMINE TMD-1 GEL SCREENING DATA

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Alamine 4D TMD-1	3.10 1.85	Shear-sensitive, weak gel forms upon standing.
Alamine 15D TMD-1	3.60 1.45	No gel, no viscosity increase.
N-3-APCHA TMD-1	3.20 1.80	Insoluable mass settles out upon standing.
Armeen C TMD-1	3.20 1.80	Formation of firm gel. Shear-sensitive to viscosity check.
Armeen O TMD-1	3.60 1.40	No gel and no viscosity increase.
Armeen L-7 TMD-1	2.60 2.40	Formation of a precipitate upon standing.
Armeen L-9 TMD-1	2.90 2.10	Formation of a precipitate upon standing.
Armeen L-11 TMD-1	3.10 1.90	No gel, only slight viscosity increase.
Armeen L-15 TMD-1	3.40 1.60	No gel, only slight viscosity increase.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
Dicyclohexylamine TMD-1	3.00 2.00	No gel, no viscosity increase.
DMAPA TMD-1	2.45 2.50	Precipitate settles out upon standing.
Duomeen C TMD-1	3.40 1.60	Formation of homogeneous and thick gel.
Diam 26 TMD-1	3.10 1.95	Globular precipitate forms upon standing.
3,3-DADPA TMD-1	1.55 3.45	No gel, slight viscosity increase.
POPDA 190 TMD-1	2.40 2.65	Thin, globular precipitate forms upon standing.
POPDA 230 TMD-1	2.60 2.40	Mass of precipitate formed upon standing.
POPDA 400 TMD-1	3.30 1.70	Mass of precipitate formed upon standing.
POPDA 1000 TMD-1	4.10 0.90	Mass of precipitate formed upon standing.
POPDA 2000 TMD-1	4.60 0.40	No gel, no viscosity increase.

Components	Gelling Components (% By Weight)	Remarks (i.e., viscosity, penetrometer reading, etc.)
POPTA 403	2.80	Globular precipitate forms
TMD-1	2.20	upon standing.

Two component systems a proprietary amine and a proprietary isocyanate.

APPENDIX G

STABILITY IN STORAGE TESTS FOR
GEL CONSTITUENTS

APPENDIX G

STABILITY IN STORAGE TESTS FOR
GEL CONSTITUENTS

Procedure for determining equivalent weight of amines (total amines):

1. Accurately weigh three grams of amine.

2. Place amine into Erlenmeyer flask. Add 40 milliliters of dry isopropanol (99%).

3. Add one milliliter of bromcresol green indicator and with agitation, titrate to yellow end point with about .5N HCl.

4. Calculate equivalent weight of the amine as follows:

$$\text{equiv wt amine} = \frac{(1,000 \text{ x (wt amine added)}}{(\text{ml of acid added) x (N of acid)}}$$

Procedure for determining equivalent weight of isocyanates:

1. Accurately weigh three grams of isocyanates to be checked.

2. Place isocyanate into Erlenmeyer flask and add 25 milliliters dry toluene.

3. Accurately weigh nine grams of dibutylamine.

4. Add amine to flask containing isocyanate and toluene and warm. Let stand for 15 minutes before titrating.

5. Add 100 milliliters of dry isopropanol (99%).

6. Add one milliliter bromcresol green indicator and titrate to yellow end point with about .5N HCl.

7. Calculate equivalent weight of isocyanate as follows:

$$\text{equiv wt isocyanate} = \frac{\text{wt isocyanate added}}{\frac{\text{wt amine added}}{\text{equiv wt of amine}} - \frac{\text{(ml of HCl) x (N of HCl}}{1,000}}$$

The equivalent weights should be determined once at the beginning of storage period for reference and then at any doubtful interval.

