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CEA - 96
Mitigating the Problem of Gas Migration

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Prepared for CEA-96 Sponsors
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MEMORANDUM

TO: All Sponsors

FROM: **Cyrus A. Irani** CAI

DATE: June 26, 2000

SUBJECT: **CEA-96 – *Mitigating the Problem of Gas Migration* Final Report**

Attached please find a paper and electronic (disc) copy of the final report covering the work done for CEA-96, "Mitigating the Problem of Gas Migration". The study evaluated commercially available (PermSeal) and unconventional (Zero Set Fluid) systems for addressing the problem of sustained behind casing pressure. Physical models investigated included capillary tubes for preliminary injectivity testing and pipe-in-pipe models for simulating the annular cement sheath encountered in field operations.

Testing with capillary tubes demonstrated that most commercial fluids could penetrate the finest capillary openings, but had the disadvantage of setting quickly with time, which limited the extent to which they could penetrate the finest fractures. This limitation was minimized by the use of a novel Zero Set Fluid involving the dissolution of very high viscosity polymers in light hydrocarbon solvents, and then delivering the polymer through solvent evaporation. These systems had the disadvantage of limited polymer loading and involved placement methodologies.

When properly executed, both systems individually and in conjunction with each other were quite effective in limiting gas migration. Combined systems were very promising in that a conventional treatment like PermSeal could be used to eliminate the bulk migration pathways, followed by the Zero Set Fluids to plug up the remaining fine pathways. In a specific case, a cement sheath with a starting permeability of 480 md, was initially reduced to 3.5 md through PermSeal injection, and to a final permeability of 0.98 md through Zero Set Fluid injection.

The offshore industry is making deliberate strides towards the implementation of new technology for addressing the issue of gas migration in existing wells. A good example is the casing annulus remediation system (CARS) being used to deliver weighted fluids above the cement sheath for gas control. With time it is anticipated that the industry will evolve to using similar techniques to deliver weighted gelling fluids, and eventually novel Zero Set type fluids in conjunction with conventional fluids to address the issue of gas migration.

Westport Technology Center appreciates this opportunity to have worked with you on addressing this very important issue. We appreciate your patience and encouragement, and look forward to working with you again on some other project.

SUMMARY

Overall Summary

Addressing the issue of gas migration behind casing in the laboratory environment is difficult for a number of reasons. Generating physical models that accurately and repeatedly duplicate field conditions is quite difficult. The cement itself is not completely set for well over 60 days, though it is thought to have 90% of its final characteristics within 45 days. Consequently, the characteristics of the model are changing during the first 45 days, making interpretation of the results difficult. Additionally, both microfine and larger fractures are encountered in the field, and the two require different solutions. For practical purposes a larger fracture can be defined as one that will take commercially available water or hydrocarbon based weighted, or gelling fluids, or a combination of the two. In practice, weighted fluids are seeing field use even though they have limited success, primarily because they do not generate a more impenetrable barrier to gas migration. Gelling fluids, which set with time, do generate more impenetrable barriers, but have the disadvantage of being more complex to implement, and have limited penetration of the finest fractures. They are also potentially more expensive than simple weighted fluids.

Microfine fractures take very little of the conventional weighted or gelling fluids. This could be primarily a viscosity limitation, though the gelling fluids do have the disadvantage of setting with time, and this limits the extent of their penetration into the finest fractures. Novel systems have been developed in the course of this study that attempts to circumvent the shortcomings of weighted or gelled fluids. These systems involve dissolving extremely viscous polymers in light solvent systems, and then destabilizing the system, usually through solvent vaporization, to deliver a viscous polymer for microfine fracture plugging. Because these are physical solutions the starting viscosity can be adjusted to facilitate penetration of microfine fractures. Because there is no chemistry involved these solutions are stable indefinitely and this permits further penetration of the microfine fractures. These fluids can be viewed as complimenting gelling fluids and will most likely be used in conjunction with them. Disadvantages to these systems are their greater complexity in preparation and placement, greater cost, and greater risk involved due to combustible nature of the solvents used.

The offshore industry is making deliberate strides towards the implementation of new technology for addressing the issue of gas migration in existing wells. A good example is the casing annulus remediation system (CARS) developed by ABB Vetco Gray for offshore introduction of healing fluids at the face of a cement sheath. A number of CARS units are in commercial use to try and eliminate behind casing gas. However, the majority of present applications exploit weighted fluids, with only a few wells having employed settable resin systems. To date the CARS applications have generated fair results. It is anticipated that industry will evolve slowly beyond weighted fluids to the use of weighted gelling fluids, and eventually to the use of novel fluids in conjunction

with weighted gelled fluids to generate a complete solution to the gas migration problem.

Physical Models Summary

The pipe-in-pipe models developed at Westport are reasonable for simulating the annular cement configuration encountered in the field. The ability to pressurize the inner pipe through fluid injection either before, during, or after the cement has set allows the generation of different fracture configurations. However, an issue of fundamental concern is that the setting of cement is a dynamic event that stretches over many days. The set curve has an exponential decay and almost 95% of the set is in place after 45 days. Consequently, interpreting the results of an experimental program directed at identifying changes in the property of the annular cement sheath can prove problematic if the base properties of the cement are themselves changing during the course of the testing. A rigorous test procedure would call for making a model and then waiting 45 days for the cement to be almost cured before initiating any testing. Unfortunately, under most testing situations, each successive model builds on what is learnt from the previous model, and waiting 45 days for one model to cure, undertaking a test program, defining the characteristics of a new model, making the model, and waiting 45 days for the model to cure, represents an unacceptable laboratory schedule. Consequently, in the course of this study, models were prepared, allowed to cure briefly, subject to some remedial action, and then promptly evaluated to address the changes in the model, in order to minimize the interference due to the changing cement characteristics. This procedure was found to work quite well without imposing an unacceptable delay in the experimental program.

Cement weight was found to be another significant consideration that will be driven by the choice of the testing to be undertaken. Cement weights in the 12.5 lbs./gal range will generate more flexible models with higher porosities that can be readily modified to generate fractures that will easily take conventional fluids. However, to duplicate the microfine fractures that will not take conventional fluids the cement has to be in at least the 14.7 lbs./gal range, and preferably in the 16.5 lbs./gal range. These heavier weight slurries will generate a very compact cement that will have an extremely low permeability; it will also be extremely difficult to fracture in a controllable fashion. However, these micro-fissures that barely take conventional fluids are exactly the kinds of flow conditions encountered in the least treatable field situations, and represent the most appropriate models for testing unconventional fluids.

One additional modification that is recommended for future studies is the interpretation of the model's characteristics. In this study we measured permeability to nitrogen and water flow to characterize the models behavior. However, in actual field practice the time for pressure buildup after the annulus has been bled down is the measured criterion, and perhaps a similar approach should be taken even in laboratory studies (in conjunction with regular permeability measurements) to evaluate pre- and post treatment model properties.

Gelling Fluids Summary

The primary gelling fluid investigated was an aqueous based fluid commercially available from Halliburton (PermSeal). The final mixture is sensitive to air and light, which shortcomings might be common to most such fluids, and it is anticipated that the manufacturer is experienced in providing a working sample in the field. The initial fluid tested in this study was an unweighted fluid that had a set time of approximately 24 hours. After some initial modifications to improve the low temperature performance of the fluid in a cement environment, a new formulation that could be weighted up to 17 ppg with common brines was tested. Combining the "lubricating" features of weighted fluids with the setting property of a gelling fluid should lead to improved fluid placement and gas sealing characteristics. Indeed, model tests with this new formulation gave good performance. Cement sheaths with initial permeabilities in excess of 20 md could be reduced to 3-4 md. By providing a more impermeable barrier to gas migration, weighted gelling fluids have distinct advantages over simpler weighted fluids, and it is expected that they will see growing use in the field.

Novel Fluids Summary

These novel systems are generated by dissolving viscous polymers (1 MM cP polydimethyl siloxane) in light hydrocarbon solvents such as ethane, propane or butane, or mixtures of these light hydrocarbons and inert gases like carbon dioxide (CO2). Plugging action is achieved by delivering the low viscosity mixture to the appropriate thief zone and then either stripping away the solvent as with the straight hydrocarbon solvent systems, or destabilizing the mixture by pressure or temperature changes as in the CO2 systems. In both systems proper placement of the mixture followed by appropriate solvent stripping action should leave behind a viscous polymer for plugging purposes. A further advantage of mixed systems that include CO2 in the formulation is that the large volumes of CO2 released with the hydrocarbon phase will act like a fire retardant blanket to minimize the combustion potential of the hydrocarbon solvent.

The primary and most significant advantage of such fluids is their time stability. Because no chemical change takes place, the fluids do not degenerate with time, which gives them a significant advantage from a placement and penetration standpoint. Another advantage of these systems is that the flowing viscosity is adjustable by controlling the amount of polymer dissolved in the solvent phase. Consequently, this combination of properties makes these novel fluids ideal candidates to clean up behind more conventional fluids. For example, based on laboratory studies a conventional gelling fluid like PermSeal can take a 25+ md permeability cement sheath to about 4 md. Additional treatment of this cement sheath with a novel fluid system can further lower the permeability to the 0.5 to 1 md range. However, at present this residual permeability of 0.5 to 1 md appears to represent some threshold value of treatment effectiveness, and we are trying to determine what its source might be.

Disadvantages to this approach are that because of the nature of the process, only limited amounts of polymer can be carried into the fissures with each application, so that repeat applications might be needed for maximizing the performance of this process. Additionally, combustible hydrocarbons at high pressure are involved, and this combination automatically creates a barrier to field implementation that needs to be overcome. It is feasible that equipment can be designed that will alleviate these concerns, and some preliminary ideas along these lines have been generated. The use of mixed solvents including CO2 should help to minimize some of these issues.

Additional / Future Work

As a consequence of this work two significant areas of interest that warrant additional study have been identified. The first deals with a better understanding of the residual permeability that seems to persist after numerous treatment approaches and cycles have been exercised. Is this a consequence of the treatment type/mechanism, or is this inherent to the cement matrix? Preliminary results from this study indicate that cement density is a significant factor, with the higher density resulting in lower gas leakage. A study that will allow the development of an understanding of the nature of this permeability, how it correlates with cement density, and how it influences pressure buildup in the annulus will prove extremely useful. Additionally, how does this permeability correlate to standard field practice where the time for gas pressure to buildup to a certain value (usually 1000 psia) is the criterion for defining when the annulus should be bled down again. Foamed cements are seeing increasing use and they are credited with a more supple matrix, which permits them to more easily accommodate physical and thermal stresses without forming fractures. What is uncertain is what a foamed cements residual permeability might be. If it exceeds that due to the formation of fractures then little is gained by the elimination of fractures.

The second issue that warrants more attention is field implementation of remedial processes. Even though steady strides are being made in developing new technologies, one example being the CARS unit mentioned earlier, fullest exploitation of the potential of these methodologies is slow in being implemented. An obvious instance would be to exploit the CARS unit to inject gelling fluids rather than just the weighted fluids being presently utilized. Unfortunately, from an operator's perspective the gelling fluids are more difficult and expensive to deal with than simple weighted fluids, and offer far more opportunities to create a messy situation if the injection step goes awry. Somehow, an incentive needs to be made available that would prompt the operators to be bolder in exploring their treatment options. If the operators are hesitant to take the next step beyond simple weighted fluids, than the more complex fluids that represent the third generation of treatment solutions (gelling fluids representing the second) are unlikely to ever be implemented.

Another opportunity for additional development work might be the design and testing of equipment that would allay the concerns operators will voice about implementing the third generation of remedial fluids. These are all hydrocarbon based systems, and operators can be expected to voice concern with regards the safety issues evolving out of the release of large volumes of these combustible gases during the implementation of this remedial treatment. The design of a closed system that would inject the polymer mixture at pressure in the first cycle, then have a condenser/compressor for capturing the hydrocarbon gases during the bleed down cycle, might help mitigate some of the concerns associated with this technology.

1. INTRODUCTION

1.1 Background

Gas migration through cement sheaths is considered one of the major problems associated with the production of gas and oil reserves. A cement slurry is placed in a wellbore to harden into an impermeable mass that seals the annulus from fluid flow and protects the casing from corrosion for the life of the well. If fluid flow does occur in the form of gas migration, expensive remedial squeeze cementing techniques are generally required. This problem can be manifested by gas pressure on the casing annulus at the surface, inter zonal communication with a loss in production, or in its worst case, a blowout. Gas entry into unset cement is the result of a complex physical and chemical process occurring after the cement slurry is placed in an annulus, and it is commonly recognized that gas migration after placement of the cement slurry is one of the biggest cementing problems facing the industry today.

Extensive investigations into the cause of gas migration have been performed by both service companies and oil companies over the past twenty-five years. A survey of the problems associated with poor primary cementing was performed recently by Westport and some interesting facts emerged. From a total of eighteen worldwide cementing experts, an estimation of the failure rate of primary cement jobs was developed. This is based upon their experiences with operations in both specific areas of the world and the general problem worldwide. A 15% failure rate is reported by the survey group. The failure ranges from a high of 40% to a low of 2%, with almost half of the participants reporting a failure between 10 and 20%. The largest contributor to this failure is fluid migration (gas or water) behind the casing. It is estimated that 35% of the failures occur because of this fluid migration.

If a primary cement job is a failure, then a squeeze cementing treatment is necessary. The cost to the operators to do the squeeze treatment involves materials and services as well as rig time. The rig time is variable depending on the location, but some average numbers can allow a cost to the industry to be calculated. Taking into account the difference in cost between squeezing offshore and onshore, the cost of poor primary cementing to the operators is $470 Million. This assumes only one squeeze treatment per problem.

If a cementing job is not a failure, the average cost of cementing is 6% of the well cost. If a problem occurs, this cost can be 20% of the total well cost, which would be one of the most significant in the drilling operations. It is imperative that if a squeeze job is necessary due to gas migration, that the success ratio be high due to this extreme cost. Unfortunately, most squeeze jobs are not very successful and have to be repeated two or three times. In light of this failure rate, it would seem clear that there is need for some new technology that will mitigate the gas migration problem in a more cost effective and permanent fashion.

1.2 Background, CEA-96 Phase I

The project "Mitigating the Problem of Gas Migration after Primary Cementing" was designated as CEA-96 and first presented to the industry at the annual meeting of the Cementing Engineers Association (CEA) in October of 1996. Initial funding of $50,00 distributed over two years was provided by the MMS with the requirement that matching funds be provided by the industry. A considerable effort was expended during 1997 to try and garner industry support. Over the course of numerous meetings, the source of reluctance on the part of potential industry sponsors was identified, and the original objectives of CEA-96 adjusted to accommodate industry concerns.

As originally defined, CEA-96 was focused on the development and evaluation of the light hydrocarbon solvent/polymer system for addressing the issue of gas migration through microfine channels. Different carrying solvents were to be evaluated for this purpose, as also realistic laboratory physical models that mimicked gas migration channels. The primary industry concern was that this focus on unknown and untried novel systems with all the attendant uncertainties for success distracted from developing a better understanding of the success and limitations of more conventional solutions for this application.

Accordingly, the original objectives were expanded to include a two pronged approach to the problem. Two potential remedial fluid systems were identified for simultaneous testing, one fluid type comprising of two or three of the commercially available water based systems that had a starting viscosity of 1 cP or greater, and the other comprising select versions of the light solvent/polymer system specifically designed to be under 0.5 cP viscosity. With this adjustment, industry interest was renewed, and at the conclusion of CEA-96 the following companies had signed on as sponsors: Amoco, Halliburton Energy Services, Intevep, MMS, Mobil, Saga, and Unocal.

