GELLED PROD® FLUID FOR HIGH TEMPERATURE FRACTURING

R. L. CLAMPITT
Phillips Petroleum Company

INTRODUCTION

The success of fracture-acidizing treatments in carbonate formations at high temperatures of 250-400°F depends upon the in-depth penetration of live acid to produce effective etching of the fracture faces. In the fracture-acidizing treatments, viscous solutions called pads are injected ahead of the acid to improve acid penetration. Fracturing fluids which remain highly viscous at elevated temperatures create fractures with high fluid conductivity in both sandstone and carbonate reservoirs. With the greater flow capacity through the fracture, the depth of fracture penetration can be extended with larger volume treatments to increase productivity of the treated well.

This paper describes the development, important characteristics, and a field test of a new high-temperature fracturing fluid called gelled PROD® fluid. The viscous fluid was developed and tested in the laboratory in a cooperative project with personnel of Drilling Specialties Company, a Phillips' subsidiary.

REQUIREMENTS OF A PAD FLUID IN FRACTURE-ACIDIZING TREATMENTS

In ultra-deep formations, such as the Ellenburger in West Texas, it is difficult to obtain deep penetration of live acid because the rate of reaction of hydrochloric acid with the carbonate rock is extremely high at the very high formation temperatures of about 350°F. The actual reaction rate is controlled by the rate of delivery of live acid to the faces of the fracture and by the rate at which the reaction products are removed to expose new surfaces for reaction with the acid.

The most successful technique developed to improve acid penetration is the injection of a viscous pad ahead of the acid. The viscous pad increases fracture width, reduces "leak-off" of the following acid, and, being substantially more viscous than the acid, causes the following live acid to finger through the pad. In addition, the viscous pad reduces the wellbore temperature. The wider fractures reduce the contact rate between live acid and the walls of the fracture, thereby increasing the penetration of the acid.

To be considered an effective fracturing fluid at high temperatures, a viscous pad fluid must satisfy the following conditions:

1. It must have a viscosity of 100-200 cp in the fracture at temperatures of 250-300°F.
2. It must be resistant to shear degradation.
3. It must be capable of being pumped down 22,500 ft of 5-in. casing at rates of 25-35 BPM with friction losses in pressure equal to or less than those of water.
4. It must provide fluid-loss control at high temperatures and pressures.
5. Its viscosity must break down in 2-24 hr to permit efficient well clean-up and minimum damage to the formation.
6. It must be economically competitive with other commercially available fracturing fluids.

PERFORMANCE OF GELLED PROD FLUID AS A VISCOUS PAD

PROD fluids contain a "high-viscosity" grade of cellulosic polymer that is readily dispersible in water. The polymer is compatible with both fresh water and oilfield brines. PROD fluids containing this polymer can be gelled by the addition of polyvalent metallic ions such as Al^{+++} or Cr^{+++}. A preferred method of gelation is to add sodium dichromate in which the chromium has a valence of +6, and then add a reducing agent such as sodium hydrosulfite or sodium thiosulfate which reduces the valence of chromium at a controlled rate from +6 to +3. Tenfold or greater increases in viscosity have been obtained with this gelation technique. The addition of chemicals that release chromic ions in the PROD fluid produces substantial crosslinking between the polymer molecules, creating a web-like network that effectively immobilizes the water. The result can be a gelled or partially gelled solution with significantly higher viscosity and gel strength than those of an ungelled polymer solution.

The process for gelling PROD fluids is easily incorporated in the preparation of a viscous fracturing fluid. The process and mechanical effects that control the rate of crosslinking and the final viscosity of the gelled fluid are: (1) the amount of solids in the water, the type of solids and pH of the water; (2) the concentration of PROD polymer; (3) the concentration of the gelation chemicals; (4) the temperature of the solution; (5) the time the PROD fluid is aged prior to addition of the crosslinking chemicals; and (6) the time and rate of shearing following the addition of the crosslinking chemicals. Fortunately, the maximum required life of a high-temperature, viscous fracturing fluid is about two hours. Therefore, it is only necessary that the gel form and provide viscosity at the required level for a short period of time; thereafter, it is desirable that the viscosity decrease or break down.