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APPENDIX H

OPTIMUM RATIO STUDIES
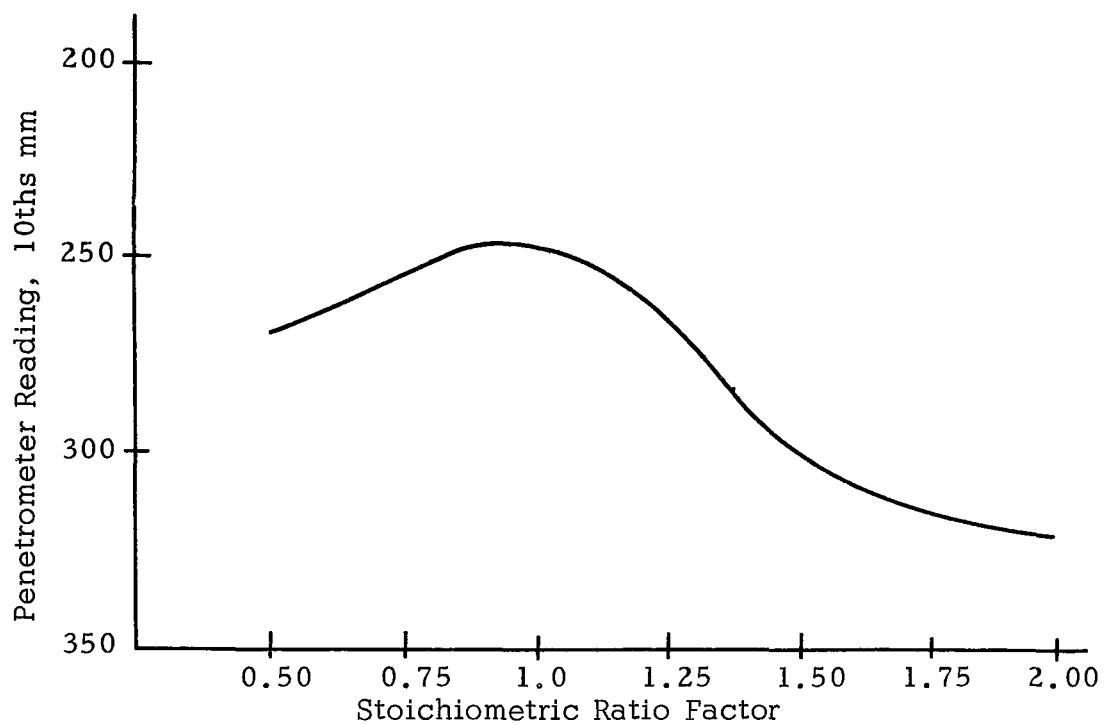
Figure H-1. Armeen C and MT-40
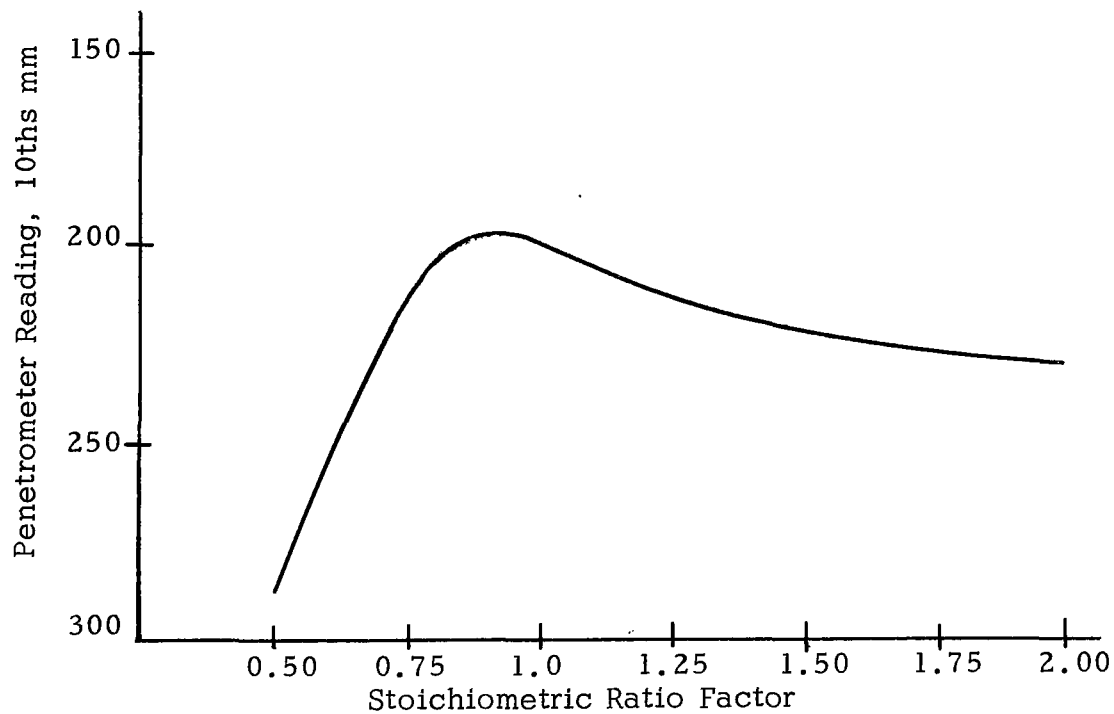
Figure H-2. Jeffamine 400 and Tonco 90
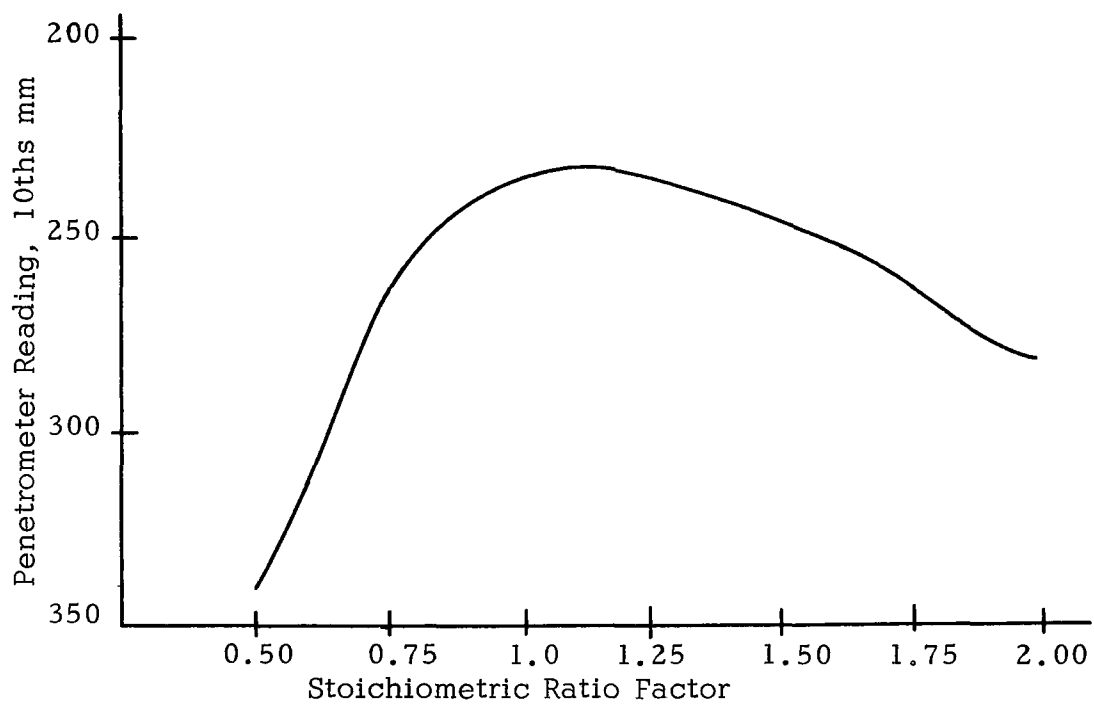
Figure H-3.   Armeen O and TDI 80/20
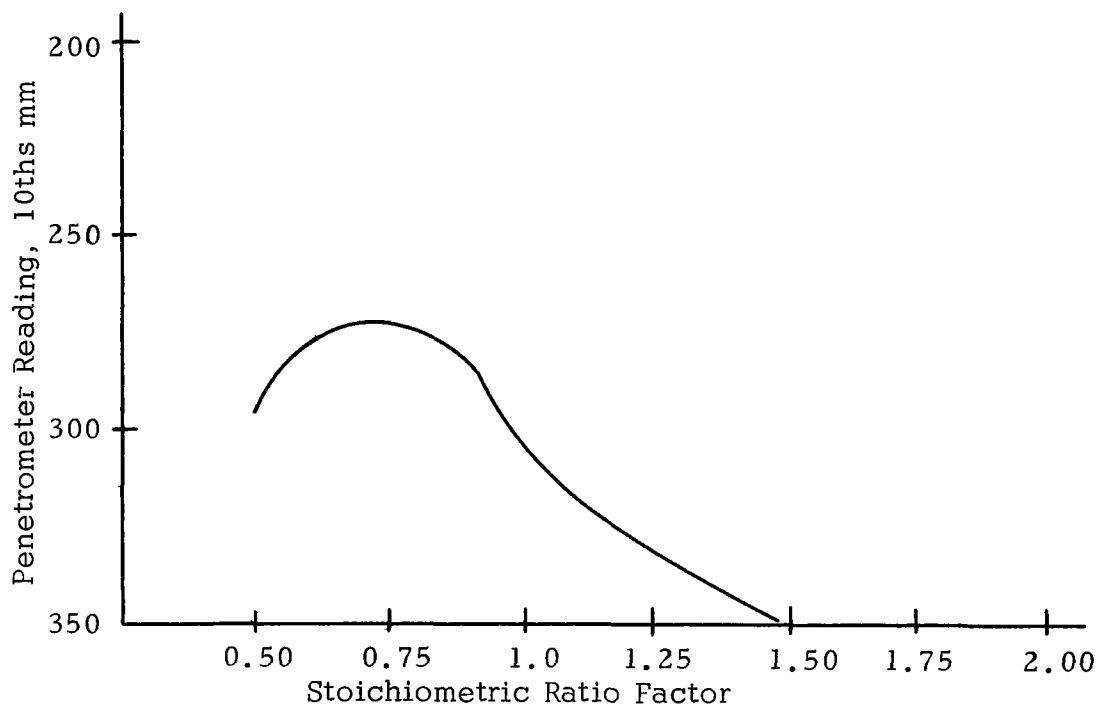
Figure H-4.   Armeen C and TDI 80/20
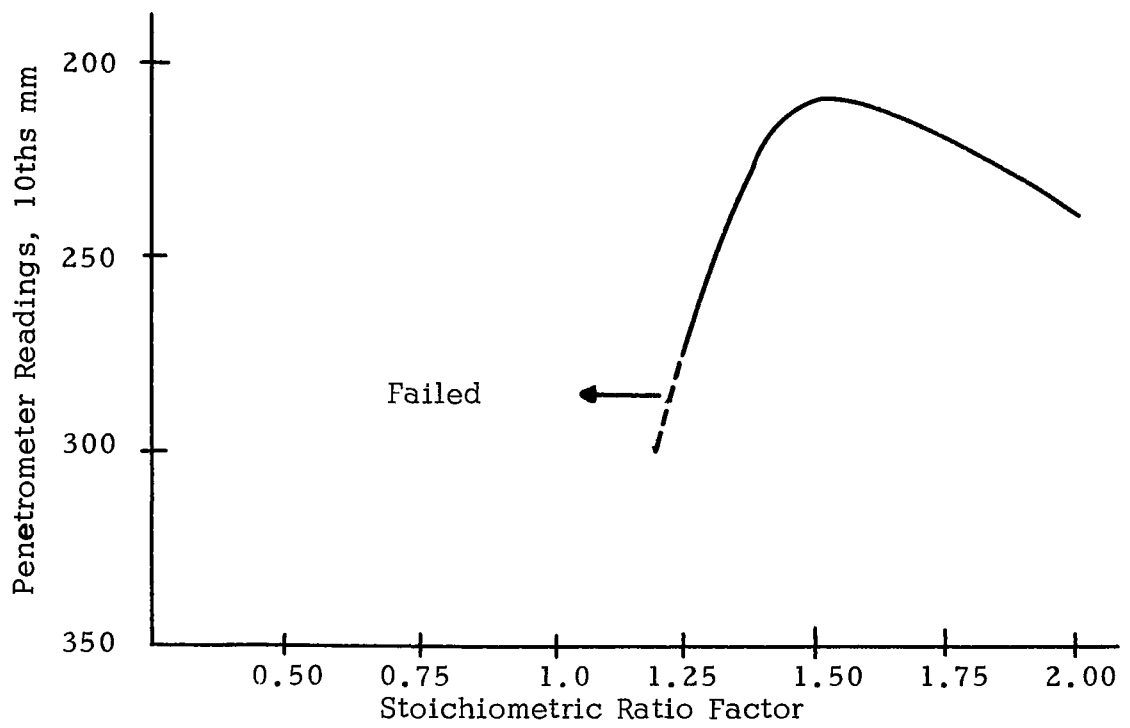
Figure H-5. Armeen L-15 and TDI 80/20
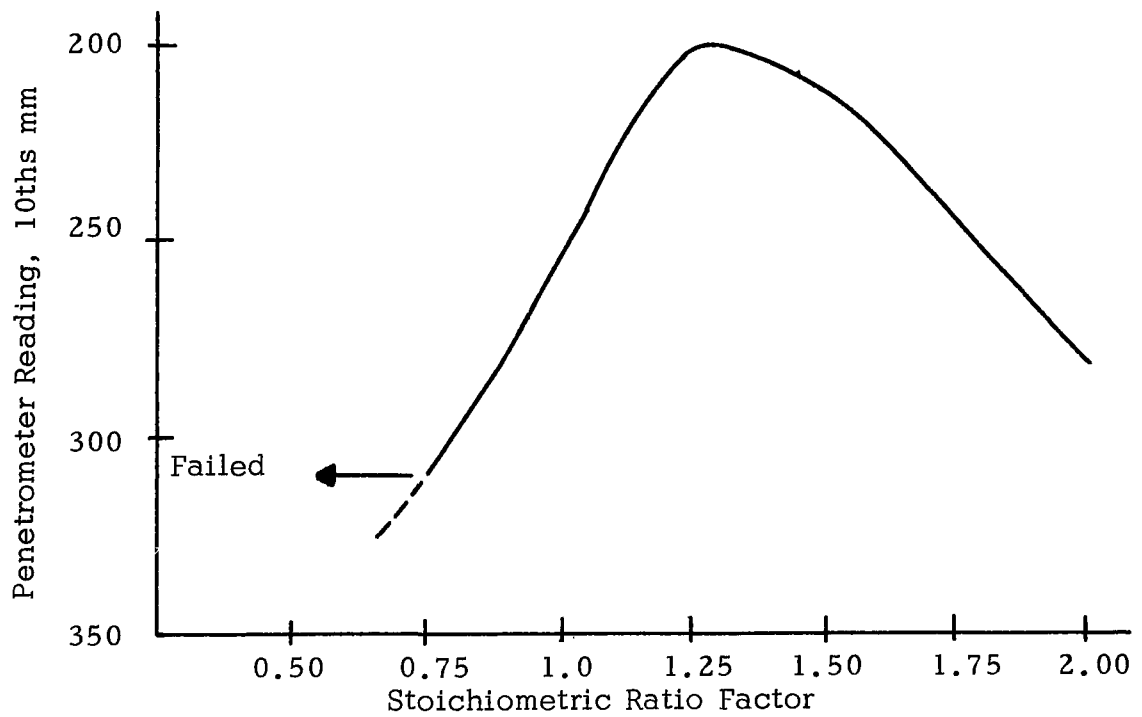
Figure H-6.   Armeen L-11 and TDI 80/20