1.3 Background, CEA-96 Phase II

The initial objective of CEA-96 (Phase I), initiated with MMS funding, was to develop a novel system for addressing the plugging of the microfine channels responsible for the behind-casing pressure problem. However, due to sponsor concerns identified above, the scope was diluted to include testing of commercially available gelling fluids.

The novel systems in question are mixtures of low viscosity solvents and high viscosity polymers. The potential solvents include carbon dioxide, lights hydrocarbons in the C2 to C5 range, heavier hydrocarbons like toluene or diesel or light naphtha cuts, and mixtures of the same. The polymer is primarily a polydimethylsiloxane polymer that can range in viscosity from 1000 cP to 1.5 million cP. The final mixture is a physical solution of the polymer in neat hydrocarbon or mixtures of hydrocarbon and an inert gas like CO2. Because no chemical change is involved, this mixture is quite stable, and in the case of neat hydrocarbons, a viscous polymer is delivered when the mixture pressure is allowed to drop below the vapor pressure of the solvent phase. When CO2 is added to the system, the solvent characteristics deteriorate, and a polymer rich phase comes out of solution at a pressure above the vapor pressure of the neat hydrocarbon component. The exact pressure at which the system destabilizes depends on the amount of CO2 present, the hydrocarbon phase, and the system temperature.

This combination of time stability and low starting viscosity makes these extremely promising systems for a number of applications including plugging microfine channels in cement sheaths. However, with the change in focus of the original CEA-96 proposal, only a limited amount of attention would be focused on these novel systems. Consequently, a second proposal was submitted to the MMS for additional funding directed solely at the study of these novel systems and their applicability to the problem of behind casing pressure. The MMS responded with a grant of $99,000 spread over two years for this study which then became Phase II of CEA-96.

2. DISCUSSION, CEA-96 PHASE I

2.1 CEA-96 Phase I, Technical Scope

Through consultation with the industry participants in the CEA-96 program it became clear that the problems associated with behind-casing pressure were extensive, extremely expensive to address or ignore, and that all the attendant issues were not well understood. An additional limitation is the lack of any significant published information on suitable models, systems, or test equipment and procedures for addressing this issue. Consequently, the sponsors of CEA-96 were constrained in using their own experiences and best judgement evolving out of consulting with other experts in the field to define the kinds of models and tests that would reasonably duplicate the gas migration problem encountered in the field. Additionally, as was indicated earlier, there was some concern within the membership that given the many uncertainties attending the understanding of the problem, the applicability of commercially available solutions deserved as much attention as any untested new concept.

Halliburton was the only oil field service company that was a participant in CEA-96, which simplified the choice of the commercially available treatments to be explored. Furthermore, after considerable discussion of the available choice of models it was concluded that initial testing of fracture sealing chemicals should be undertaken in capillary tubes. Capillary tubes represented a simple and reproducible model for preliminary screening of the stability and injectibility of the commercial and novel systems being considered for addressing the gas migration problem. Following the review of the capillary testing results, the membership identified a pipe-in-pipe model as a follow up system for simulating field conditions. Details of the design, testing, and results are discussed separately below.

2.2 CEA-96 Phase I, Capillary Tube Tests

2.2.1 Objective / Summary

The objective of this stage of testing was to provide a preliminary screening mechanism to evaluate several fluids as plugging agents for gas migration channels in a cement sheath. Testing involved establishing flow and plugging characteristics of four commercially available water based fluids in capillary tubes. Except for the microfine cement, all the fluid systems showed reasonable penetration of the capillary tubes and fairly robust plugging after setting. This was somewhat surprising because it was not intuitively anticipatetd that these gelling fluids would readilly penetrate the smallest diameter capillary tubes. A low viscosity hydrocarbon fluid carrying polymer was also tested and showed inconclusive results. The poor performance of this novel fluid system is discussed and options for modifying the performance are presented.

2.2.2 Capillary Tube Test Procedure

Four commercially available sealing fluid systems identified as Injectrol, PermSeal, Stratolock and MicroMatrix cement were tested. Testing involved injection of the fluids through capillary tubes. Tubes of four different diameter were selected for this study. The inside diameters were 0.04, 0.02, 0.01, and 0.005 in. Each tube was five feet long, and the bundle of tubes was contained in a manifold equipped with valves etc. to facilitate experimentation (Figure 1).

Preliminary evaluation of the system called for mixing the components of the sealing fluids to the manufacturers specifications and pouring the contents into an airtight container. For the gell systems a marble or other dense round object was included to facilitate the mixing and subsequent evaluation of the fluid. By visually recording the gelling and initial set time of the fluids an appreciation of the fluid's behavior was developed.

The actual test procedure called for the following steps:

1. Mix desired system (conditions vary for each system).

2. Pour fluid into pressure vessel. Retain a small sample of the test fluid in a sealed container for monitoring.

3. Pressurize vessel to approximately 10 psia.

4. Open manifold valve to the 0.04 inch ID capillary tube and establish flow. Record flow rate. If flow is not obtained increase pressure incrementally up to 1000 psi. If no flow is visible at 1000 psi differential pressure, maintain pressure for 1 hour or until flow is established.

5. Close manifold valve and place end cap on the opposite end of the tubing to lock fluid in place.

6. Use steps 4. & 5. for the fluid injection of the 0.02, 0.01 & 0.005 inch ID tubing.

7. After approximately 24 hours gelling period, detach the manifold assembly and apply nitrogen pressure to the returns end of the tubing in 100 psi increments up to 1000 psi.

8. Monitor the flow of gas or displacement of the system from the injection end of the tubing. (It may be necessary to use a surfactant solution to detect gas flow).

9. If flow is detected or system is displaced, use wet test meter to determine gas flow rate.

10. To determine the penetration of a system in a particular tube size, apply 200 psi nitrogen pressure to the returns end of the tubing and cut into 2 inch sections beginning from the initial injection point until obtaining gas flow.

2.2.3 Test Results with Conventional Fluids

Test #1
System: Injectrol
Maximum Differential Pressure: 1000 psi
Temperature: 75°F

The Injectrol system was successful at penetrating the three largest (0.04, 0.02 and 0.01 inch inside diameter) tubes. At 1000 psi differential pressure, fluid returns were seen instantaneously. Maximum differential pressure (1000 psi) was maintained on the smallest (0.005 inch inside diameter) tube for one hour with no fluid returns.

After approximately twenty-four hours nitrogen pressure was applied in 100 psi increments up to 1000 psi to determine the sealing capabilities of the fluid. The system was designed to have a pump time of two hours. A sample of the test fluid was visually evaluated before determining sealing capabilities, to insure the system was adequately set. The Injectrol system was pushed out of the 0.04 and 0.02 inch tubes at 573 and 694 psi. The two smallest (0.01 & 0.005 inch) tubes maintained 1000 psi for 15 minutes at which time the pressure was released.

The 0.005 inch tube was cut into two inch sections, starting from the initial point of injection, while maintaining 200 psi nitrogen pressure on the returns end. The fluid penetration was determined to be 34 inches.

Test #2
System: PermSeal
Maximum Differential Pressure: 1000 psi
Temperature: 76°F

The PermSeal system was successful at penetrating all of the capillary tubes. The injection pressure was less than 10 psi for the three largest (0.04, 0.02 and 0.01 inch inside diameter) capillary tubes and approximately 500 psi for the smallest 0.005 inch tube. At these pressures adequate flow was established to insure full penetration of the tubes in less than one minute.

The PermSeal system was able to withstand the maximum differential pressure of 1000 psi outlined in testing protocol across all four tubes.

Test #3
System: Stratolock
Maximum Differential Pressure: 1000 psi
Temperature: 78°F

The Stratolock system also penetrated all of the capillary tubes. Flow was established at 10 psi in the two largest (0.04 & 0.02 inch) tubes in less than one minute. The pressure was increased to 300 psi on the 0.01 inch tube before flow was established. When injecting the system into the 0.005 inch tube, it was necessary to increase the pressure to 1000 psi to establish flow.

The Stratolock system was able to withstand the maximum differential pressure of 1000 psi outlined in testing protocol across all four tubes.

Test #4
System: MicroMatrix Cement
Maximum Differential Pressure: 1000 psi
Temperature: 76°F

The MicroMatrix cement was unable to penetrate the three smallest (0.02, 0.01 & 0.005 inch) capillary tubes with 1000 psi differential pressure for one hour. Flow was established with the 0.04 inch capillary tube at 50 psi in less than a minute.

The three smallest capillary tubes were able to withstand the maximum differential pressure of 1000 psi outlined in testing protocol. A surfactant solution was used to detect gas flow from the cement in the 0.04 inch tube at 700 psi.

After the sealing capabilities of the fluids were determined, the 0.02, 0.01 and 0.005 inch capillary tubes were cut into two inch sections, starting from the initial point of injection, while maintaining 200 psi nitrogen pressure on the returns end. The cement penetrated 24 inches into the 0.02 and 0.01 inch tubes, while the 0.005 inch tube had less than 2 inches of penetration.

TABLE 1
Capillary Tube Testing with Conventional Fluids Results Summary

System Test #	Tube Size (in ID)	Tube Length (in)	Injection Pressure (psi)	Penetration (in)	Maximum Pressure (psi)
Injectrol # 1	0.04	60	1000	60	573
	0.02	60	1000	60	694
	0.01	66	1000	66	1000
	0.005	66	1000	34	1000
PermSeal # 2	0.04	60	8.5	60	1000
	0.02	60	8.5	60	1000
	0.01	60	9.8	60	1000
	0.005	60	501.5	60	1000
Stratolock # 3	0.04	60	10	60	1000
	0.02	60	10	60	1000
	0.01	60	299	60	1000
	0.005	60	1000	60	1000
MicroMatrix Cement #4	0.04	60	50	60	706
	0.02	60	1000	24	1000
	0.01	60	1000	24	1000
	0.05	60	1000	2	1000

2.2.3 Capillary Tube Testing with Non-Conventional Fluids
System: Low Viscosity Polymer Solution
Temperature: 76°F

A low viscosity fluid system was also tested. The solution was a 95 wt.% mix of butane and the 600K cSt. polydimethylsiloxane system with a starting viscosity in the 0.5 cP range. This mixture was flowed through the two smallest diameter (5 ft. long) capillary tubes under pressure sufficient to keep the solvent from vaporizing. When the tubes were full, further injection was stopped, and the pressure in the tubes allowed to drop slowly to atmospheric to bleed off the solvent and leave the polymer behind. After the bleed down step, nitrogen injection was initiated to detect tube plugging, but no resistance to gas flow was observed. A much longer capillary tube (25 ft., 0.05 inch diameter) was prepared and the tests repeated using numerous placement techniques, but again proved unsuccessful.

Certain characteristics of the low viscosity fluids might limit their performance under certain test conditions. A primary consideration has to be the very low concentration of plugging agent being carried in the solvent phase in order to generate the low desired injection viscosity. In particular, during these series of tests the injected solution contained only 5 wt.% of the polymer, which, coupled with the very small volume of mixture contained in the capillary tube, resulted in extremely small quantities of polymer being available for plugging action.

A second significant consideration has to be the delivery mechanism. In previous uses for these low viscosity fluids the delivery mechanism was through the destabilization of a carrying fluid that caused polymer to drop out of solution. Furthermore, the polymer precipitation was taking place in a complex and tight rock matrix where separate channels were available for the carrier gas and deposited polymer to follow divergent paths through the matrix, and gas flow velocities were quite low. Consequently, the flowing gas stream could leave behind the deposited polymer, unlike the case of the capillary tube where all the deposited polymer would be in the path of the fast moving ejected gas stream. Repeated plugging mixture injections could also be exploited to plug a specific channel.

Because of pressure constraints that pertain to this application, the entire polymer carrying and deposition mechanism has been changed relative to previous applications. Solvent vaporization rather than phase destabilization is now the mechanism for polymer delivery, and the smooth continuous bore of the capillary tube offers no capture mechanism for retaining polymer solution during the bleed down step. These considerations might be specific to this test procedure, or may require unique ways of rethinking how this concept might work better for this application. Certainly moving from capillary tubes to more realistic cement filled models should provide considerable insight as to what modifications these systems will require.

Additionally, perhaps the most significant advantage of these systems, namely their time stability, was not adequately exploited during these studies. The two most serious disadvantages conventional water based gelling fluids are thought to have for this application is their high (relatively speaking, 1 to 3 cP range) starting viscosity and their limited gelling time. This high starting viscosity was originally thought to limit the ability of these fluids to penetrate the extremely fine microfractures responsible for the most difficult to treat gas migration problems. This low penetration coupled with their fast gelling time (<24 hours) limited the effectiveness of these primarily water based gelling systems for addressing the gas migration problem. Consequently, the novel compositions developed for this application were initially geared to be low viscosity systems to ensure penetration through the fine capillaries. However, the capillary tube experiments with conventional fluids indicated that viscosity was not as severe a constraint as time stability. Consequently, far more concentrated/viscous solutions of polymers could have been tested because their time stability would have allowed for penetration, while also offering more polymer for plugging action.

2.3 CEA-96 Phase I, Testing in Pipe-in-Pipe Models

2.3.1 Testing in Pipe-in-Pipe Models, Introduction

At the completion of the capillary tube testing phase, a sponsors meeting was held to review the results and define the next mode of testing. The capillary tube tests had demonstrated that most of the commercially available sealing fluids had effectively penetrated and sealed even the finest capillaries under investigation. Based on these results it was concluded that further testing should be undertaken on more representative cement models. One of the options under consideration had been a slurry model cell recommended by Halliburton. However, during discussions directed at setting up the laboratory program it was concluded that the repeatability of the slurry test cell was questionable, and this program was abandoned.

A parallel approach under consideration was to use pipe-in-pipe models to mimic the physical configuration encountered in the field. Accordingly, the pipe-in-pipe model incorporated a hollow inner tube (2.5"od) centered within an outer metal tube (4" id.), with the annular space between the tubes filled with cement. This setup was considered to provide a significant amount of flexibility in that the inner tube could be pressurized before the cement was poured and set, following which releasing the pressure on the tube would cause it to pull away from the cement sheath and create micro-channels for gas migration. Along the same lines, the inner tube can be left unpressurized while the cement is setting, and pressurized after the cement sets in order to create micro-fine fractures in the cement. However, the cement itself poses issues that deserve separate treatment below.

The procedure followed with the models was to characterize them in terms of permeability to nitrogen and water flow, subject them to some remedial action, and then reevaluate the model permeability in order to quantify the improvement. Accordingly, models with high nitrogen permeability (> 100 md) were usually subject to more conventional remedial fluids, whereas models with lower nitrogen permeability (<100 md) were subject to remedial treatment using the unconventional hydrocarbon solvent carried treatments. For practical purposes it needs to be kept in mind that even though such permeability measurements are feasible in the laboratory, they are not feasible in a field situation. Accordingly, in field practice, the time for pressure buildup to some preset level after the annulus has been completely bled down is the criterion used to quantify the gas migration problem. It is recommended that perhaps a similar approach should be taken even in laboratory studies (in conjunction with regular permeability measurements) to evaluate pre- and post treatment model properties. This would give a means to correlate measured gas permeabilities to actual pressure buildup in the annulus.

Anecdotal contentions of the personnel who work with gas migration related issues in the field substantiate this position. The conventional wisdom is that if the remedial fluid can be pumped through the gas passages, then the conventional gelling type fluids will effectively seal the gas passages. However, the finest gas migration channels, identified by the longest delays in pressure buildup in a closed annulus, pose the least successful option for treatment with conventional fluids because of limited penetration in the allowable time. It is recommended that future laboratory studies should attempt to quantify these various observations.