The two fracture-fluid compositions with PROD gels shown below were developed and tested for "ad hoc" experiments in the laboratory specifically for fracture-acidizing in the Gomez Field. The compositions do not necessarily represent an optimization of the gelation technique but were selected and evaluated in the laboratory over a short period of time and judged to be suitable for conditions in the Gomez Field.

Preparation No. 1 - Retarded Gelation	Lb/1000 Gal.
Concentration of PROD in Tap Water	40
Concentration of Sodium Dichromate ($Na_2Cr_2O_7 \cdot 2\,H_2O$)	12
Concentration of Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5\,H_2O$)	78

Properties - Gel begins to form after 6 minutes at a mixing water temperature of 130°F. Gel is stable at room temperature for several days and is stable at 250° for about 2 hours.

Preparation No. 2 - Rapid Gelation	Lb/1000 Gal.
Concentration of PROD polymer in Tap Water	40
Concentration of Sodium Dichromate ($Na_2\ Cr_2\ O_7 \cdot 2\,H_2O$)	12
Concentration of Sodium Hydrosulfite ($Na_2\ S_2\ O_4$)	12

Properties - Gel begins to form after 1 minute at a mixing water temperature of 130°F. Gel is stable at room temperature for an indefinite period and stable at 250°F for 2 hours or more.

Fluid properties and pumping characteristics of the solutions of PROD gel follow.

Viscosity at Elevated Temperatures

The gelled PROD composition utilizing sodium thiosulfate as the reducing agent (Preparation No. 1) was considered *a retarded gelation* system at 130°F because approximately six minutes of time elapsed before there was a noticeable increase in viscosity. The composition utilizing sodium hydrosulfite was considered a *rapid gelation* system because a viscosity increase was observed in less than one minute. Compared in Fig. 1 are the viscosities of the two gelled PROD systems at temperatures ranging to 300°F. The rapid gelation system gelled while in turbulent flow at 130°F 16 hours prior to the time that the viscosities shown on Fig. 1 were measured. The preparation was cooled to room temperature and a sample placed into the cup of a high-temperature, high-pressure Model 50 Fann viscometer. Viscosities then were measured as the sample was heated from room temperature to 300°F over a 20-minute period. The retarded system was prepared by adding the gelation chemicals to the PROD solution at 120°F immediately before the sample was placed in the cup of the Model 50 Fann viscometer. The viscosities shown in Fig. 1 were measured as gelation occurred and as the solution was heated to simulate treatment in a deep gas well in the Gomez Field. Figure 2 shows the viscosity as a function of time and temperature for the retarded gelation system.

Figure 3 provides an estimate of the decrease of the temperature at various distances from the wellbore with time for a pumping rate of 25 BPM for a 200 cp fracturing fluid in a formation with a rock temperature of 350°F. Table 1 presents viscosities at elevated temperatures through a