APPENDIX I

GEL STRENGTH VERSUS PERCENT GELLING AGENT
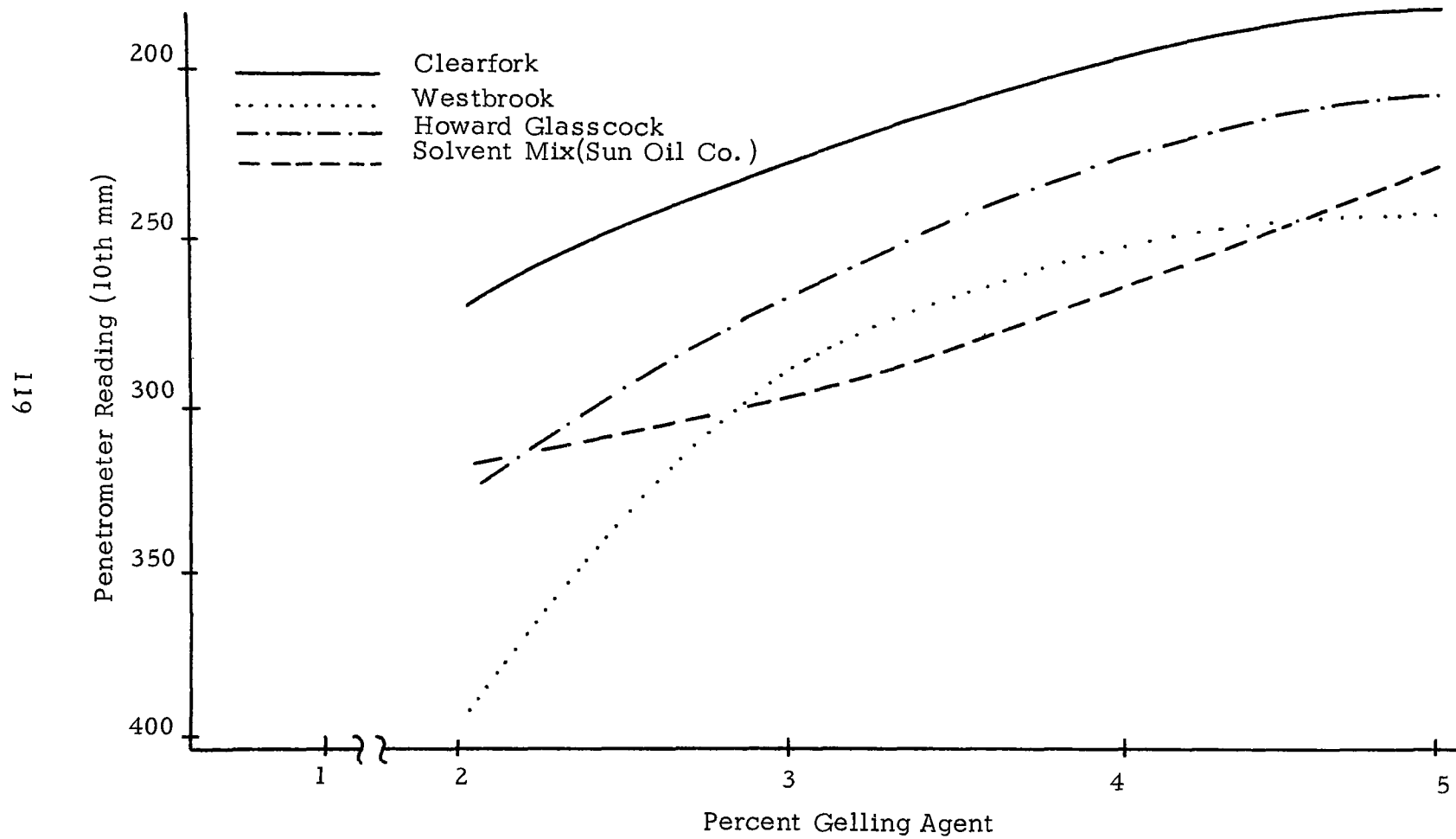
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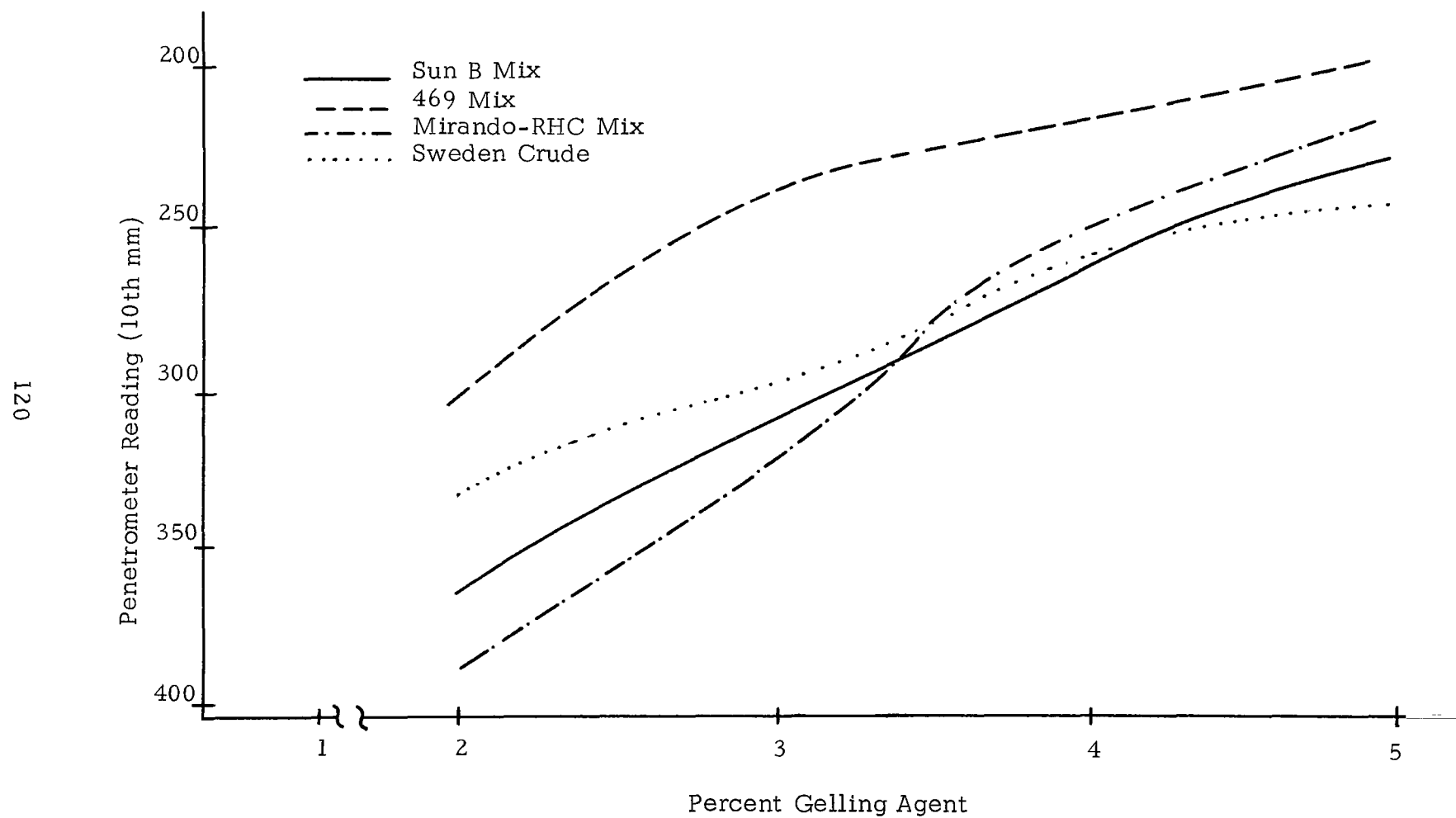