2.3.2 Testing in Pipe-in-Pipe Models, Cement Composition

An issue of fundamental concern to studies such as this is the cement set time. The setting of cement is a dynamic event that stretches over many days. The set curve shows exponential behavior with almost 95% of the set in place by about 45 days. Consequently, interpreting the results of an experimental program directed at identifying changes in the property of the annular cement sheath can prove problematic if the base properties of the cement are themselves changing during the course of the testing. A rigorous test procedure would call for making a model and then waiting 45 days for the cement to be almost cured before initiating any testing. Unfortunately, under most testing situations, each successive model builds on what is learnt from the previous model, and waiting 45 days for one model to cure, undertaking a test program, defining the characteristics of a new model, making the model, and waiting 45 days for the model to cure, represents an unacceptable laboratory schedule. Consequently, in the course of this study, models were prepared, allowed to cure briefly, subject to some remedial action, and then promptly evaluated to address the changes in the model, in order to minimize the interference due to the changing cement characteristics. This procedure was found to work quite well without imposing an unacceptable delay in the experimental program.

Cement weight was found to be another significant consideration that will be driven by the choice of the testing to be undertaken. Cement weights in the 12.5 lbs./gal range will generate more flexible models with higher porosities that can be readily modified to generate fractures that will easily take conventional fluids. However, to duplicate the microfine fractures that will not take conventional fluids the cement has to be in at least the 14.7 lbs./gal range, and preferably in the 16.5 lbs./gal range. These heavier weight slurries will generate a very compact cement that will have an extremely low permeability; it will also be extremely difficult to fracture in a controllable fashion. However, these micro-fissures that barely take conventional fluids are exactly the kinds of flow conditions encountered in the least treatable field situations, and represent the most appropriate models for testing unconventional fluids.

2.3.3 Testing in Pipe-in-Pipe Models, Model Histories

Four physically similar pipe-in-pipe models incorporating a 3 ft. length of hollow inner tube (2.5" od) centered within a 3 ft. long outer metal tube (4" id.), were prepared and tested. A schematic of the pipe-in-pipe model is presented in Figure 1. The model was stood vertical and a few inches of the lower section of the annular space filled with sand to provide a buffer for accessing the cement sheath from the bottom. A sufficient quantity of cement was then poured so as to fill the model and leave a couple of inches exposed on top for access. Different cement batches were used with each model to generate different flow and fracture characteristics as desired for specific fluid testing. Some of the models were tested repeatedly with different remedial fluids in order to maximize their contribution. A brief history of the models as prepared chronically is presented below and summarizes the cement used, the model characteristics, remedial fluid used in the testing, and the results obtained.

MODEL #1

Slurry: Class H + 0.5% Halad 344 +1% $CaCl_2$ @16.5 lbs./gal.
Cement had a compressive strength of 4000 psia after seven days.

The inner pipe had been machined to yield at 10,000 psia and thus generate micro-fractures. However, when taken to 12,500 psia and held for 5 minutes no fractures were generated. The measured initial permeability to nitrogen was 69 md at 500 psia, and the water permeability was measured at 0.2 md at 500 psia. This model was considered adequate for testing with the unconventional systems and a mixture that was 90 wt.% butane + 10 Wt.% 1MM cP polymer was prepared. This mixture was injected into the model in repeated 20 cc batches in the top down mode. After each 40 cc injection the model pressure was bled down to eliminate the butane carrier phase and leave behind polymer for plugging. A total of 10 such cycles (400 cc of solution) was injected, after which the model was bled down completely and the closing nitrogen permeability was measured to give 4 md at 500 psia.

These results were found to be quite encouraging because they indicated that the unconventional plugging systems could effectively reduce the permeability by better than 90%. Some of this decrease (perhaps 20%) could be attributed to the continued shrinkage of the cement, but the rest had to come from the plugging agent injected. This continuous change in the properties of the cement sheath is apparent because a nitrogen permeability check a few months later showed a distinct improvement to 0.15 md at 1000 psi nitrogen. The top of the model was cut off to expose the cement top for observation and 2 or 3 extremely tiny bubble streams were observed during nitrogen injection.

Permeability History:

6/1/99	Initial permeability measurement gave 69 md at 500 psia N2; 0.2 md at 500 psia H2O.
6/16/99	Post treatment check gave 4 md at 500 psia N2
9/23/99	Routine check gave 0.15 md @ 1000 psia.

MODEL #2

Slurry: Class H + 4% Bentonite @ 12.4 lbs./gal.

The model was filled with slurry and the inside tube pressurized to 7000 psi for 7 days while the slurry set. The pressure on the inside tube was then released, but had to be re-pressurized to 6000 psi to control gas flow during nitrogen injection for permeability measurement. Subsequently, the 6000 psia pressure was locked in throughout the testing period. Permeability measured was 260 md to nitrogen and 4 md to water at 500 psi. Primary passage for gas was between the outer pipe and the cement sheath. This unusually high permeability was directly attributable to the low mud weight, which, gave rise to significant amounts of matrix permeability in addition to fracture permeability.

Because of the excessive permeability this model was considered an excellent candidate for treatment with conventional gelling fluids like PermSeal. A 200 cc batch of PermSeal was prepared for injection. The PermSeal was flowed into the top of the model above the cement sheath and nitrogen pressure was applied to flow the PermSeal into the model. System returns were collected from the bottom of the model to evaluate the set time for the treatment. After several days the PermSeal had not set in most of the samples collected and showed only minimal gellation in the other samples. This implied that the PermSeal formulation under investigation was inadequate for the desired plugging action, and the test was terminated. The model was flushed with water to eliminate ungelled residual PermSeal in preparation for further testing.

The manufacturer of PermSeal was contacted with regards the unexpected failure, and it was concluded that a combination of low temperature and interaction with cement was responsible for the problem. After considerable laboratory testing by the manufacturer a modified formulation for PermSeal was recommended for testing. This new formulation of PermSeal gave good plugging action. After plugging action was complete, the model permeability was checked by nitrogen injection. Gas flow was first observed at 400 psi. At 500 psi, permeability to nitrogen was 5 md, which is a significant reduction from the originally measured 260 md at 500 psi nitrogen.

Removing the top end cap and observing the gas flow indicated that the primary gas passage remained between outer pipe and cement sheath.

Four months later the model permeability was routinely tested again and showed 480 md to nitrogen at 100 psi. This represents a significant deterioration over the last measured value and demonstrates the disadvantage of working with an uncured cement sheath that is still in transition. These low weight cements give rise to quite porous finished products, and their drying characteristics may be responsible for these deteriorating properties. However, in its present configuration this model seemed ideally suited for a second remedial treatment with PermSeal, which program was initiated.

First, all residual liquids were blown out of the model by nitrogen injection from the top. Next, water was injected from the bottom until it first showed at the top of the cement sheath. The measured volume of injected water was 113 cc. Nitrogen was now reinjected from the top and 71.43 cc of water were recovered before gas breakthrough. A 300cc batch of PermSeal (new formulation) was prepared, poured onto the top of the cement sheath, the top fitting on the model closed, and nitrogen injection on top initiated. After 75 cc of liquid had been recovered from the bottom, a sample of the fluid was tested in sunlight and gelled. An additional 20 cc of liquid was pumped out, the bottom of the model was locked in, the top of the model was exposed to recover the excess PermSeal, and the model was allowed to stand for 24 hours. A nitrogen injection permeability check gave 3.81 md between 200 and 500 psia, and 3.5 md between 500 and 1000 psia.

Given the range of residual permeability in the model, it was considered an ideal candidate for further treatment using the novel light solvent approach. A similar procedure to that presented above was repeated. Nitrogen was injected from the top to clear the model, and water was next injected from the bottom till it just showed at the cement top. There was a dead space of 400 cc between the cement top and the top of the model, and this was filled with sand to minimize the dead space. The model took 130.45 cc water to the cement top and an additional 120.32 cc to the top of the sandpack. The model was pressurized with water to 3000 psia in preparation for a polymer plugging treatment.

In a separate pressure vessel a mixture of 15g of polymer (1 MM cP polydimethylsiloxane) + 59.85 g butane + 225.15g CO2 was prepared. The pressure vessel was equipped with a piston, and water was injected under the piston to take the mixture pressure to 3000 psia. The mixture was rocked at 3000 psia to make single phase, and then injected into the top of the model against the water pressure in the model. At a constant pressure of 3000 psia water was removed from the bottom and the plugging mixture injected from the top. 185.06 cc of the mixture had been injected when gas breakthrough was observed at the bottom. The model was closed out at the bottom and the pressure slowly bled down from the top to destabilize the mixture for polymer delivery and continuous bleeding to eliminate the solvent phase. The nitrogen permeability of the treated model was measured to be 2.41 md between 300 and 500 psia.

The lowered permeability indicated that some improvement was being observed due to the polymer inclusion step, and the treatment was repeated following the steps indicated above. 173.29 cc water was injected from the bottom before water breakthrough was observed at the top of the cement. 173.58 cc of plugging mixture was next injected from the top before gas breakthrough was observed at the bottom. The pressure was again bled down and nitrogen permeability between 300 and 500 psia was determined to be 0.98 md. These results are encouraging for they imply that a dual treatment incorporating a mixture of commercially available water based gelling fluids such as PermSeal and the more exotic hydrocarbon solvent based polymer plugging fluids can effectively reduce cement permeability to very low values.

This cycle was repeated a third time but no further improvement was observed. This residual permeability deserves additional attention as it may be responsible for the smallest but most persistent gas leakage observed in the field, while also proving least treatable. Understanding the nature of this residual permeability will provide clues to new treatment processes or identify a residual permeability that may only be treatable by bleeding down the annulus.

MODEL #3

Slurry: Class H + 4% Bentonite @ 12.4 lbs./gal.

In spite of the model number (#3) this was one of the earlier models tested, and consequently had a number of learning issues associated with it. This was also a low cement weight system and based on our experiences with Model # 2, problems of excessive porosity and permeability could be expected, and were encountered. The inner tube was initially pressurized to 7000 psi and the annulus filled with cement. After the cement set, while maintaining pressure on the inner tube, the permeability was measured to be 11 md to nitrogen and 2 md to water at 100 psi. Physical observations of the top of the cement column during nitrogen injection indicated that the model had high bulk permeability (lots of bubbles across the entire cross sectional area) rather than specific channels. Based on our present knowledge of these models and available remedial techniques, this would have been an ideal candidate for preliminary treatment with the water based gelling fluids prior to testing with the polymer systems. Unfortunately, it was only tested with the polymer systems, and the results were disappointing.

Test 1: 230 cc's of the polymer system (130 cc of 80% Butane & 600,000 cP polymer) was displaced into the cement sheath top down. After the polymer had been displaced the remaining pressure was bled from the top of the model to drop out the polymer. No post treatment improvement in nitrogen permeability was detected.

Test 2: The polymer system (80% Butane & 600,000 cP polymer) was displaced into the model top down, and the pressure was bled off at the top and bottom of the model simultaneously. No post treatment improvement in nitrogen permeability was detected.

Test 3: The polymer system (90% Butane & 1,000,000 cP polymer) was displaced into the model from the bottom. 280 cc's of the polymer system was displaced into the model while slowly bleeding the pressure from the top of the model. No post treatment improvement in nitrogen permeability was detected.

As the above three tests indicate, a number of different placement schemes were attempted to try and improve on the performance of the treatment. Continued failure of the treatment steps prompted a closer scrutiny of the model's physical properties, including porosity through water injection. With the model completely blown down with nitrogen, water was injected from the bottom, and 448.15 cc went in before the first show of water at the cement top. When pushed out again with nitrogen, 422.66 cc of water were recovered. Essentially, this model took 2.5 times the water taken up by Model # 2, indicating significant open internal volume and very large channels, both of which would be extremely adverse to the performance of the polymer plugging scheme. For these reasons this model would have been an excellent candidate for pretreatment with PermSeal before subjecting it to the hydrocarbon/polymer treatment.

Permeability Track:

2/1/99	Init. Check. 11 md to N2 and 2 md to water at 100 psi
Test #1	3/2/99
Test #2	3/8/99
Test #3	4/13/99
10/13/99	220.5 md to N2 @ 100 psi
12/6/99	202 mD to N2 at 100 psi.

MODEL #4

Slurry is a Class H + 4% Bentonite @ 14.7 lbs./gal.

This was a higher density cement system aimed at generating a tighter pack. The inner tube was initially left unpressurized. After the slurry set, the inside tube was pressurized to 2000 psia for 5 minutes and the nitrogen permeability checked. No change in permeability was noticed and the pressurization step was repeated in 1000 psi intervals up to 8000 psi with repeated checks on the permeability. Permeability at the 8000 psia step was 6.8 md at 500 psi nitrogen, and 3.5 md at 500 psi water. With this particular model it was decided to make the starting permeability as tight as possible so as to try and duplicate the worst case in the field. Accordingly, the inner tube of the model was further pressurized to 10,000 psia and the nitrogen permeability determined to be 1.47 md at 207 psia, and 2.53 md at 306 psia.

At this low permeability it was considered unlikely that the commercial gelling fluids (PermSeal) would have any significant penetration in the allocated time because of increasing viscosity due to the gellation process. Consequently, a low viscosity polymer system was picked for remedial treatment. The specific system chosen was 4 wt.% of the 1 MM cP polydimethylsiloxane polymer in butane solution. This mixture had an ambient (69.3F) temperature viscosity of 0.6 cP at 1111 psia and 0.83 cP at 2108 psia. 100 cc of the mixture were injected into the model in a top down mode and the pressure bled down to allow polymer deposition to take place. This procedure was repeated twice more for a total of three cycles (300 cc). After treatment the model permeability to nitrogen was checked and gave 0.0479 md at 344 psia and 0.0993 md at 912 psia.

These are encouraging results because they indicate that with these higher density cements the permeability can be reduced to very low values. What is lacking is an ability to correlate this permeability to the measured pressure recovery rate exploited in field practice to define the extent of the gas migration problem.

2.4 CEA-96 Phase II, Novel Zero Set Polymer Plugging Fluids

2.4.1 CEA-96 Phase II, Background

The technology for generating low viscosity plugging fluids for gas migration channels in cement sheaths has its origins in the need to viscosify gases like carbon dioxide (CO2). CO2 is frequently injected into oil bearing formations for purposes of improved oil recovery. However, the difference in viscosity between the injected CO2 and the in-place reservoir fluids leads to fingering and early breakthrough of the gas. Consequently, there was a need to develop a technology for viscosifying CO2 to bring it up to the 1 cP range. Adding a cosolvent comprising a light hydrocarbon like propane or butane to the CO2 phase facilitated the dissolution of high viscosity polymers of the polydimethylsiloxane family to generate the desired viscosity increase. A significant advancement in the evolution of this technology was the realization that this combination of ingredients offered a mechanism for carrying a high viscosity polymer as a much lower viscosity fluids to some appropriate thief zone. With the fluid properly placed in the thief zone, the stability of the system can be adjusted either through external means or through the natural change in environment during placement, to force precipitation of the polymer for plugging purposes.

A request by the MMS for novel ideas to address the problem of behind casing pressure and the attendant problem of gas migration through microfine fractures in the annular cement sheath between the casing and the formation, lead to the initiation of CEA-96. As initially envisioned, CEA-96 would attempt to apply the polymer delivery system described above to addressing the problem of sustained casing pressure (SCP). Consequenty, the project “Mitigating the Problem of Gas Migration after Primary Cementing” was designated as CEA-96 and first presented to the industry at the Cementing Engineers Association (CEA) annual meeting in October of 1996. Initial funding of $50,00 distributed over two years was provided by the MMS with the requirement that matching funds be provided by industrial sponsors. A considerable effort was expended during 1997 to try and garner industry support. Over the course of numerous meetings, the source of reluctance on the part of potential industry sponsors was identified, and the original objectives of CEA-96 adjusted to accommodate industry concerns.