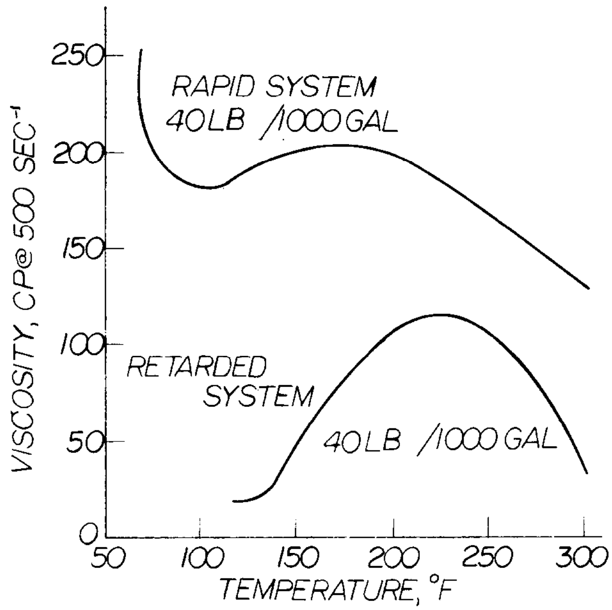

FIG. 1—MEASURED VISCOSITY DURING SIMULATED TREATMENT OF GOMEZ FIELD GAS WELL

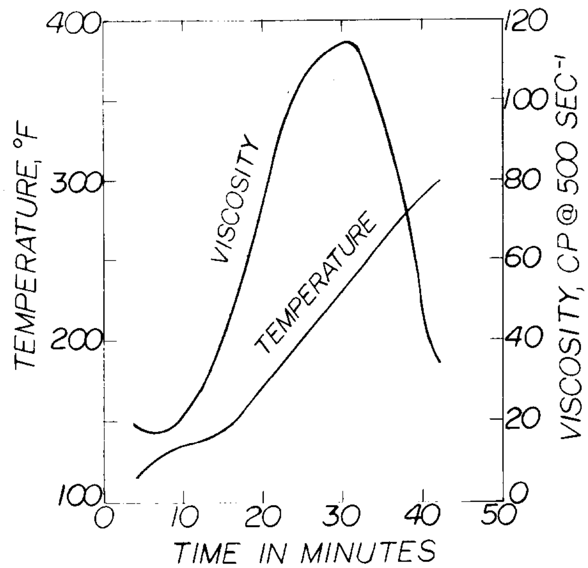

FIG. 2—MEASURED VISCOSITIES AS GELATION OCCURRED IN SIMULATED DEEP WELL TREATMENT

wide range of shear rates that would be encountered in vertical fractures during fracture-acidizing treatments using the retarded gelation system. The PROD gel satisfactorily met the viscosity requirement of 100-200 cp needed at shear rates of 170 sec^{-1} or less in a fracture, and at average temperatures of 250-275°F following a preflush to lower the temperature in the fracture.

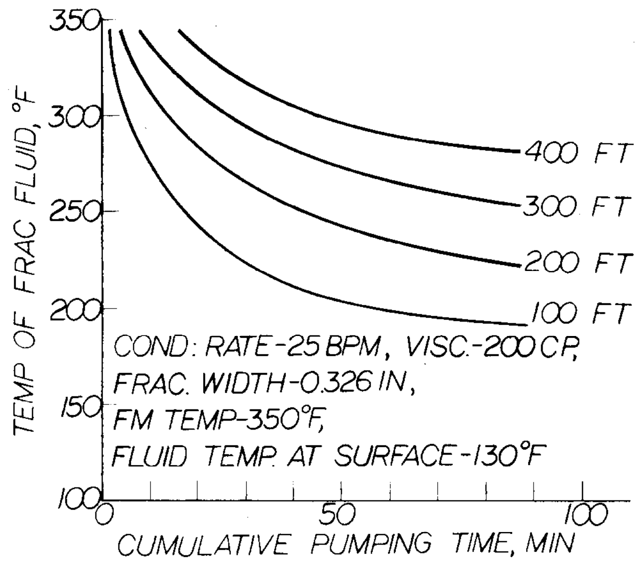

FIG. 3—TEMPERATURE OF FLUID IN FRACTURE AT VARIOUS DISTANCES FROM WELLBORE

The characteristic of shear thinning with increasing shear rates for PROD gel shown by the data in Table 1 is typical of most commercially available fracturing fluids. During a fracture treatment the PROD gel would be exposed to a wide range of shear rates during flow through pipe, perforations, the vertical fractures, and through the pores along the fracture face. Therefore, when considering the viscous behavior of PROD gel, the shear rate must be either calculated or estimated under the simulated treatment conditions.