Figure I-2. Armeen L-11 and TDI 80/20
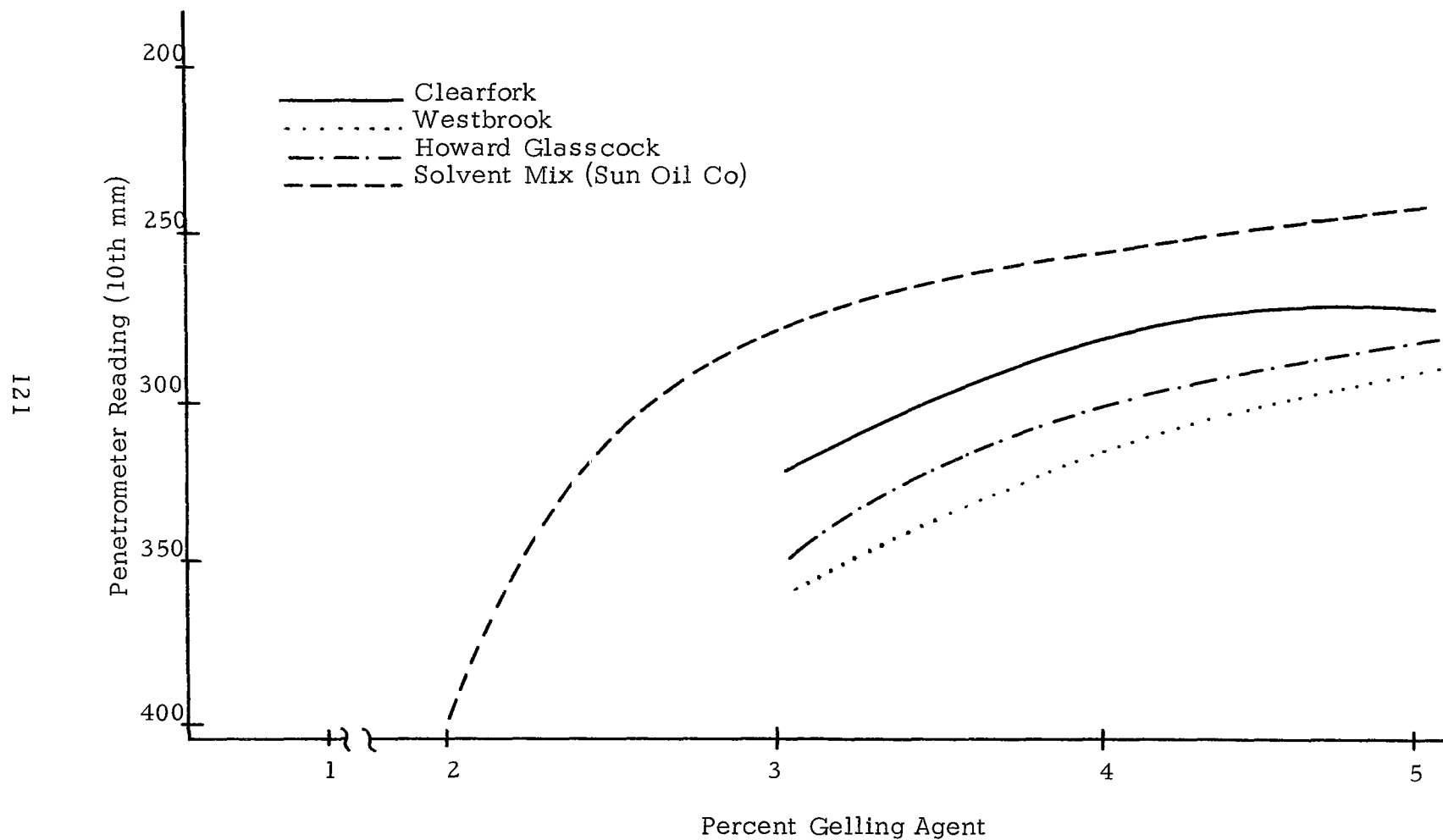
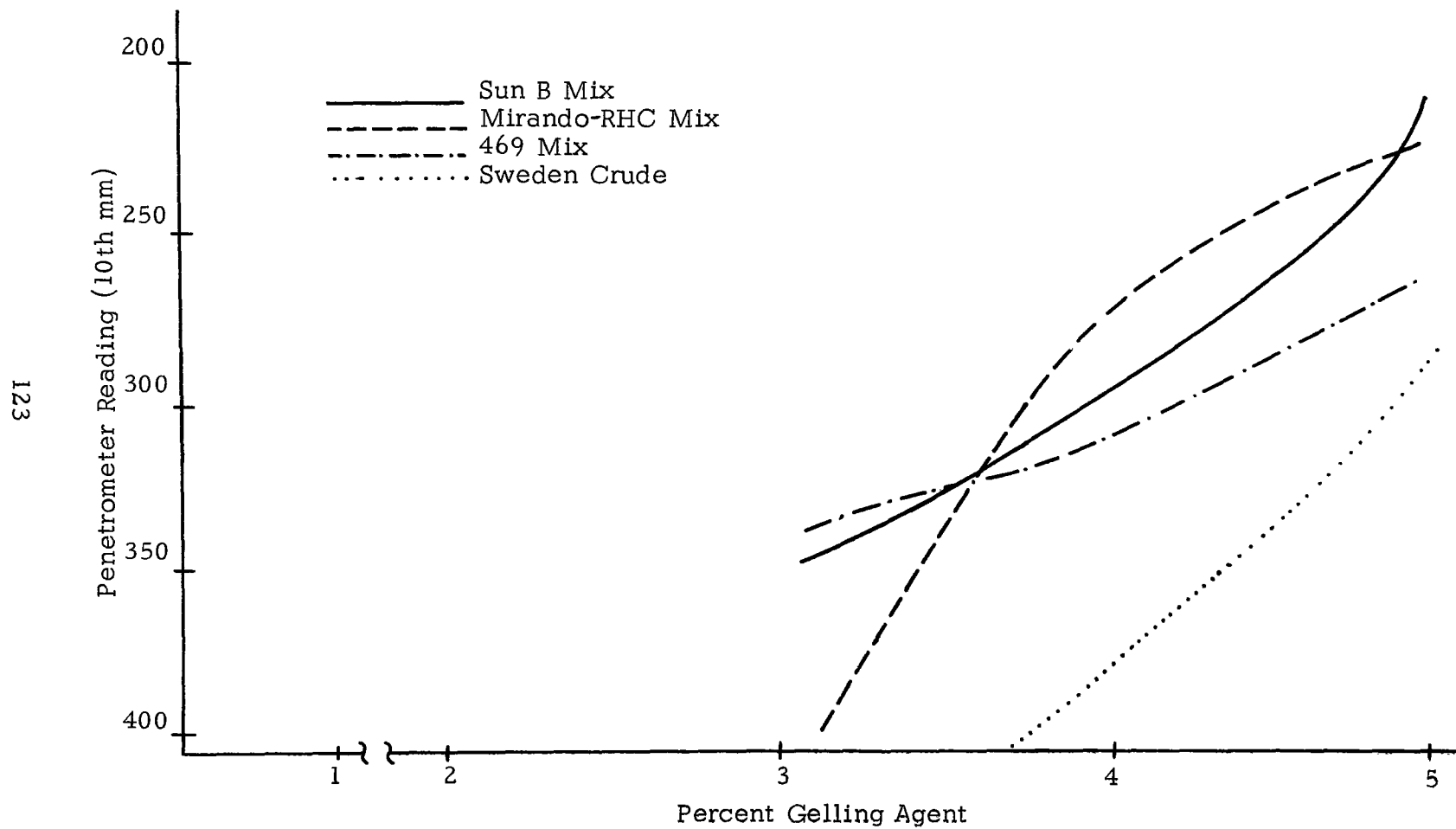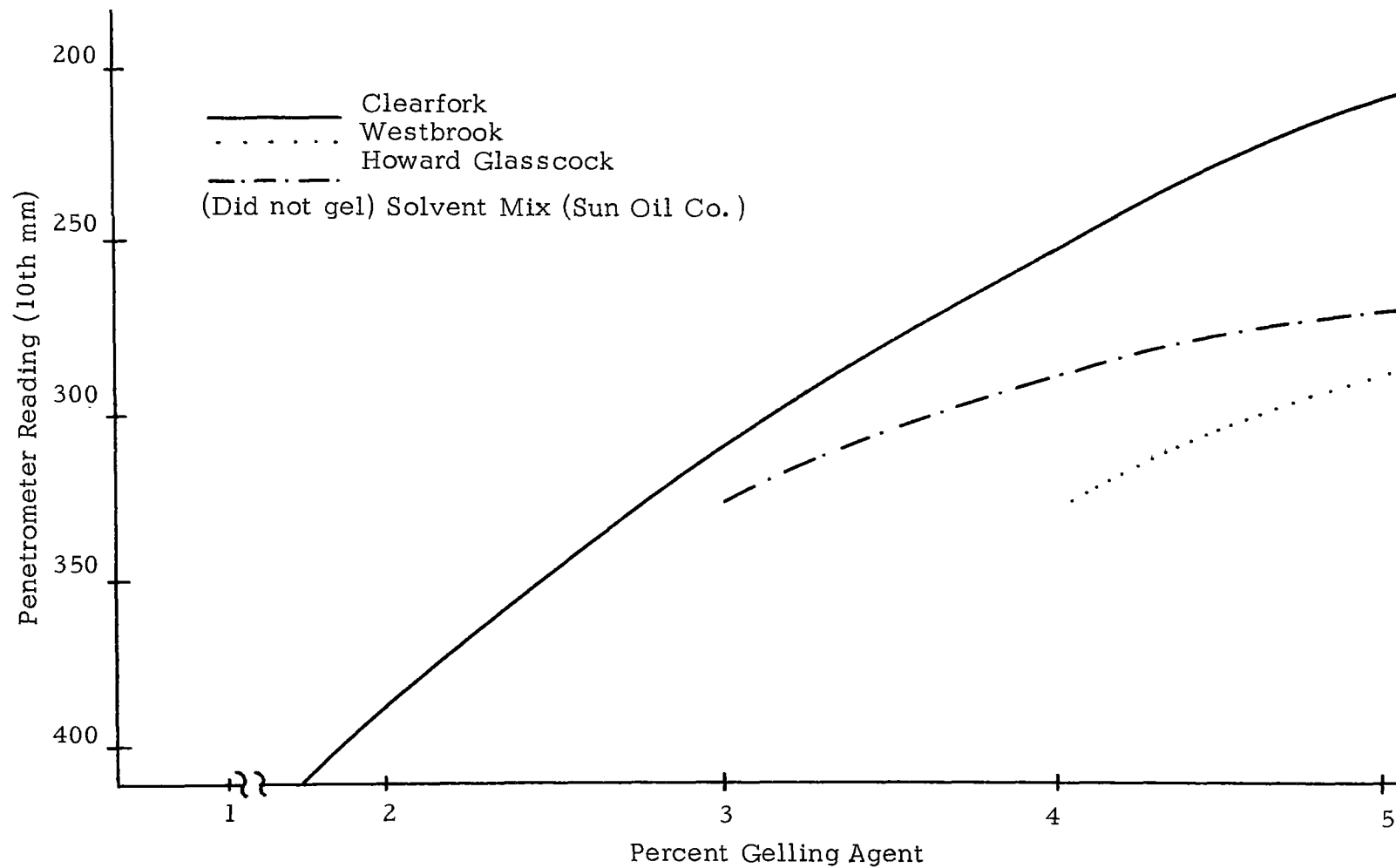