As originally defined, CEA-96 was focused on the development and evaluation of the light solvent/polymer system for addressing the issue of gas migration through microfine channels. Different carrying solvents were to be evaluated for this purpose, as also realistic laboratory physical models that mimicked gas migration channels. The primary industry concern was that this focus on unknown and untried novel systems with all the attendant uncertainties for success distracted from developing a better understanding of the success and limitations of more conventional solutions for this application.

Accordingly, the original objectives were expanded to include a two pronged approach to the problem. Two potential remedial fluid systems were identified for simultaneous testing, one fluid type comprising of a commercially available water based systems that had a starting viscosity of 1 cP or greater, and the other comprising select versions of the light hydrocarbon solvent/polymer system specifically designed to be under 0.5 cP viscosity. With this adjustment, industry interest was renewed, and the following companies signed on as sponsors: Amoco, Halliburton Energy Services, Intevep, MMS, Mobil, Saga, and Unocal.

This change in emphasis of the original CEA-96 proposal was crucial in order to capture industry interest and continued support for addressing the significant problems associated with SCP/gas migration. Unfortunately, this change in focus had also significantly diluted the resources available for exploring the novel low viscosity fluids. These systems are complex, not well understood, and difficult to interpret and implement. However, they have two significant advantages over the more conventional water based fluids that warrants their further study. They can be formulated to deliver viscosities< 1 cP, and, far more significantly, they are time stable (hence the zero set designation), which allows for much greater penetration before plugging is activated.

In order to further investigate the potential of these fluids, a separate proposal was submitted to the MMS in 1998. Subsequently, the project entitled “Low Viscosity Fluids for Plugging Microfine Fractures" was funded by the MMS ($100,000 over two years) with the express commitment that these funds would only be directed at expanding the data base and developing interpretive skills that would enhance the field implementation of these novel systems. As such, the Zero Set Fluids (ZSF) project would significantly compliment CEA-96, and it was designated as CEA-96, Phase II.

2.4.2 CEA-96 Phase II, Discussion

The primary polymer under consideration for the ZSF systems was polydimethylsiloxane. Considerable prior experience had been developed with this polymer in potential solvent systems, and this polymer is the only one capable of significant solubility in mixtures of hydrocarbons and inert gases like carbon dioxide.

Some preliminary experiments were conducted with the 600,000 cP starting viscosity polymer, but it became quickly obvious that for maximum plugging efficacy the highest viscosity polymers were crucial, and all the later work was done using the 1 MM cP polymer.

Two distinct solvent systems for dissolving the polymer were explored. The first used light neat hydrocarbon systems like ethane, propane, and butane. These mixtures are simple to prepare and maintain and require nothing more than dissolving the polymer in the pressurized liquid solvent phase. Polymer delivery is achieved through solvent vaporization when system pressure is released. The second solvent system involved mixtures of the same three hydrocarbons with an inert gas like carbon dioxide. Both solvent systems have unique advantages and disadvantages and they are discussed separately.

The initial focus of this study was to develop low viscosity fluids (0.5 cP and less) to augment the commercially available fluids that tend to be water based and in the viscosity range of 1+ cP. The expectation was that some of the fractures could prove too small to readily take 1+cP fluids, and consequently, the ability to inject a fluid with a viscosity less than 1 cP that can still deliver plugging action could prove desirable in certain situations. Additionally, because a very large number of solvent and polymer combinations are possible, and each could have a unique application, an equally significant objective was to try and develop some correlation scheme that would provide a reasonable (90%+) first pass prediction of what the viscosity of a particular solvent + polymer mixture would be. Such a correlation would improve significantly on the entirely empirical approach being presently practiced, and could greatly reduce the amount of work needed to produce a particular solution.

However, the capillary tube experiments with conventional fluids clearly demonstrated that starting viscosity was not an impediment to penetration of even the smallest diameter capillary tubes, but rather the quick set time of the conventional gelling fluids limited their penetration. Consequently, this program was adjusted to focus more on the zero set time feature of these novel fluids and to minimize the emphasis on the low viscosity approach. This was a very significant paradigm shift, as the plugging action would be significantly influenced by the amount and viscosity of the polymer phase deposited. Consequently the focus was shifted to the 1 MM cP polymer in order to deliver the highest viscosity plug, and the limitation on the low starting viscosity was lifted in order to deliver the maximum amount of polymer feasible. Essentially, by lifting the limitation on the low starting viscosity, the most powerful feature of these fluids, namely their zero set time ability could be exploited.

2.4.3 CEA-96 Phase II, Neat Hydrocarbon Solvent Systems

As discussed above, this method exploits neat light hydrocarbon solvents, and this study was focused on ethane, propane and butane. Methane is not a viable choice because it can not be condensed at reasonable conditions to give a liquid like solvent phase. Pentane and higher molecular weight hydrocarbons lack the volatility at ambient conditions to be easily stripped from the polymer. Consequently, all the C2, C3, and C4 hydrocarbons including isomers and mixtures of them are the most viable candidates for this application. The data collected included phase behavior and viscosity measurements, and the two are treated separately below.

The actual choice of solvent for a particular application would be dictated by physical circumstance, namely application temperature and pressure. For example, at 70 °F the vapor pressure for butane is 32 psia, propane is 122 psia, and ethane is 560 psia. Consequently, for an application at 70 °F where the pressure would be in the 100 psia range, propane would be the solvent of choice. With butane the solvent phase would not vaporize, whereas with ethane the mixture would need to be injected at a significantly higher pressure than necessary to keep the solvent liquid during placement. With propane the mixture would be injected at a pressure just high enough to keep the propane liquid during placement, following which the pressure would bleed down to the vapor pressure allowing the solvent to evaporate and leave behind the polymer.

2.4.3.1 Neat Hydrocarbon Solvent Systems – Phase Behavior

Of the three neat solvents tested (ethane, propane, and butane), only ethane gave interesting phase behavior. Both propane and butane are extremely good solvents even at high temperatures, so that the polymer and solvent were completely miscible in all proportions and the only phase behavior was the shrinkage of any given solution as the solvent evaporated. Ethane, however, is not a strong solvent for these polymers, and whereas the polymer is completely soluble at ambient conditions, this is not the case at higher temperatures. Consequently, phase behavior measurements with the ethane system involve determining the critical opalescence pressure (COP) as a function of temperature.

Polymer dissolved in the ethane phase at ambient temperature and a pressure above the solvent vapor pressure represents a clear solution. However, if at constant pressure, the temperature of the mixture is raised, the solvent characteristics of the ethane deteriorate and the polymer can no longer be maintained in solution. In simple terms the solvent characteristics are dictated by the close proximity of the solvent molecules to each other which tend to give it a more liquid like character. As the temperature is raised, the energy of the molecules increase affecting their close packing and hence their liquid like characteristics. Increasing the pressure counters this effect by forcing a tighter packing on the molecules. Consequently, a solution of polymer in ethane at ambient temperature and pressure just above the vapor pressure can be expected to destabilize as the temperature is raised, or if the pressure is lowered at some fixed high temperature.

This lack of solubility initially manifests itself as sub-micron particles of polymer in suspension in a continuous solvent phase. The polymer particle size is such that light can be scattered, and this scattering effect gives rise to the critical opalescence phenomena. Essentially, critical opalescence identifies the first set of temperature and pressure conditions at which the solution is destabilized and solvent swollen polymer particles are generated. These tiny particles are unlikely to generate plugging, but are the precursors of the larger more viscous droplets that will eventually generate a plugging phase. In the phase behavior cell, as the pressure is lowered below the COP the particles of polymer phase grow in size until they form a second lower phase of polymer swollen with solvent. Further decrease in pressure results in continued stripping of the solvent from the lower phase until finally a viscous polymer remains for plugging purposes. This solvent stripping process is augmented by increase in temperature.

Experimentally the COP studies call for placing known amounts of polymer and solvent (ethane) in a phase behavior cell at ambient temperature, making the system one phase at some high pressure, usually 10,000 psi, and slowly lowering the pressure while carefully monitoring the system to see if a second phase forms. The pressure at which critical opalescence (the first indications of a second phase) is observed is noted, and the system raised to some higher temperature and the process repeated. This data is used to generate a plot of COP vs. temperature for a given system and composition. The 300,000 cSt polymer was studied in ethane and data for the 10, 20, and 30 wt.% polymer in ethane are presented in Tables 2, 3, and 4. This type of data is needed in order to develop a correlation for interpreting and predicting the behavior of such systems. Because a large combination of solvents (C2 through C5 hydrocarbons), cosolvents (CO2, C1, N2, etc.), and polymers (100 cP to 1 MM +cP polydimethylsiloxanes) are available, some mechanism for developing a semi-quantitative means for predicting the properties of a given mixture, or predicting the ratio of the components needed for developing certain mixture properties, can prove very useful.

2.4.3.2 Hydrocarbon Solvent + Cosolvent Systems – Phase Behavior

As pointed out above, with neat hydrocarbon systems there is only limited latitude in how the phase behavior of a given system can be influenced by temperature or pressure. With ethane there is some immiscibility as the temperature increases, but with propane and butane the pressure has to be below the vapor pressure of the solvent at the application temperature in order for solvent stripping and polymer deposition to take place. However, with any of these systems, the addition of a poor cosolvent like CO2 or N2 significantly affects the phase behavior of the mixture, and much more latitude is available in selecting the conditions at which polymer deposition can take place. This is primarily because a gas like CO2 is a poor solvent for the polymer, but being completely miscible with the light hydrocarbon it works to negatively affect the solvent properties of the light hydrocarbon and allows phase separation to take place in an otherwise completely miscible system. Consequently, even though the pure propane and butane systems would show no critical opalescence behavior at elevated temperatures, both systems would show distinct phase separation even at low temperatures once the solvent characteristics of the hydrocarbon phase were compromised by inert gas addition.

COP measurements for the CO2+ethane system are presented in Tables 5, 6, and 7 and plotted in Figures 2, 3, and 4. All the data are summarized in Figure 5. In the three cases the weight % ethane increases from 15.31% to 20.73% to 34.34%. As expected, increasing the ethane concentration lowers the COP at the same temperature. Such mixed systems have considerable advantages over straight solvent systems because they allow the flexibility to modify the properties of a system to deliver a COP at any desired temperature and pressure.

This flexibility is even more pronounced when CO2 is added to propane or butane systems. Recall that due to the solvent strength of propane and butane no COP is observed with the straight hydrocarbon solvents. However, the addition of CO2 sufficiently disrupts the solvent capacity of the neat solvents to generate systems with distinct COP. Propane offers the greatest flexibility as shown in Tables 8 (15.5%), 9 (24.1%) and 10 (28.9 %) and plotted in Figure 6. At the higher concentrations of propane systems can be generated that give COP well below 1000 psi. The advantages of these mixed systems over neat hydrocarbon systems is that the user is no longer dependent on just vaporization to facilitate polymer deposition. Instead, at some low pressure above the solvent vaporization pressure, polymer separation takes place and plugging action starts before solvent vaporization is completed. These systems have the added advantage that during the venting stage the high CO2 content offers a non-flammable blanket to minimize the fire hazard of the pure solvent system. This is a significant issue, because the offshore operators are quite concerned about any risk to their operations posed by the presence of flammable vapors.

Data for the CO2+ butane system are presented in Tables 11 and 12 and plotted in Figure 7. At 15 wt.% butane COP is observed across a broad range of temperatures starting at ambient (Table 11). However, at 26 % butane the solvent mixture is sufficiently enriched so that no COP is observed until 131.72 F. This is to be expected as butane is a very good solvent for these polymers, and enriching the CO2 with butane imparts this improved solvency to the mixed phase. It is only at higher temperatures that the solvent tendencies of the butane and CO2 mixture deteriorate sufficiently so as to generate a COP. However, it is a weak effect because only minimal pressure (872 psia) is required before the solvent molecules are sufficiently compressed to give a homogeneous solution. With increasing temperature the COP pressure increases, but this is expected. Similarly, at a higher butane content COP would be first observed at a higher temperature, and this is indeed seen to be the case. These data were used to assist in the design and testing of a number of unconventional fluid plugging systems in the pipe-in-pipe models.

2.4.4 CEA-96 Phase II, Viscosity Measurements

Viscosity measurements were undertaken on a number of the mixtures in order to characterize the systems being studied and to assist with development of appropriate correlations. Viscosity measurements were made on polydimethylsiloxane polymers dissolved in light hydrocarbon solvents, or in mixed solvents involving hydrocarbons and CO2. The procedure followed was to prepare a homogeneous mixture of the polymer and solvent by combining the components in the appropriate proportions in a pressure vessel and mixing vigorously to make the system one phase. With pure hydrocarbon solvents the pressure was maintained at least 200 psi above the vapor pressure of the hydrocarbon. With mixed systems involving CO2 and hydrocarbon, the system pressure was maintained at a value sufficient to dissolve the polymer in the weaker solvent system. The appropriate pressure would have been previously determined during COP studies of the selected system, and the pressure during mixing would be at least 500 psi above the corresponding COP pressure.

The procedure called for preparing mixtures of the polymer and solvents in high pressure containers and agitating to make single phase. The mixtures are then transferred at pressure to a capillary viscometer for viscosity measurements. As the name implies, the capillary viscometer uses a capillary tube located in a constant temperature bath (+/- 0.1°C) for measurement purposes. The tube is calibrated using known fluids to obtain the tube constant. The sample is transferred at pressure into two pressure vessels connected to the two ends of the capillary tube. The pressure vessels and transfer lines are filled with mercury for pressure maintenance during transfer and filling. The working of the capillary tube requires a specially designed push-pull pump that works to move mercury back and forth between the two sample cylinders. The movement of the mercury in turn moves the sample floating on top of the mercury back and forth through the capillary tube. The pressure drop across the tube during sample flow is measured for a given flow rate by pressure gauges located at both ends of the tube. The measured pressure drop at a known flow rate in conjunction with the tube calibration gives the sample viscosity.

Initial studies were directed at understanding how the viscosity of the polymer would be influenced by temperature and solvent dilution. Tables 13 through 18 and Figures 8 through 13 show the influence of temperature and solvent (toluene) on a wide range of polymers. Comparing the results in Tables 13, 15 and 17 it is noticed that for all three polymers the polymer viscosity at 224°F is only 25% of the viscosity at 70°F. Unfortunately, the effect of solvent is even more pronounced. In all three cases the presence of 25 wt% solvent (toluene) reduces the polymer viscosity to only 13% of its undiluted value. Consequently, in order to get maximum plugging it is crucial to start with the highest viscosity polymer and to use the most volatile solvent. The higher the starting viscosity of the polymer the more effectively the thinning effect of temperature can be counteracted. The more volatile the solvent, the less stays behind to create a significant thinning effect on the delivered polymer.

Viscosity measurements on the 300K cP polymer dissolved in ethane are presented in Tables 19, 20 and 21, and plotted in Figures 14,15 and 16 for the 90, 80 and 70 Wt.% ethane cases for three temperatures. As can be expected, the viscosity increases with pressure, decreases with temperature, and decreases with increasing ethane concentration. Similar viscosity data for the 600K cP polymer in ethane are presented in Table 22. Additional viscosity measurements were made on specific systems being considered for injection in the pipe-in-pipe models. Table 23 presents viscosity measurements on a mixture of 4 wt.% of the 1 MM cP polymer dissolved in butane. The data is plotted in Figure 17.

As indicated above, there is considerable advantage to injecting a mixture with a high loading of very high viscosity polymer in order to maximize the amount of polymer delivered for plugging action. Consequently, a mixture containing 14 wt.% 1MM cP polymer in 30 wt.% butane and 56 wt.% CO2 prepared for phase behavior testing, was transferred to the viscometer for viscosity measurements. Viscosity data for this system is presented in Table 24 and plotted in Figure 18. At 70°F and 5000 psia the system viscosity is 6.31 cP which is quite workable and injectable. As expected, the viscosity falls with increasing temperature. At the highest temperature (228°F) the system goes two phase at some pressure between 3236 psia and 2114 psia, as manifest by the fact that a light gas with a very low viscosity of 0.08 cP registers first, followed by a much thicker fluid with a viscosity of 184 cP. If the pressure were allowed to continue to fall, this separation would continue, and the viscosity of the lower phase would continue to increase until plugging action started.