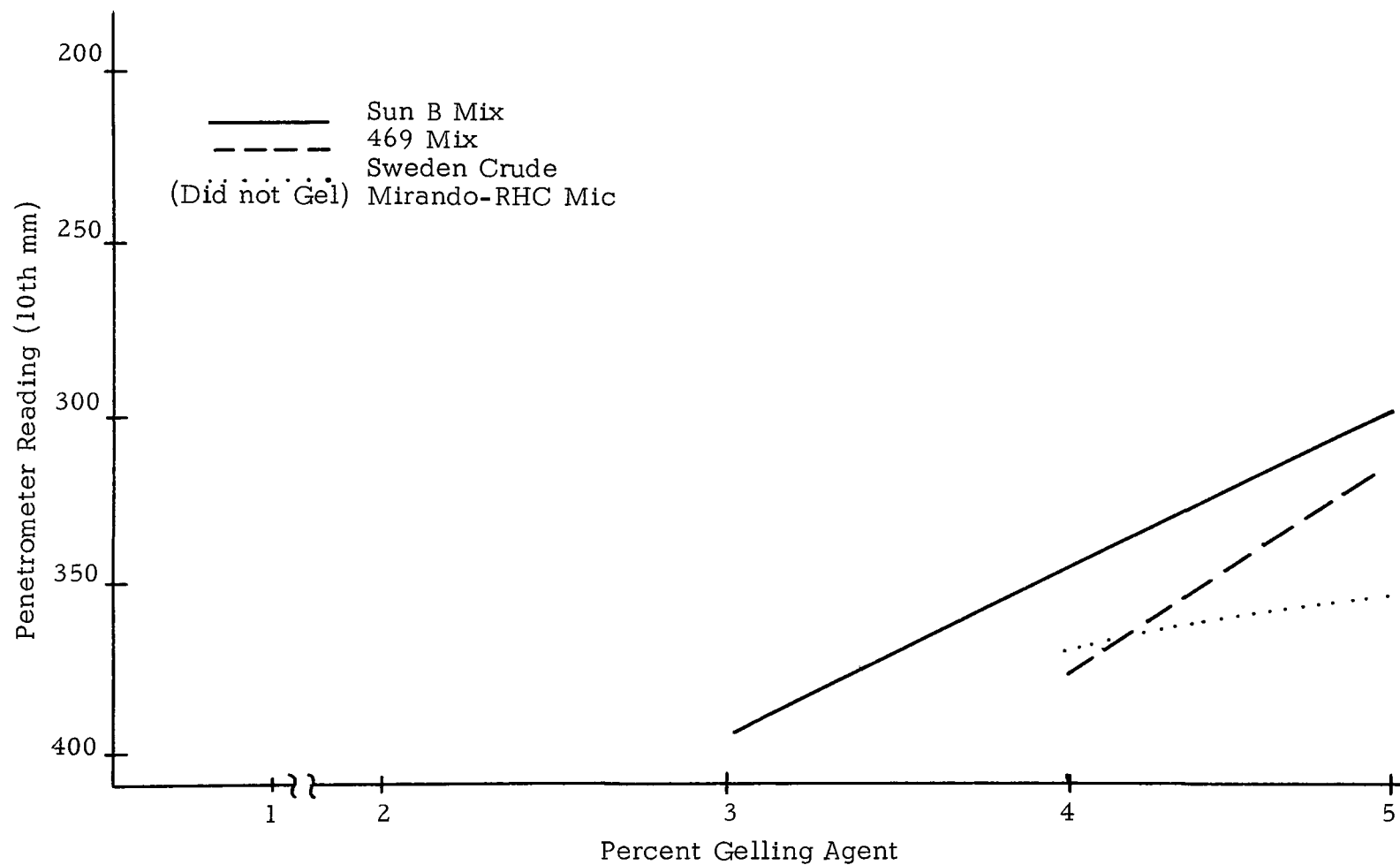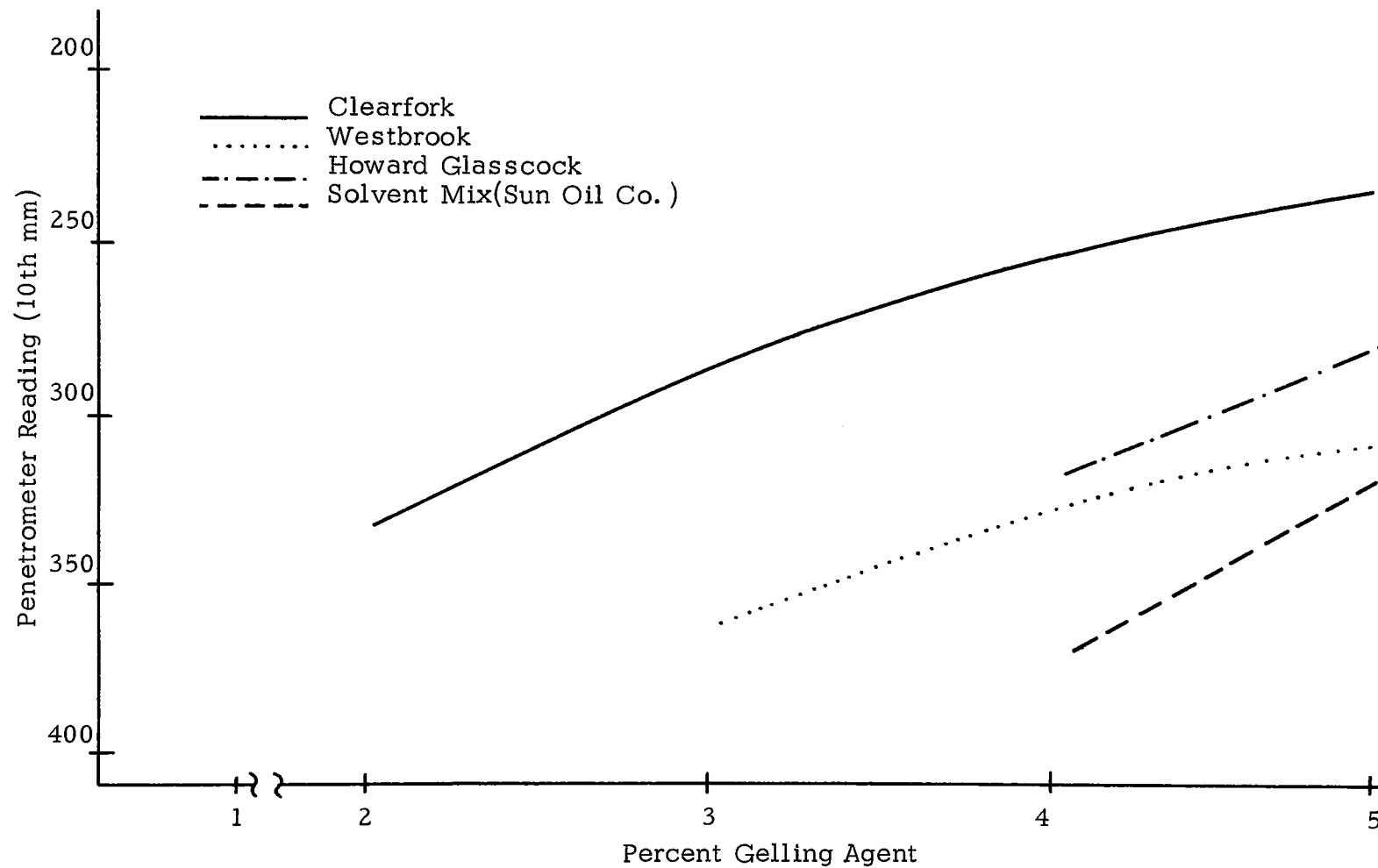Figure I -3. Armeen C and MT-40
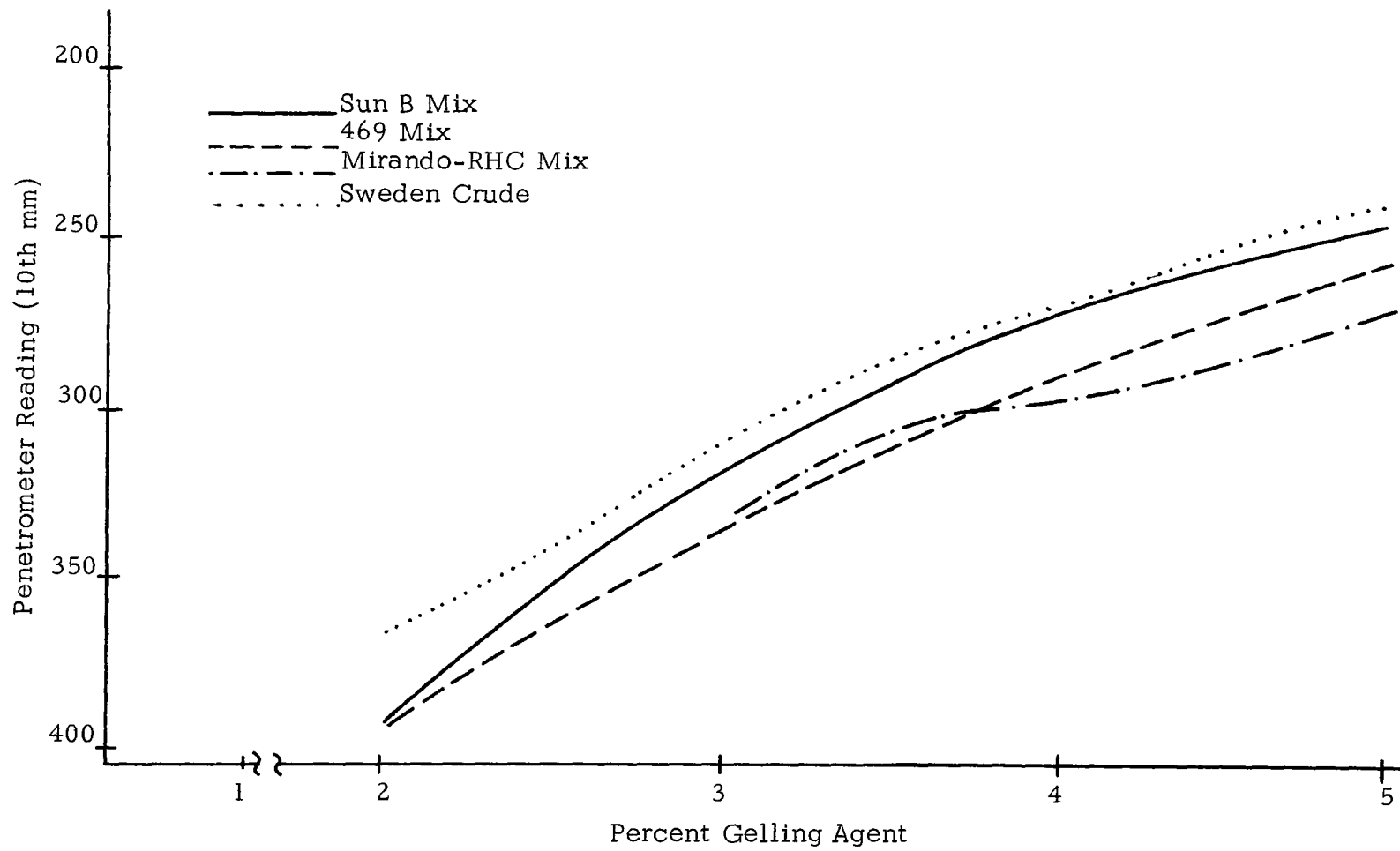
Figure I-4. Armeen C and MT - 40

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Figure I- 5. Jeffamine 400 and Octadecyl Isocyanate
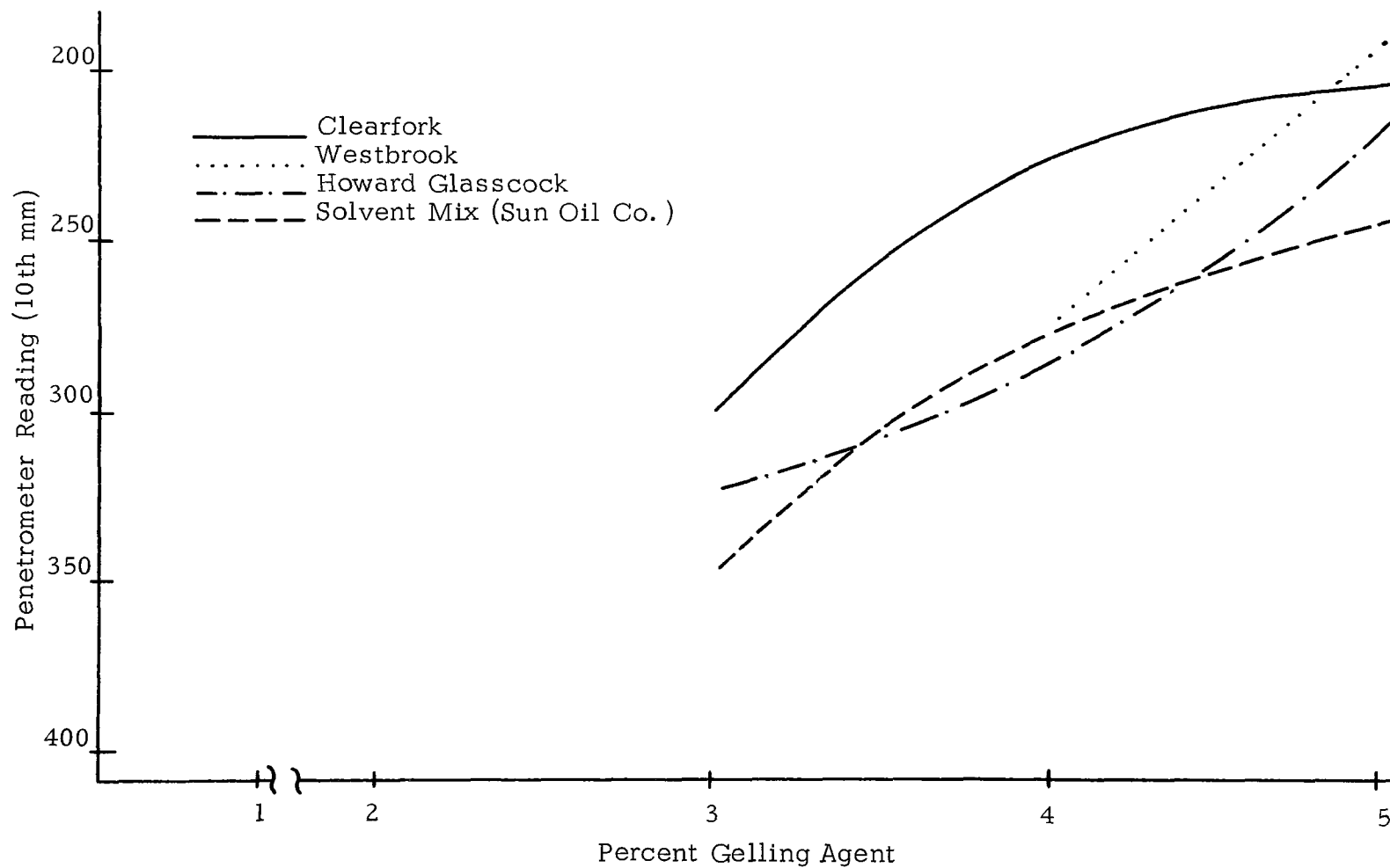
Figure I -6. Jeffamine 400 and Octadecyl Isocyanate