2.5 Correlation

2.5.1 Introduction

In general, viscosity of liquid mixtures can not be predicted from pure component properties with high levels of accuracy. The molecular theory used to predict low pressure gas mixture viscosity can not be extended directly to liquid mixtures. In particular, at low temperature, the viscosity is dependent on the structure of the liquid, and therefore it's composition. In some extreme cases, liquid mixtures that have polar components or some degree of association may exhibit extreme behavior (maximum, minimum and/or inflection point). Furthermore, the viscosity of a low pressure gas is due to momentum transfer by collisions between molecules moving randomly between layers moving at different velocities. Liquids may exhibit similar behavior, however viscosity of liquid is exceedingly impacted by the interaction forces between the closed arranged liquid molecules. Therefore, no theory reduces to a simple form that allows predicting of liquid viscosity from basic thermodynamic or physical laws, and an empirical approach is necessary.

Liquid viscosity correlations can be generalized in two forms as follow:

$$f(\eta_m)_L = \sum_i \sum_j x_i x_j f(\eta_{ij})_L \qquad (1)$$

Or

$$f(\eta_m)_L = \sum_i x_i f(\eta_i)_L \qquad (2)$$

In these formulations $f(\eta_{ij})_L$ may be η_L, $\ln \eta_L$, $\frac{1}{\ln \eta_L}$, etc., and x_i may be the liquid volume, weight, or mole fraction.

2.5.2 Viscosity of Polymer-Hydrocarbon Mixtures

In an attempt to develop or adapt a successful approach for predicting polymer-hydrocarbon mixture viscosities, several correlations have been tested. We found that the two-parameter correlation suggested by Lobe[+] was successful. This correlation has the following form.

$$\upsilon_m = \sum_{i=1}^{n} \phi_i \upsilon_i \exp\left(\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\alpha_j \phi_j}{RT} \right) \qquad (3)$$

Where:

υ_m = kinematic viscosity, $\frac{\eta}{\rho}$, cSt

ρ = density, gm/cc

ϕ_j = volume fraction of component j

α_j = characterstics viscosity parameter for j in mixture, cal/g-mol K

R = gas constant cal/g-mol K

T = temperature, K

To use Equation 3 for an n-component mixture, at least n mixture viscosity values must be known to obtain α_j values. Equation 3 will yield an equation that can accommodate non-homogeneous mixtures that exhibit minimum, maximum, and inflection point in their mixture viscosity. For a binary mixture, the correlation in Equation 3 can be written as

$$\upsilon_m = \phi_a \upsilon_a e^{\alpha_b^* \phi_b} + \phi_b \upsilon_b e^{\alpha_a^* \phi_a} \qquad (4)$$

where $\alpha_a^* = \frac{\alpha_a}{RT}$, and $\alpha_b^* = \frac{\alpha_b}{RT}$. If the component a is choosen to be the component with lesser kinematic viscosity, and if the mixture viscosity is a monotonic function of composition, then α_a^* and α_b^* can be correlated with kinematic viscosity ratio as follows:

$$\alpha_a^* = A \ln\left(\frac{\upsilon_b}{\upsilon_a} \right) \qquad (5)$$

and

[+] Reid, R.C., Prausnitz, J.M., and T.K Sherwood (1977): *The Properties of Gases and Liquids*. 3rd edition, McGraw-Hill Book Company.

$$\alpha_b^* = B\ln\left(\frac{\upsilon_b}{\upsilon_a}\right) + \left(C\ln\left(\frac{\upsilon_b}{\upsilon_a}\right)\right)^n \qquad (6)$$

In Equations 5 and 6, A, B, C, and n are parameters to be optimized. After the evaluation of these parameters, it is possible to estimate the binary-hydrocarbon mixture viscosity from pure component kinematic viscosity.

2.5.3 Discussion of the Results

As a first test, the system ethane-600K polymer was choosen for this excersize. Figure 3, shows the experimental data for the 600K polymer viscosity versus temperature along with the polynomial that best fits the data. While the density of the polymer is considered constant (0.978 gm/cc) at different pressure and temperature, the density and viscosity of ethane are evaluated from an Equation of State. Table 25 shows the relevant pure component properties of ethane.

TABLE 25
Ethane Viscosity and Density at Different Pressure and Temperature

Temp. (°F)	Pressure (psia)	Viscosity (cP)	Density (g/cc)
61	3000	0.0770	0.4342
100	3000	0.0642	0.4069
150	3000	0.0507	0.3642
61	7241	0.1074	0.4852
61	3000	0.0785	0.4380
61	2000	0.0691	0.4185
150	7000	0.0770	0.4369
150	5000	0.0656	0.4095
150	3000	0.0507	0.3642
62.2	7000	0.1056	0.4826
62.2	3000	0.0781	0.4371
62.2	2000	0.0687	0.4173
67	7000	0.1044	0.4801
67	5000	0.0919	0.4608
67	3000	0.0768	0.4334
67	2000	0.0672	0.4128

The density of the mixture is calculated from the densities and the weight fractions of the pure components as follows:

$$\rho_m = \sum_{i=1}^{n} w_i \rho_i$$

The experimental measurement of the mixture viscosity at different composition, pressure, and temperature is depicted in Table 26.

TABLE 26
Mixture Viscosities at Different Pressure, Temperature, and Ethane Concentration

Ethane Weight %	Temp (°F)	Pressure (psia)	Experimental Viscosity (cP)	Calculated Viscosity (cP)
70	66	3000	21.3	20.88
70	100	3000	11.6	13.29
70	150	3000	8.5	6.69
80	61	7241	6.5	6.79
80	61	3000	3.5	3.97
80	61	2000	2.7	3.17
80	150	7000	3.8	3.15
80	150	5000	2.7	2.33
80	150	3000	1.4	1.40
85	62.2	7000	3.5	2.89
85	62.2	3000	1.9	1.79
85	62.2	2000	1.5	1.44
85	150	7000	1.6	1.45
85	150	5000	1.1	1.10
85	150	3000	0.69	0.69
90	67	7000	1.1	1.22
90	67	5000	0.89	1.01
90	67	3000	0.63	0.77
90	67	2000	0.46	0.63
90	150	7000	0.78	0.66
90	150	5000	0.55	0.51
90	150	3000	0.28	0.33

Using the data of Figure 19 and Tables 25 and 26, the parameters of Equations 4 to 6 were optimized to the following values:

$A = -0.652672$
$B = 1.153765$
$C = 2.792576$
$n = 0.682431$

The calculated mixture viscosity values from these parameters are also presented in Table 26. Figure 20 shows the degree of spread of the data around the 45 degree line. The average absolute error in the calculated data of Table 26 and Figure 20 is 11.7%.

2.5.4 Recommendation

Examination of the data in Table 26, indicates that the highest error in the viscosity data is encountered where the impact of pressure and temperature is high on the molar volume of the mixture. Since the assumption in this calculation is based on additive mixtures, which is not the case, it is recommended that the density of the mixture be measured at the reported experimental conditions. The correlation parameters can be improved with the density data, and the model would have better accuracy and predictive capability.

2.5.4 Future Plans

Continue development of the correlation approach to encompass more polymer/solvent systems. The ultimate goal is to come as close as possible to generating one correlation for the bulk of the systems.

Generate viscosity, density, and phase behavior data as needed for evaluating the 1 million cSt. polymer systems for this application. Incorporate these results into the correlation effort.

TABLE 2

Ethane (90 wt.%) + 300 K cP Polymer

Temperature (F)	Pressure (psia)	Sample Volume (cc)	Liquid Vol. Fraction
67	4000	34.02	
67	3000	35.18	
67	2000	36.81	
67	1165	39.05	0.379
67	550	48.19	0.154
150	5000	37.17	
150	4000	38.76	
150	3000	41.40	
150	2680	42.52	0.316
150	1785	50.12	0.138
200	6000	38.17	
200	5000	39.92	
200	4000	42.49	
200	3453	44.46	0.183
200	2393	52.53	0.133

TABLE 3

Ethane (80 wt.%) + 300 K cP Polymer

Temperature (F)	Pressure (psia)	Sample Volume (cc)	Liquid Vol. Fraction
74	4000	34.02	
74	3000	35.00	
74	2000	36.45	
74	1126	38.76	0.902
74	700	41.30	0.376
155	5000	37.03	
155	4000	38.45	
155	3000	40.73	0.000
155	2637	42.83	0.448
155	1999	48.67	0.292
200	6000	38.23	
200	5000	39.83	
200	4000	42.24	
200	3260	44.85	0.509
200	2345	52.30	0.237

TABLE 4

Ethane (70 wt.%) + 300 K cP Polymer

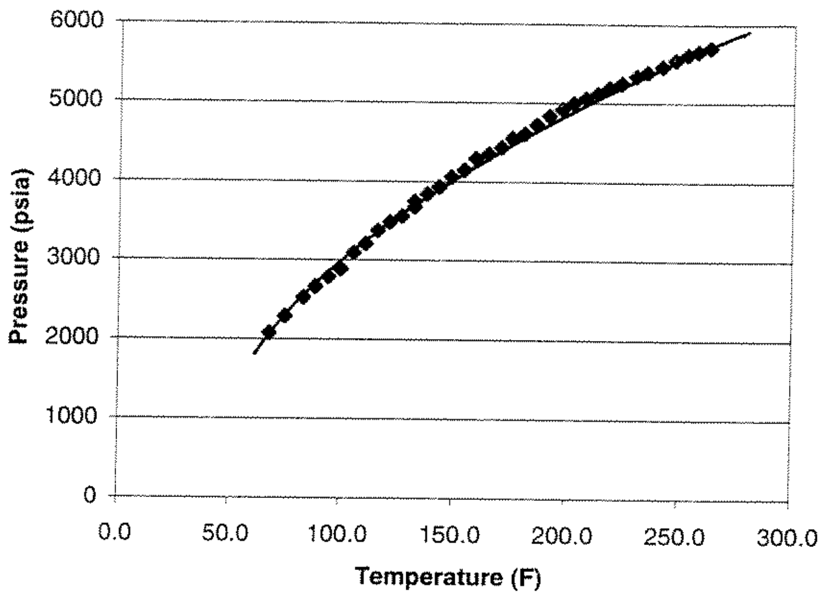
Temperature (F)	Pressure (psia)	Sample Volume (cc)	Liquid Vol. Fraction
69.1	4000	34.02	
69.1	3000	34.85	
69.1	2000	36.30	
69.1	1500	37.04	
69.1	1300	37.52	
69.1	1122	37.69	0.883
69.1	1000	38.57	0.520
69.1	800	39.30	0.422
69.1	551	64.12	0.226
88	1566	38.22	0.863
108	4000	35.76	
108	3000	36.78	
108	2000	38.41	
108	1956	38.90	0.907
128	2320	39.52	0.907
148	4000	37.47	
148	3000	38.91	
148	2667	40.33	0.895
168	2995	41.07	0.899
168	4000	39.75	
188	3257	41.88	0.895
200	6000	37.37	
200	5000	38.62	
200	4000	40.55	
200	3390	42.32	0.895
200	3000	44.23	0.450
200	2500	48.09	0.294

TABLE 5

COP Measurements in C2+CO2

Temperature (F)	Critical Opalesc. Pressure (psia)
68.2	2079
75.2	2290
83.5	2526
88.7	2662
94.5	2789
99.9	2887
105.6	3093
110.8	3210
116.2	3377
121.6	3484
127.0	3563
132.4	3678
132.4	3749
138.0	3847
143.2	3935
148.5	4062
154.2	4150
159.1	4297
164.8	4356
170.4	4438
175.1	4556
180.7	4611
185.9	4726
191.5	4840
197.1	4930
202.1	5001
207.5	5061
212.7	5122
217.9	5197
223.5	5254
229.8	5346
234.7	5395
241.3	5466
247.1	5550
252.5	5620
257.2	5661
262.6	5707

Figure 2. COP vs Temperature



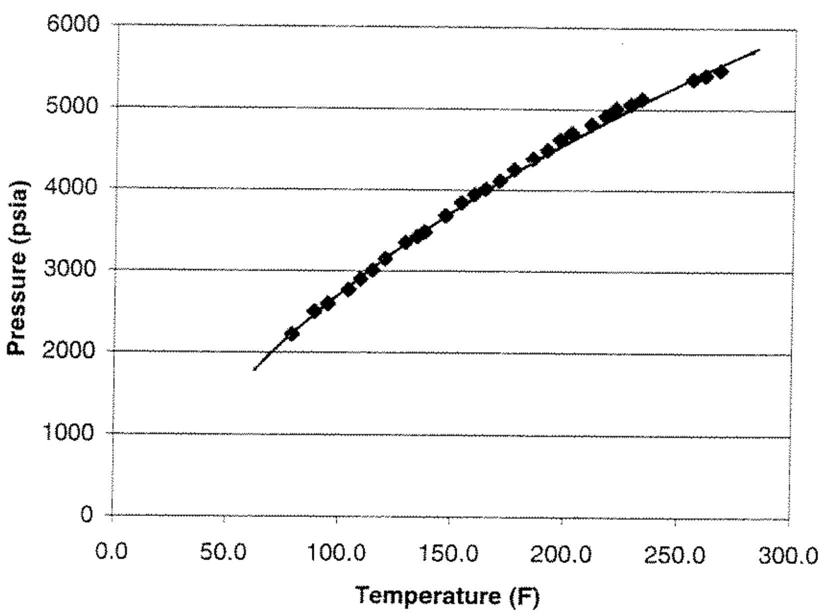
. % Polym* = 16.94
Wt. % CO2 = 67.75
Wt.% Ethane = 15.31

TABLE 6

COP Measurements in C2+CO2

Temperature (F)	Critical Opalesc. Pressure (psia)
79.2	2220
88.9	2500
94.8	2600
103.8	2770
109.2	2901
114.6	3010
120.4	3150
129.4	3350
134.8	3427
137.8	3480
146.8	3680
153.7	3844
159.4	3944
164.5	4015
170.8	4115
177.1	4255
185.4	4390
191.5	4497
196.9	4625
201.9	4710
210.6	4815
216.7	4925
221.2	5015
227.7	5064
232.5	5131
255.0	5374
260.4	5420
266.7	5486

Figure 3. COP vs. Temperature



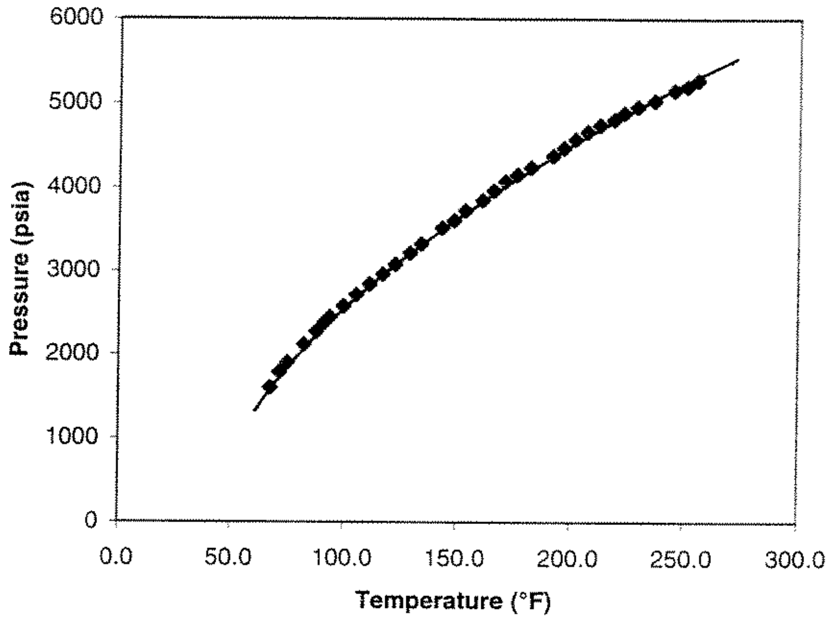
Wt. % Polym* = 17.89
Wt. % CO2 = 61.38
Wt.% Ethane = 20.73

TABLE 7

COP Measurements in C2+CO2

Temperature (F)	Critical Opalesc. Pressure (psia)
67.3	1605
71.2	1790
74.8	1908
82.2	2123
87.6	2277
91.2	2386
93.6	2454
99.7	2582
105.3	2720
111.2	2849
117.0	2967
122.5	3084
129.0	3221
134.06	3329
143.24	3523
148.46	3612
153.5	3729
160.88	3856
165.92	3972
170.78	4081
176	4160
181.94	4248
191.48	4385
196.34	4479
201.38	4581
206.78	4674
212.18	4752
218.48	4816
222.8	4894
228.74	4968
236.12	5040
244.94	5159
250.52	5209
255.2	5282

Figure 4. COP vs Temperature



Wt. % Polym* = 14.82
Wt. % CO2 = 50.85
Wt.% Ethane = 34.34

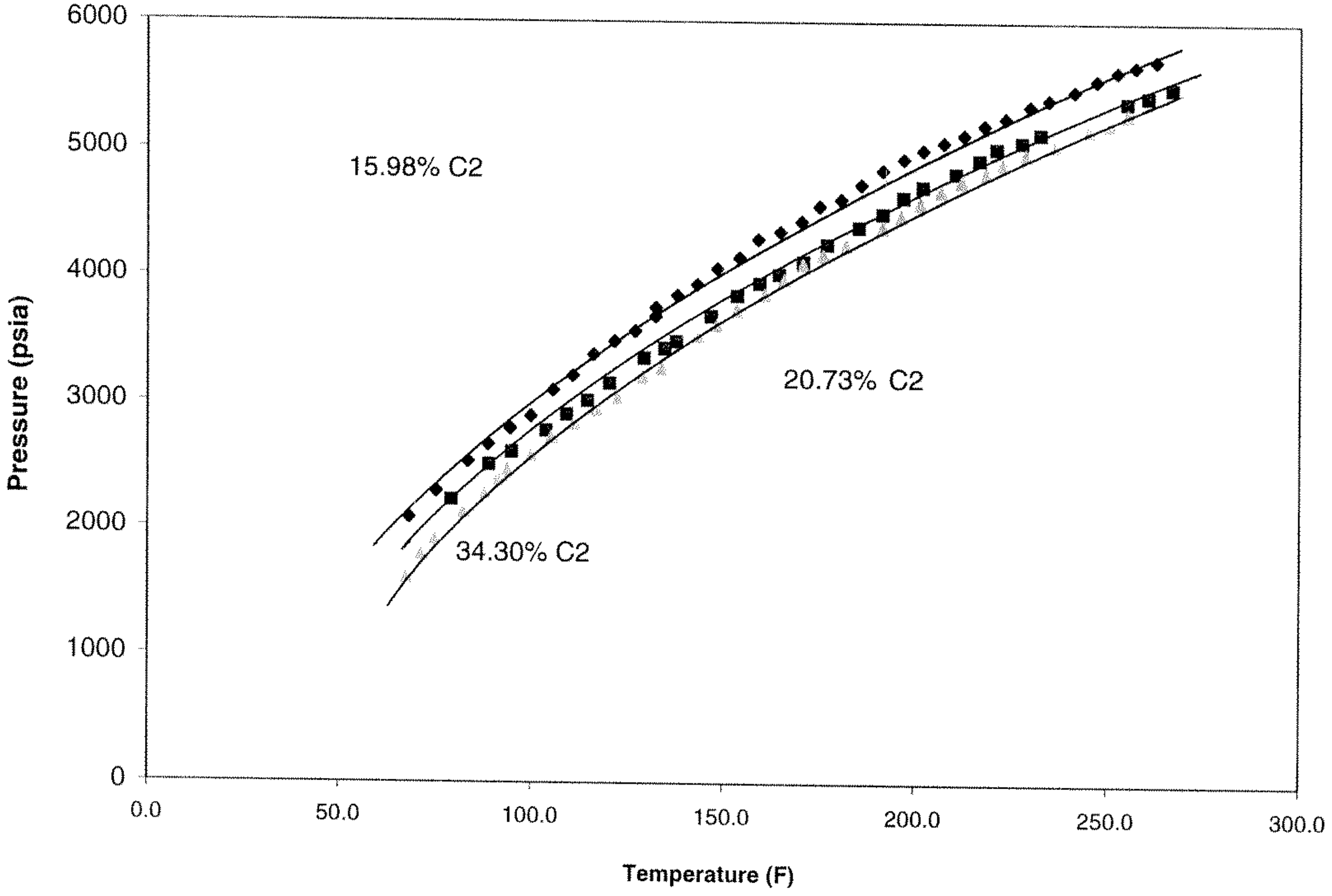


Figure 5. COP vs Temperature Comparisons

TABLE 8

COP Measurements in C3+CO2

Temperature (F)	Critical Opalesc. Pressure (psia)
65.5	1319
110.7	2603
115.7	2760
121.1	2897
126.5	3004
131.9	3112
137.7	3230
158.9	3698
164.3	3822
169.9	3881
175.1	3984
180.5	4101
185.9	4166
191.3	4292
196.52	4370
202.1	4483
207.5	4503
212.9	4599
218.3	4637
223.7	4718
229.1	4747

Wt. % Polym* = 16.91
Wt. % CO2 = 67.62
Wt. % Propane = 15.48

TABLE 9

COP Measurements in C3+CO2

Temperature (F)	Critical Opalesc. Pressure (psia)
62.4	547
64.8	664
70.3	733
76.3	859
81.9	956
87.3	1046
101.7	1438
106.9	1553
112.1	1646
118.0	1793
123.4	1938
128.8	2006
133.7	2153
139.46	2237
152.42	2582
157.46	2705
161.96	2857
167.9	2877
172.76	2975
179.96	3083
186.44	3220
193.64	3328
197.78	3435
203.18	3502
208.4	3582
213.8	3675
219.2	3771
224.6	3876
233.24	3977

Wt. % Polym* = 56.82
Wt. % CO2 = 14.21
Wt.%Propane = 28.97

TABLE 10

COP Measurements in C3+CO2

Temperature (F)	Critical Opalesc. Pressure (psia)
70.7	713
76.1	821
81.7	987
86.9	1056
92.3	1183
98.1	1379
103.3	1443
108.5	1620
114.1	1722
119.3	1805
126.5	1903
131.9	2113
137.3	2160
144.5	2371
149.9	2505
155.3	2626
160.7	2709
166.1	2799
171.5	2892
176.9	3009
182.3	3078
187.7	3216
193.1	3298
198.5	3394
203.9	3509
209.3	3558
214.7	3661
220.1	3773
225.5	3849
230.9	3940
233.78	3986.00

Wt. % Polym* = 28.68
Wt. % CO2 = 47.234
Wt. % Propane = 24.08

Figure 6. COP Measurements in CO2 + C3

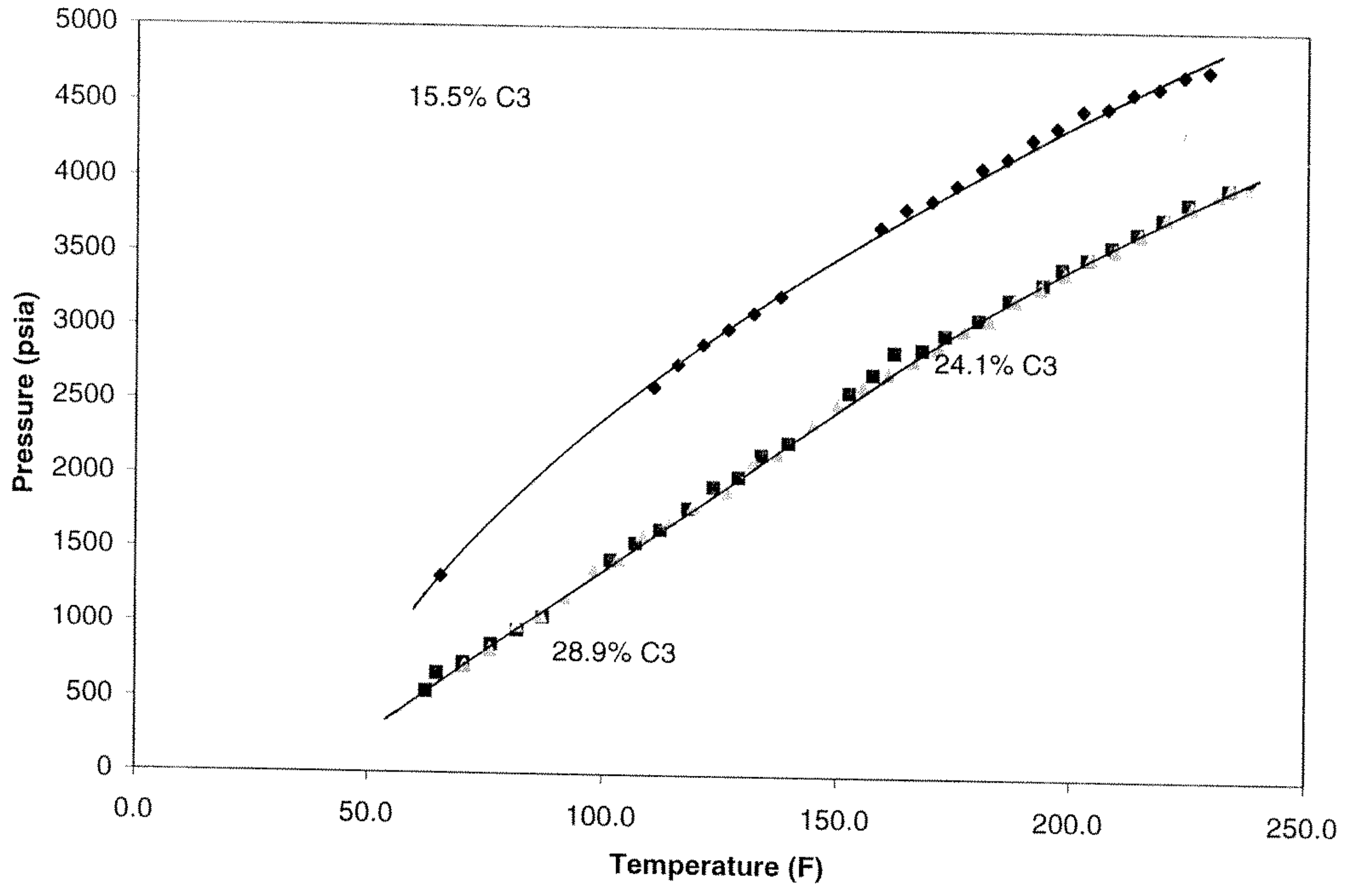


TABLE 11

Phase Behavior for the CO2+Butane System

Component	Wt. %	Temperature (F)	Pressure (psia)	Sample Volume (cc)	Poly. Phase Volume (cc)	Polym. Relat. Volume Fract.
Polymer	16.99	68.5	1220			
CO2	67.98	77.0	1499			
Butane	15.02	81.1	1717			
		86.0	1768			
		91.4	1973			
		96.8	2075			
		102.2	2196			
		107.6	2294			
		113.0	2412			
		122.4	2773			
		140.0	3286			
		161.8	3951			
		167.2	4145			
		177.4	4588			
		184.8	4853			
		190.2	5154			
		195.1	5447			
		200.5	5692			
		205.9	5935			
		211.3	6170			
		216.7	6517			
		222.1	6926			
		227.5	7283			
		231.1	7575			
		236.5	8098			
		68.20	1150	26.76	21.193	0.311
		68.20	1125	26.53	21.011	0.308
		68.20	1109	26.59	21.055	0.309
Polymer	17.49	147.7	7973	17.96	7.67	0.427
CO2	69.98	147.7	4002	21.19	7.69	0.363
Butane	12.52	147.7	1020	83.82	2.08	0.025

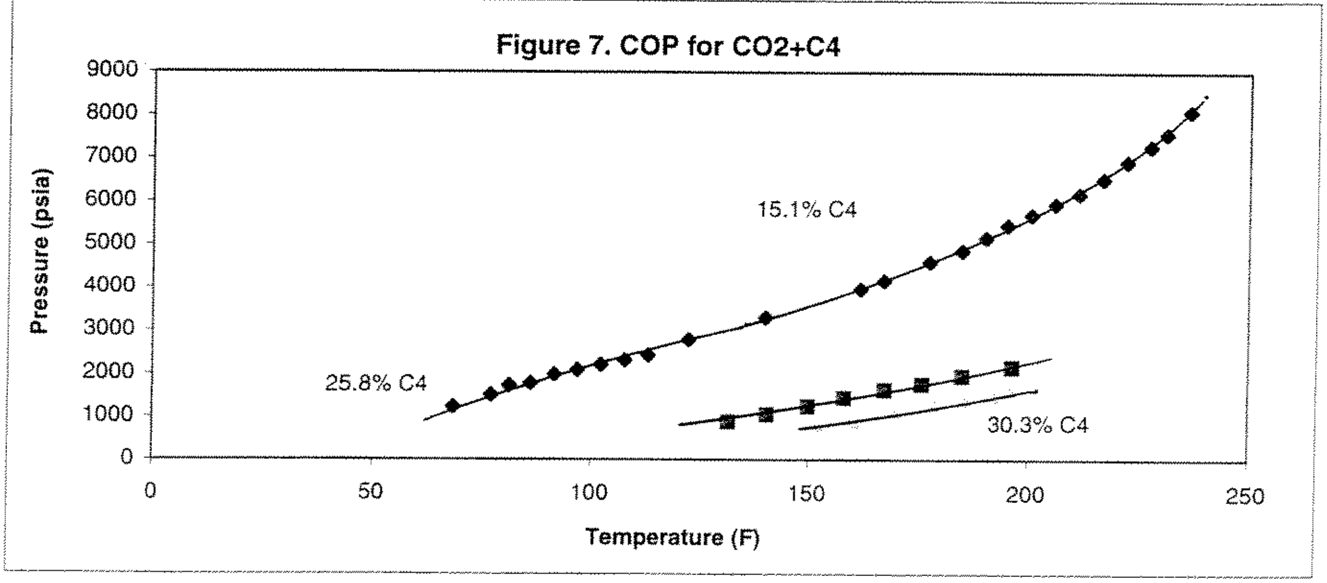


Figure 7. COP for CO2+C4

TABLE 12

Phase Behavior for the CO2+Butane System

Component	Wt. %	Temperature (F)	Pressure (psia)	Sample Volume (cc)	Poly. Phase Volume (cc)	Polym. Relat. Volume Fract.
Polymer	14.48	131.72	872	COP		
CO2	59.72	140.54	1049	COP		
Butane	25.79	149.90	1236	COP		
		158.18	1429	COP		
		167.54	1615	COP		
		176.00	1748	COP		
		185.00	1935	COP		
		196.34	2140	COP		
		196.34	2114	49.32	9.64	0.195
		196.34	1341	53.83	10.02	0.186
		196.34	988	97.93	8.25	0.084
Polymer	13.66	151.88	793	COP		
CO2	56.32	160.34	889	COP		
Butane	30.03	169.16	1104	COP		
		178.70	1272	COP		
		185.36	1389	COP		
		192.02	1488	COP		
		195.80	1595	COP		
		195.80	1008	60.05	11.260	0.187
		195.80	956	96.36	13.210	0.137