Figure I -7. Armeen L-15 and TDI 80/20

Figure I-8. Armeen L-15 and TDI 80/20

Figure I -9. Armeen O and TDI 80/20
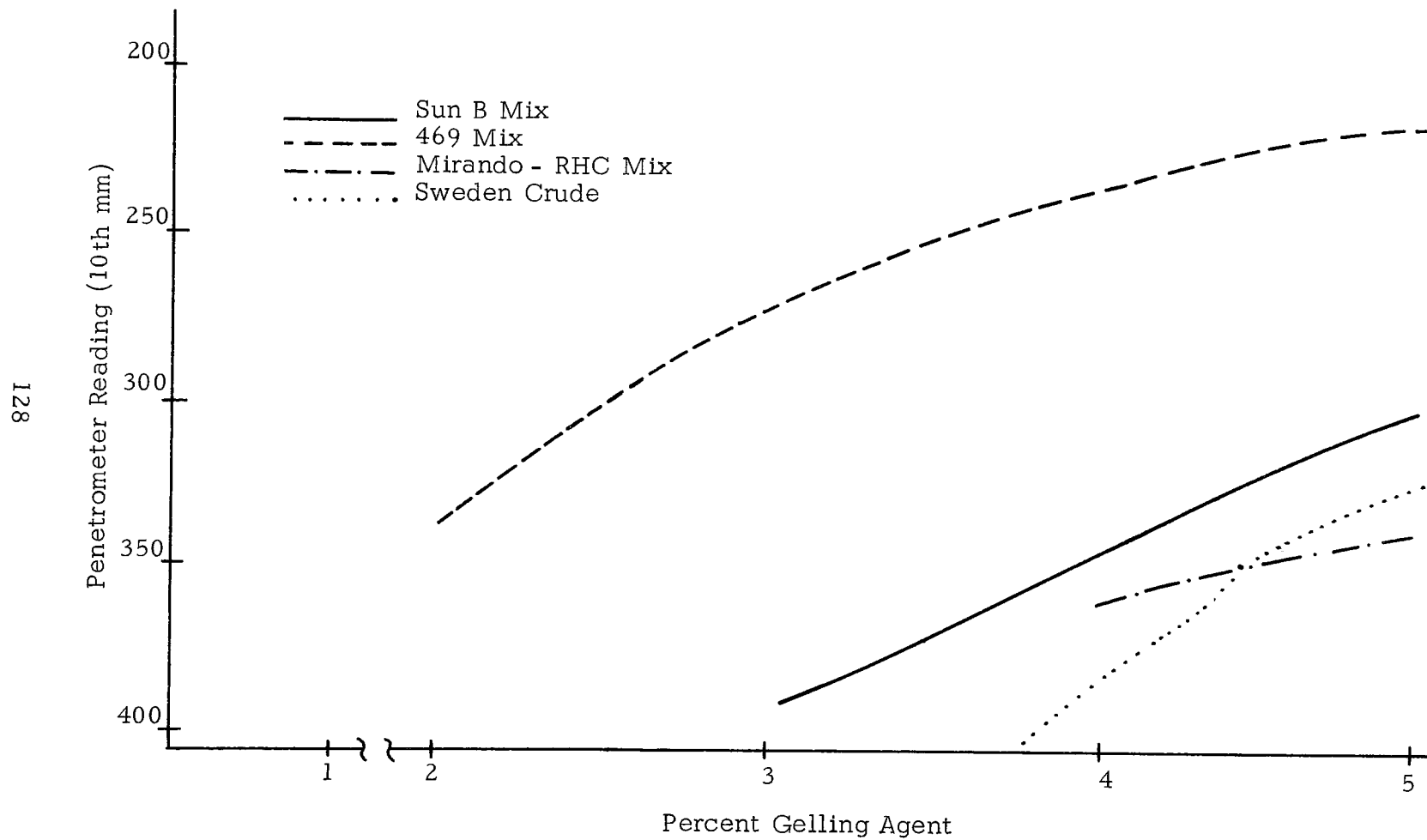
Figure I -10. Armeen O and TDI 80/20

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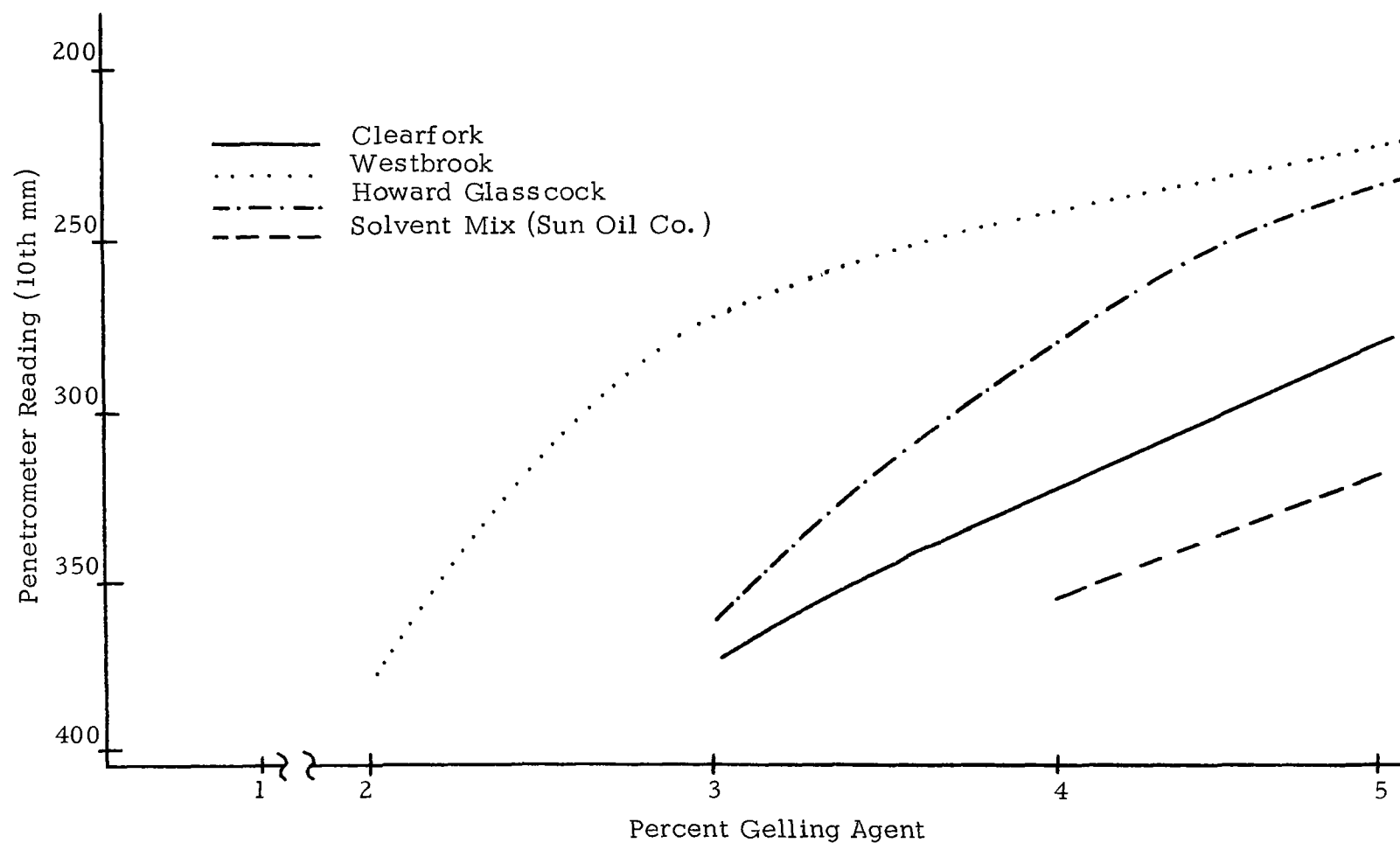
Figure I-11. Armeen C and TDI 80/20
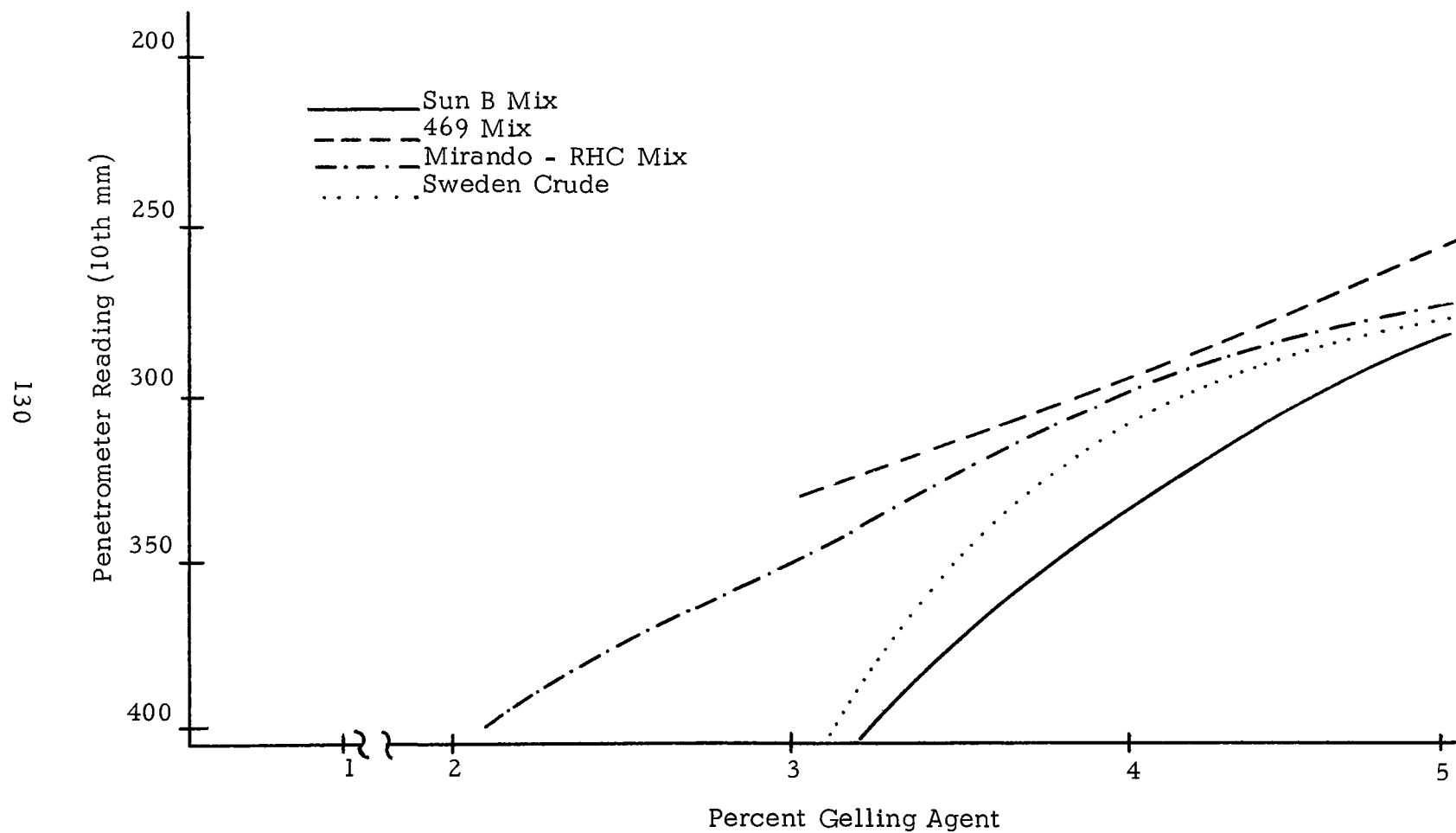
Figure I-12. Armeen C and TDI 80/20

APPENDIX J

GEL AGENT DISPENSING CONCEPTS

TABLE J-I.   GEL AGENT DISPENSING CONCEPTS

Concept	Advantages	Disadvantages
1. Rotating Nozzle Use of injection nozzles which are canted and designed to rotate horizontally on the discharge line. One agent is discharged from the nozzles during travel vertically from bottom to top of tank. Crude from tank is used to flush agent from the discharge system. Second agent is discharged from nozzles during travel from bottom to top of tank·	Can be portable or permanent ship equipment. Oil gelled in bulk process.	Theoretical analysis of dispersion limits impossible. Testing series is required to define equipment parameters. Operating limits are defined by gelling time.
2. Recirculation Pump oil out of tank. Mix in gel agents and return to tank.	All oil treated discretely and uniformly. Can be permanent or portable system. Simple installation. No obstructions in tank.	High lift for oil removal pump. Pump suction needs to vary for different oil levels. Some dilution between treated and untreated oil.
3. Recirculation With Air Pump oil out of tank, mix in gel agents and air and return to tank. Gelled oil floats on oil.	All oil treated uniformly. Could be permanent or portable system. Simple installation. No obstructions in tank. Minimum dilution between gelled and ungelled oil.	High lift for oil removal pump. Auxiliary power is needed. Pump suction level needs to be variable for different oil levels. Is not known if gelled oil with air floats in oil.

Concept	Advantages	Disadvantages
4. Vertical Diffuser Diffuser pad, plate or pipes adjacent to outer hull - to distribute gel agents next to possible holes.	Near possible leak. Gel minimum crude oil. No major obstruction added to tank.	Permanent installation only. Can not be used for portable. Needed in every tank. Possibility of damage in collision since near outer shell. Cannot distribute gel agents to entire tank.
5. Horizontal Diffuser Lattice work of pipes with set nozzles are placed at bottom of tank. Air injected with agents to foam or lighten gelled crude to make it float.	No interference between gelled oil and gelling process. No major obstruction added to tank. May possibly be able to add portable system to tanks as needed.	Difficult to adopt as portable system. Lattice may not be in oil layer after leak started. Floating gel may not seal leak in bottom of tank until much loss has occurred. Auxiliary power is needed to pump agents. It is not known if air mixed with gel agents floats on oil.
6. Submersible Pump Use submersible pump lowered in tank of crude oil, inject air and gelling agents into pump to gel and float crude oil.	No installation in tanks is required. Minimum mixing of gelled and ungelled oil.	Very high horsepower is required to agitate entire tank. Air may not float gel.

Concept	Advantages	Disadvantages
7. <u>Propeller Mixer</u> Use portable or permanent propeller type mixer in tank. Gel agents dispensing into vortex by rotating blades.	Simple installation. Portable or permanent system possible.	High horsepower to achieve good mix. Installation difficult.
8. <u>High Velocity Jets</u> High velocity jets, powered by gas generator (propellant, gun or rocket) or explosive . Locate tanks of chemical on deck for movement to leaking tank.	No external power source necessary. Possible to direct toward leak.	Tank very heavy and difficult to move in a possible no power condition. Possible hazard with explosives and crude oil. Good mixing of agents and crude not possible from single application point.
9. <u>Honeycomb</u> Honeycomb with gel agents in the cells are placed at bottom of tank. Agents are released at emergency by ultrasonic generator or other means.	Always in tank ready to go. No movement of materials or equipment during emergency.	Five percent of ship capacity permanently lost by carrying agents to gel all tanks. No way to mix gel agents into crude. Danger of rupturing cells during tank cleaning. No way to check for deterioration of gel agents. Special equipment necessary to break Honeycomb.

Concept	Advantages	Disadvantages
10. Encapsulated Agents Gel agents are encapsulated in beads of wax, polyethylene, gelatin, etc. Pour into tank at time of emergency. Agents are released by dissolving capsule. Destroy capsule by ultrasonic or crushing.	No handling of liquids. Simple application method. No ship modification is required.	Not possible to get uniform distribution in crude oil tank density of crude oil varies. No way to control sinking of beads in fluid.
11. Tapes Tapes made of little bags of gelling agent. Tapes are dispensed into tank in proportion to capacity of tank. Tapes are dissolved or run through rollers to expel gelling agents.	No liquids to handle. Very minor ship tank modifications.	No positive or complete mix possible.
12. Horizontal Diffuser - Top of Tank Lattice work of pipes with jet nozzles are placed at top of tank.	Always out of water layer. Can be permanent simple installation. No major obstruction added to tank. Could be portable.	Adequate mixing in all parts of tank probably not attainable. Too much gelling possible in same area.

Concept	Advantages	Disadvantages
13. Discharge Overboard Pump oil out of leaking tanks. Gel oil and discharge overboard.	Oil is removed from leaking tank. Good mixing of oil and gel agent. All oil is treated. No dilution of gelled oil after mix. Gelled oil easy to harvest. Gelled oil on water is not spread over large area. Could use as permanent or portable system. Simple installation. No obstructions in tank.	High lift for oil removal pump. Need special equipment to harvest. Pump suction needs change for changing oil levels Hoist is needed to place pump in place. If we could pump out of tank, we could just as easily put ungelled oil into a barge for salvage rather than putting gelled oil on water.
14. Endless Belt Endless moving belt to carry gelling chemicals down tank wall.		No way to mix gel agents with all the oil in the tank. Expensive installation.
15. Diaphragm. Construct loose vertical diaphragm in tank, pump oil from one side of diaphragm, add gelling agents and return to other side.	Complete isolation of crude oil and gelled crude. Prevents loss of oil in itself.	Obstructions in tank prevents this method. Probably expensive.

Concept	Advantages	Disadvantages
16. Random Cylinders Chemicals are stored in alternate ends of cylinder with offset nozzle on each end. Compressed gas is stored to expel gel agents and at same time impart rotational or random movement of cylinder. Many small cylinders are used to gel oil.	No alternate power source needed.	Large number of devices are needed to gel large tank. Device needs to be extra heavy to permanently store compressed gas. Device is presently not in state-of-art of chemical dispensing, much development is needed.