TABLE 13

12.5K cP. Polymer Viscosity

Temperature (°F)	Viscosity (cP)
70.5	11100
73	10900
90.6	9200
110	7900
140.2	6200
224	2800

Figure 8. Effect of Temperature on 12.5 CP Polymer Viscosity

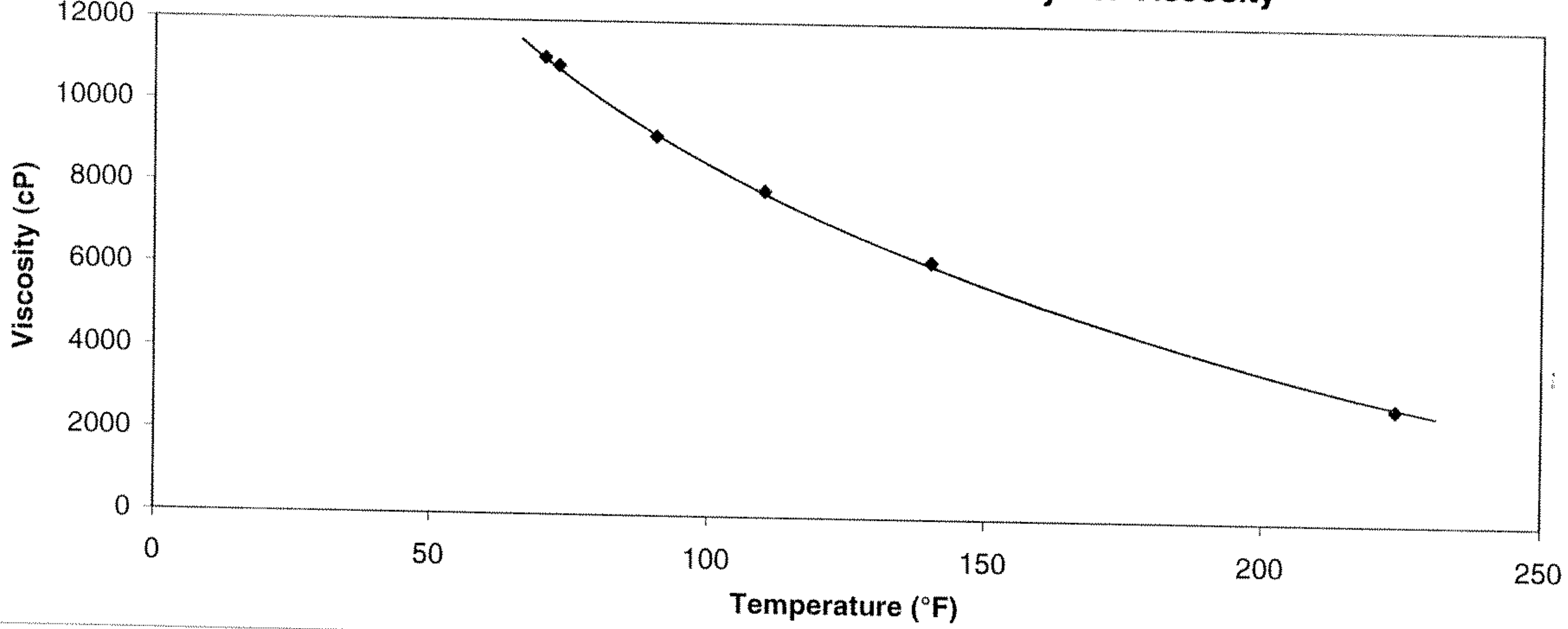


TABLE 14

12.5K cP. Polymer Viscosity

Weight % Polymer *	Viscosity (cP)
100	11100
75	1560
50	244
25	34

* In toluene

Figure 9. 12.5K cP Viscosity vs. Toluene Conc.

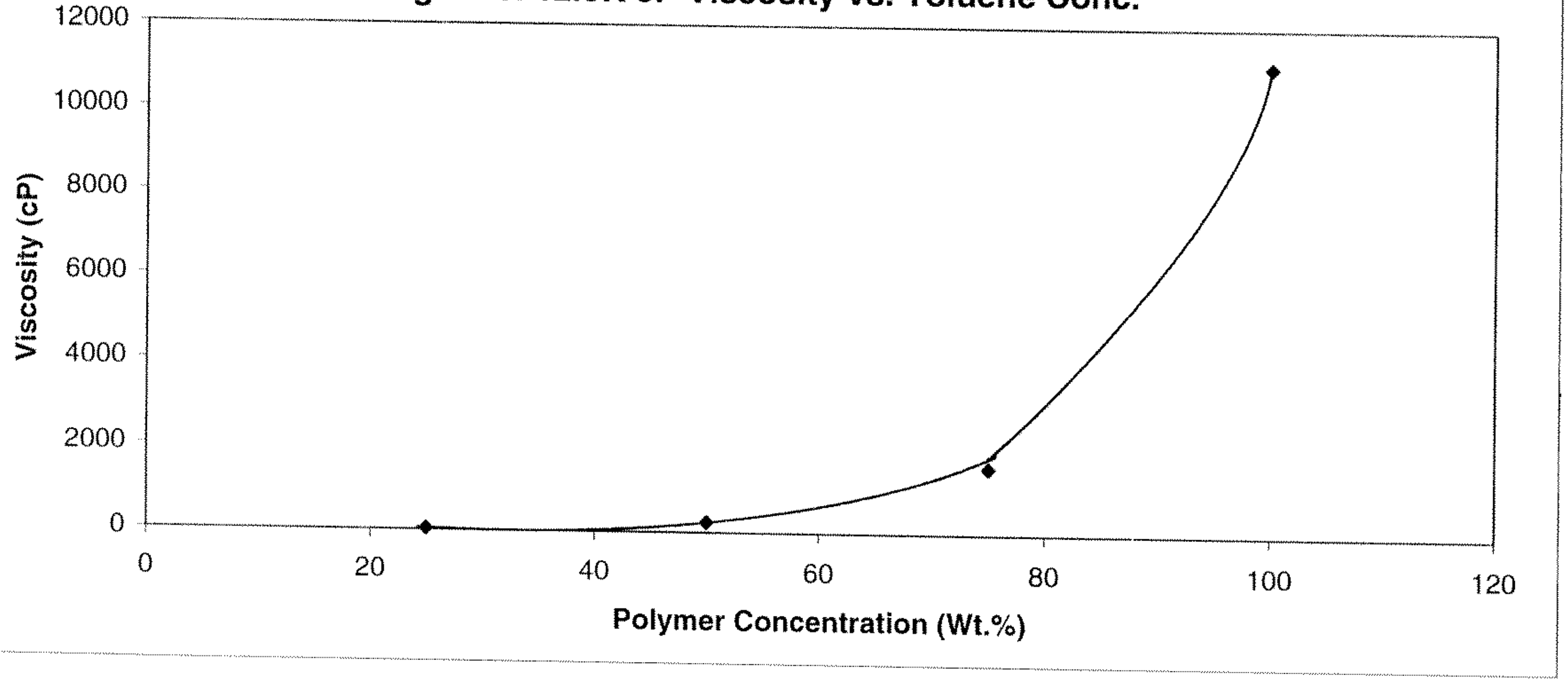


TABLE 15

100K cP. Polymer Viscosity

Temperature (°F)	Viscosity (cP)
70.5	104000
73	103000
90.6	86300
110	74600
140	56900
224	28000

Figure 10. Viscosity of 100K cP Polymer vs Temperature

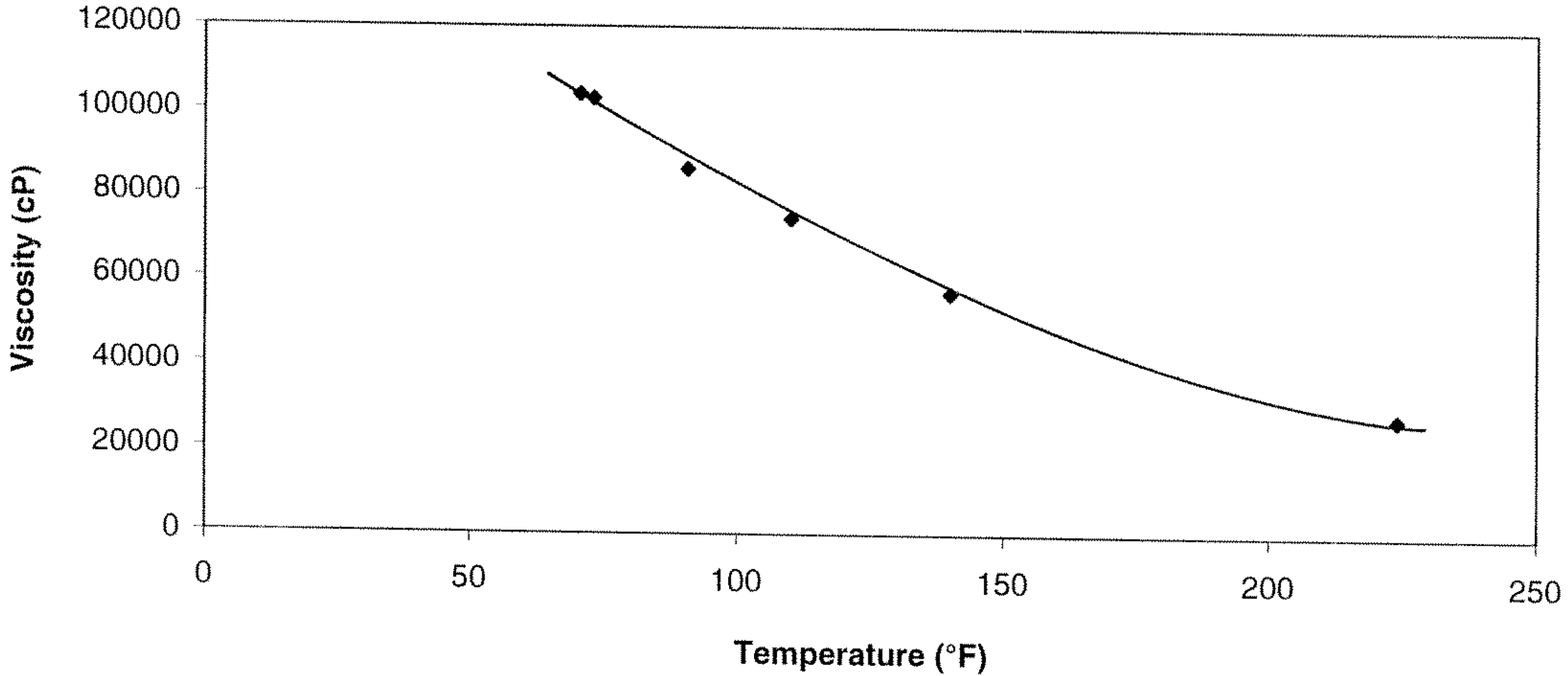


TABLE 16

100 K cP. Polymer Viscosity

Weight % Polymer *	Viscosity (cP)
100	11100
75	1560
50	244
25	34

* In toluene

Figure 11. 100K cP Polymer Viscosity vs Toluene Concentration

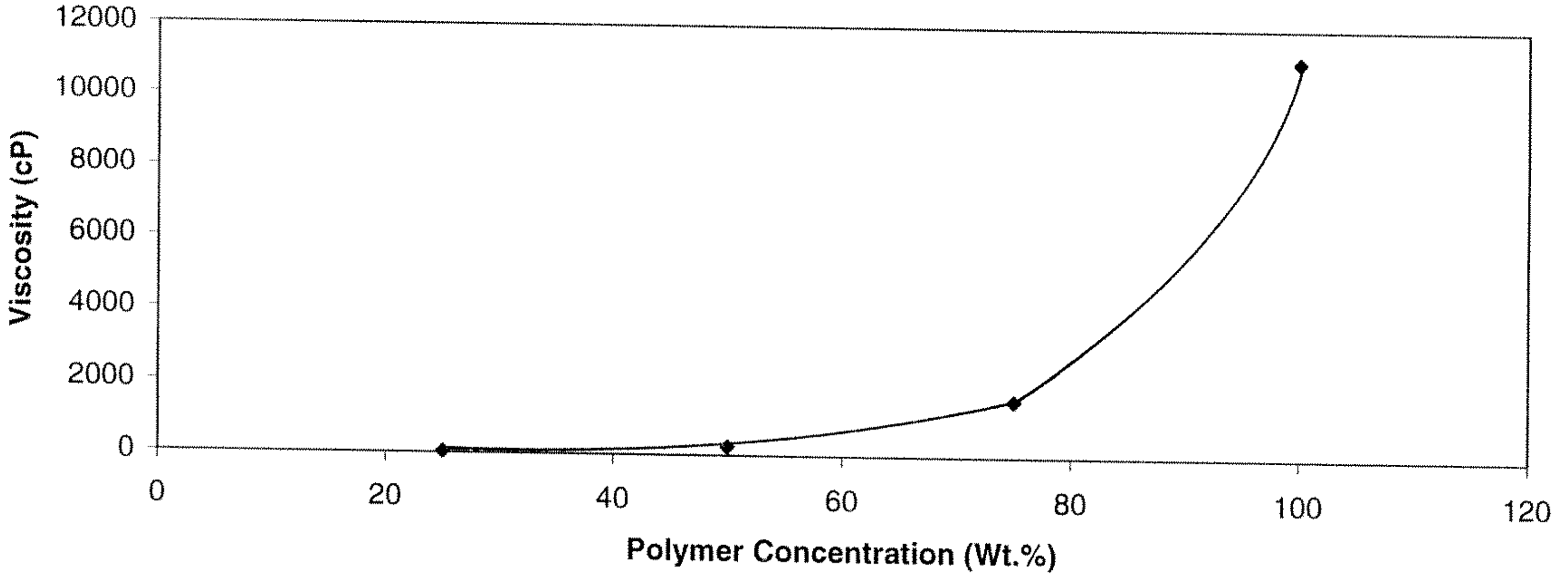


TABLE 17

600K cP. Polymer Viscosity

Temperature (°F)	Viscosity (cP)
70.5	602000
90.3	504000
110	425000
140	332000
224	153000

Figure 12. Viscosity,100K cP Polymer vs Temperature

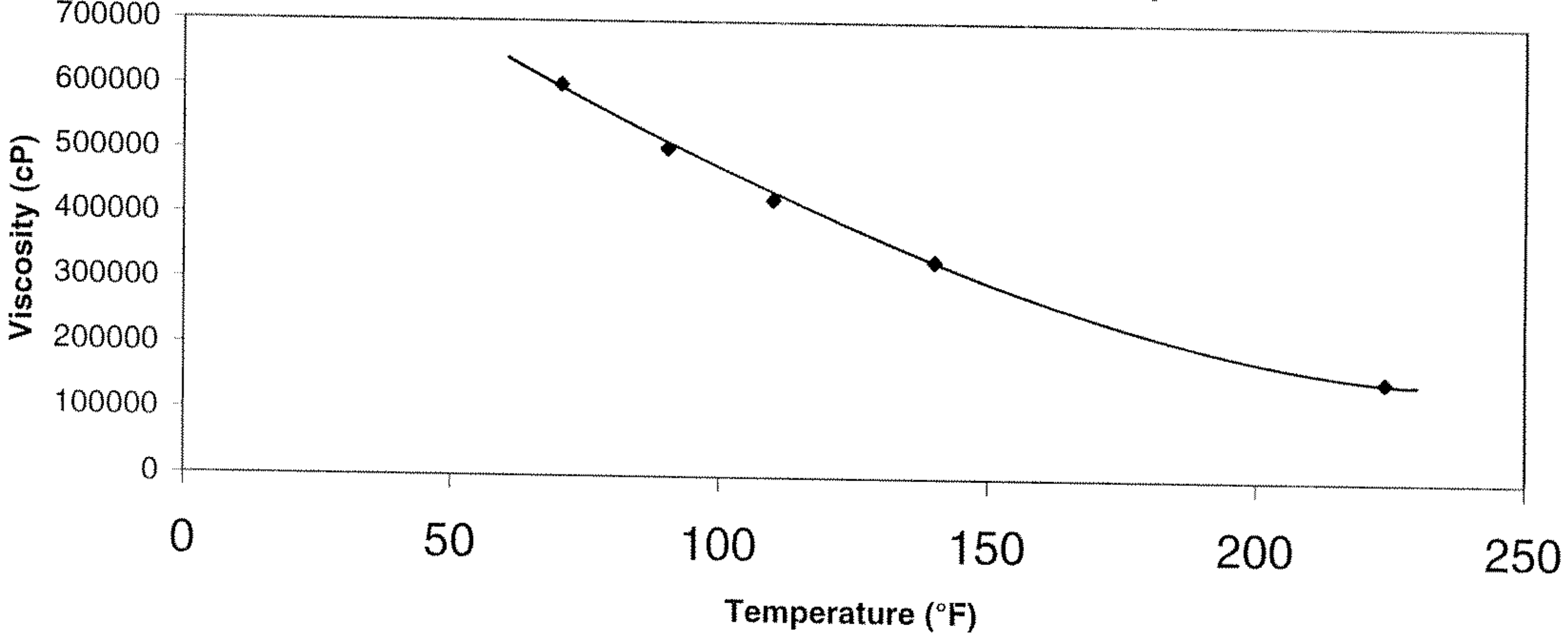


TABLE 18

600 K cP. Polymer Viscosity

Weight % Polymer *	Viscosity (cP)
100	602000
75	79700
50	8460
25	370

* In toluene

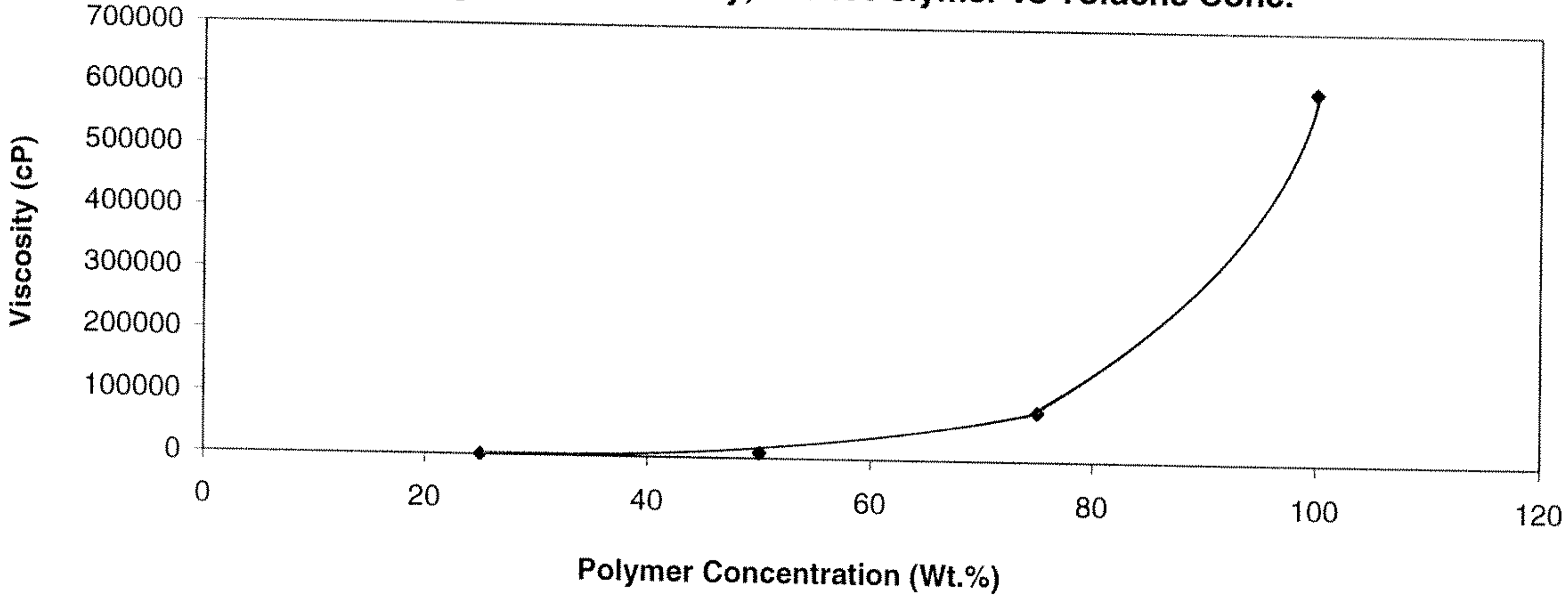


Figure 13. Viscosity, 600 K Polymer vs Toluene Conc.

TABLE 19

300K cP Polymer in Ethane
90 wt.% Ethane - 10 Wt.% Polymer

Temperature (F)	Pressure (psia)	Viscosity (cP)
200	6000	0.52
200	5000	0.41
200	4000	0.28
150	5000	0.54
150	4000	0.42
150	3000	0.28
68	4000	0.78
68	3000	0.64
68	2000	0.48

Figure 14. Viscosity of 300K cP (10 Wt.%) Polymer in Ethane (90 Wt.%)

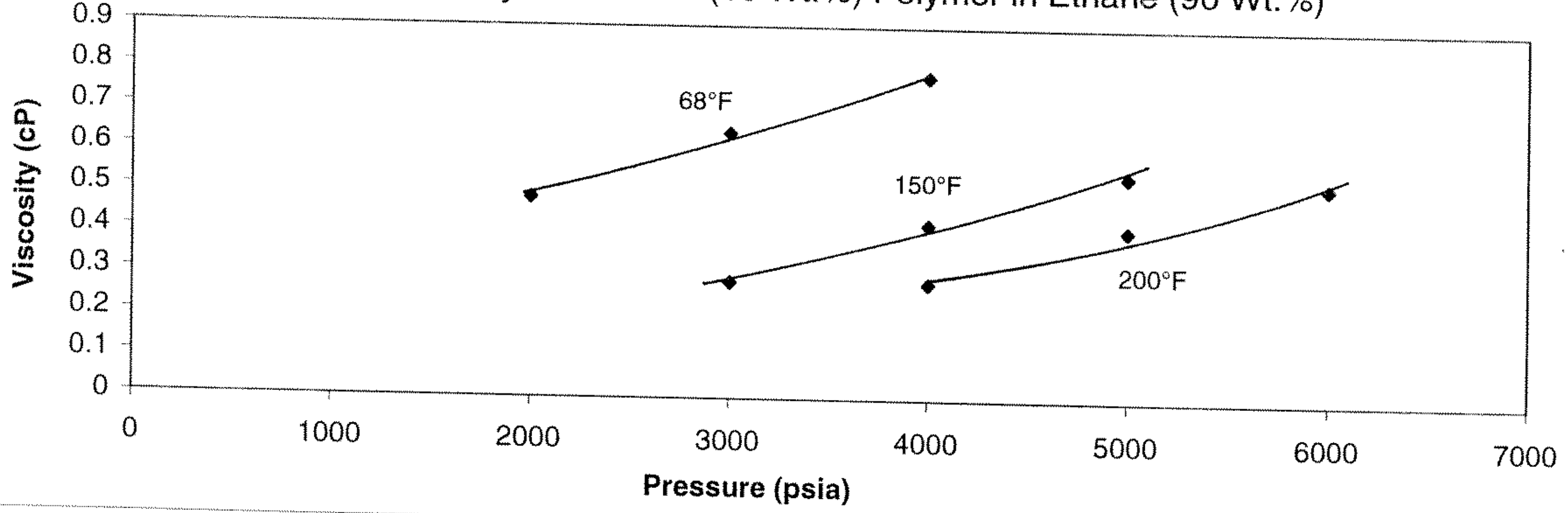


TABLE 20

300K cP Polymer in Ethane
80 wt.% Ethane - 20 Wt.% Polymer

Temperature (F)	Pressure (psia)	Viscosity (cP)
200	6000	2.09
200	5000	1.53
200	4000	1.11
150	5000	2.25
150	4000	1.66
150	3000	1.11
69	4000	3.35
69	3000	2.91
69	2000	2.43

Figure 15. Viscosity of 300K Polymer (80Wt.%) in C3 (20Wt. %)

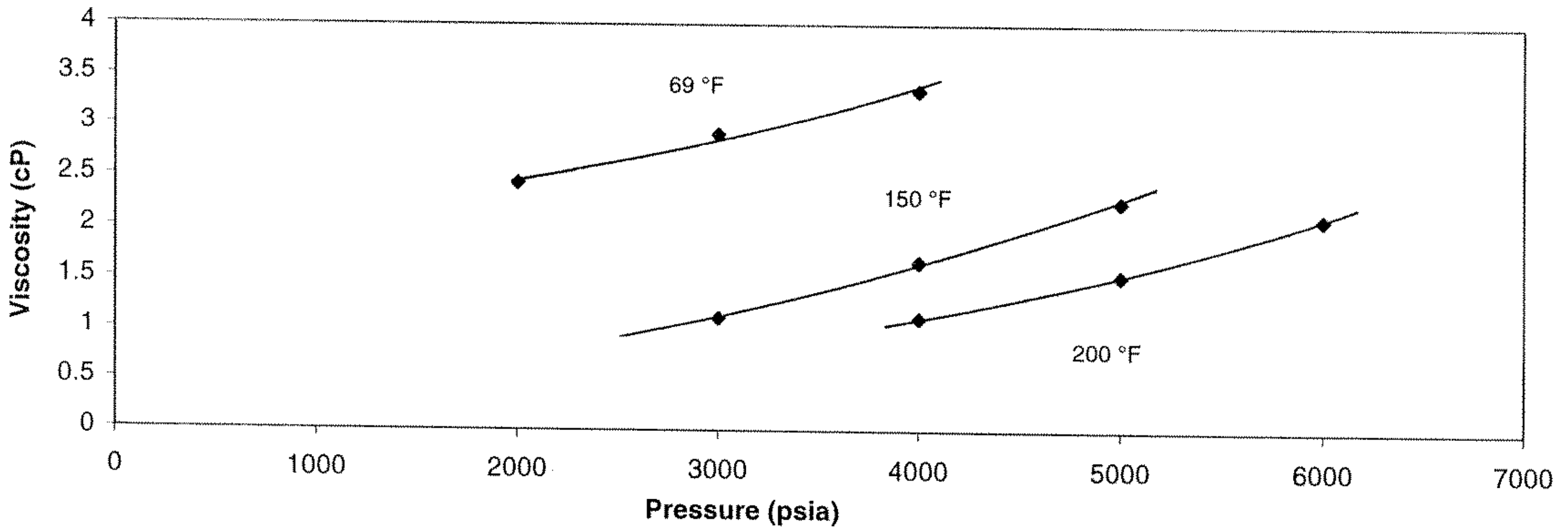


TABLE 21

300K cP Polymer in Ethane
70 wt.% Ethane - 30 Wt.% Polymer

Temperature (F)	Pressure (psia)	Viscosity (cP)
200	6000	4.27
200	5000	3.31
200	4000	2.3
150	5000	5.36
150	4000	4.21
150	3000	3.06
67	4000	8.68
67	3000	7.22
67	2000	5.65

Figure 16. Viscosities, 300K cP Polymer (30 Wt.%) in Ethane (70 Wt.%)

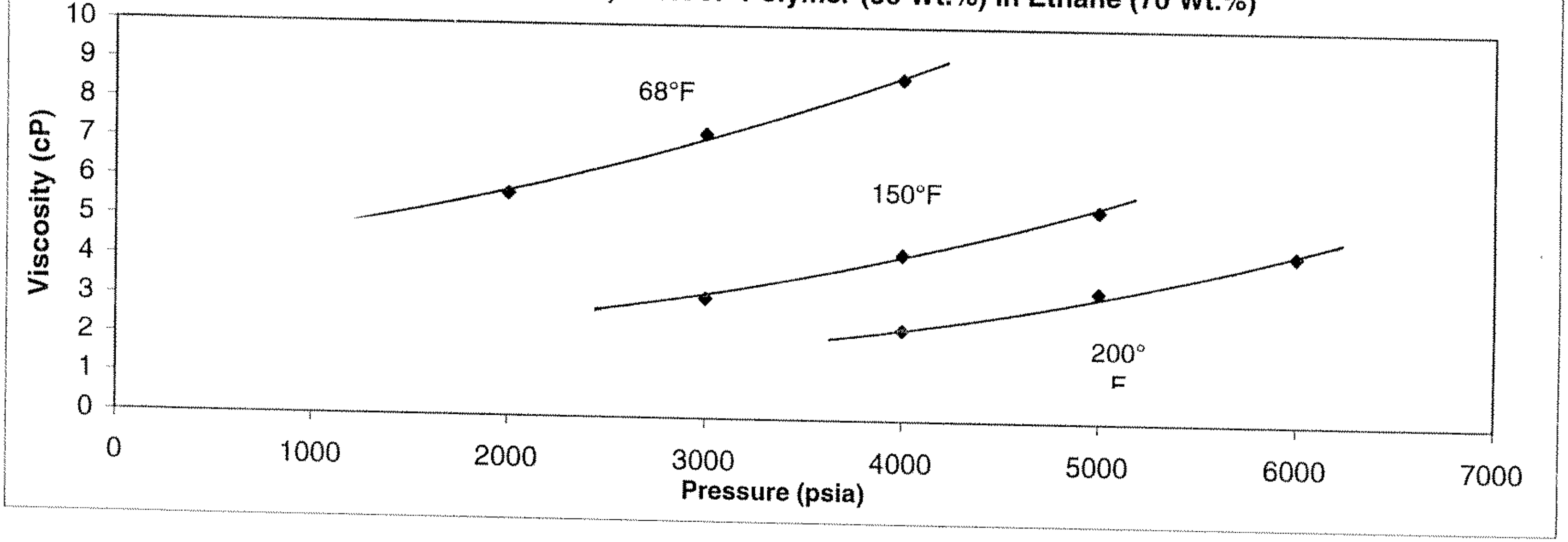


TABLE 22

600K cSt. Polymer in Ethane

Ethane (Wt.%)	Temperature (F)	Pressure (psia)	Viscosity (cP)
70	66	3000	21.3
70	100	3000	11.6
70	150	3000	8.5
80	61	7241	6.5
80	61	3000	3.5
80	61	2000	2.7
80	150	7000	3.8
80	150	5000	2.7
80	150	3000	1.4
85	62.2	7000	3.5
85	62.2	3000	1.9
85	62.2	2000	1.5
85	150	7000	1.6
85	150	5000	1.1
85	150	3000	0.69
90	67	7000	1.1
90	67	5000	0.89
90	67	3000	0.63
90	67	2000	0.46
90	150	7000	0.78
90	150	5000	0.55
90	150	3000	0.28

TABLE 23

Viscosity of 1 MM cP Polymer in Butane*

Temperature (°F)	Pressure (psia)	Viscosity (cP)
69.3	5015	1.02
	4119	0.97
	3125	0.91
	2108	0.82
	1111	0.65
138.92	5142	0.75
	4069	0.69
	3105	0.63
	2160	0.56
	1189	0.46

*4 Wt.% Polymer in butane

Figure 17. Viscosity, 1MM cP Polymer in Butane