TABLE 1—APPARENT VISCOSITIES OF GELLED PROD FLUID AT VARIOUS SHEAR RATES AND TEMPERATURES

Shear Rate,	Apparent Viscosity of Retarded Gelation Preparation, cp		
sec^{-1}	200°F	250°F	300°F
1	18680	9067	310
10	3067	1906	127
200	292	251	40
1000	83	84	21

Shear Resistance

It is important that a pad fluid be resistant to shear degradation such as would be experienced in pumping the fluid at high rates with shear rates of 500 to 10,000 sec^{-1} through pipe and through the perforations into the formation. A solution of PROD gel (40 lb/1000 gal.) was judged to be very shear-resistant in comparison with other commercially available gelled solutions. This conclusion was drawn after a sample of PROD gel had been cycled through a gear pump 15 times which simulated a very severe shear-rate condition. The PROD gel remained highly viscous and exhibited high gel strengths upon setting.

Pumpability

Measurements of the pressure loss due to friction in pipe were made in Halliburton's research facilities in Duncan, Oklahoma, to determine if the solutions of PROD gel in tap water (City of Duncan) would gel while moving through pipe in turbulent flow, and to determine the friction losses that could be expected in fracture-treating a well through 5 and 5-1/2 in. casing in the Gomez Field. The information in Table 2 compares the estimated pressure losses for fresh water, ungelled PROD polymer, and PROD gel prepared by the retarded gelation system. During turbulent flow in a nominal 1-in. pipe loop held at a constant temperature of 130°F, gelation of the PROD solution occurred after six minutes. It was concluded that PROD gel could be pumped with less friction loss than water at the rates of flow used in fracture treatments.

TABLE 2—COMPARISON OF PRESSURE DROPS IN 5-1/2 IN. PIPE DUE TO FRICTION PREDICTED(1) FOR WATER, UNGELLED AND GELLED PROD SOLUTIONS UTILIZING THE RETARDED PREPARATION

Injection Rate BPM	Total Pressure Drop (ΔP_f), psi
Fresh Water	
25	2420
30	3390
UNGELLED PROD Solution(2)	
25	1762
30	2151
Gelled PROD Solution(3)	
25	2141
30	2540

(1) The friction loss predictions are based upon injecting fluids into a well 22,500 ft deep where 17,000 ft are 5-1/2 in, 23 lb/ft and 5500 ft are 5-in., 23.2 lb/ft steel casing, and the surface injection fluid temperature will be 130°F, the formation temperature at 22,500 ft will be 350°F. These conditions are an approximate simulation of the equipment in Phillips' gas wells in the Gomez Field, Pecos County, Texas.

(2) Solution consisted of 40 lb/1000 gal. of PROD polymer dissolved in Duncan tap water.

(3) Solution contained 40 lb PROD polymer, 12 lb sodium dichromate and 78 lb sodium thiosulfate per 1000 gal.

Fluid Loss Control at Elevated Temperatures

One measure of the efficiency of a viscous fracturing fluid is the quantity of fluid that is lost by "leak-off" into the matrix of the formation while the fluid is moving through the fracture at low shear rates. The rate of leak-off is difficult to measure in the laboratory because it is dependent upon: (1) rock characteristics such as size of the pores and presence of hair-line fractures or vugs; (2) the wall-building characteristics of the fracturing fluid; and (3) the temperature and rate of shear which controls the viscosity of the viscous fluid as it enters the pores.

In designing a fracture treatment it is necessary to estimate a composite fluid-loss coefficient that takes into account the fluid-loss coefficient for a wall-building fluid (C_w) and the fluid-loss coefficient for a viscosity-controlled fluid (C_v). The results of two laboratory fluid-loss tests on cores were used in estimating a composite fluid-loss coefficient of 0.0055 ft/$min^{1/2}$ for the two PROD gel preparations. The fluid-loss tests were run at 260°F on limestone cores having low permeabilities from 0.1 to 5.0 md.

The fluid-loss characteristics of gelled PROD were satisfactory for treating the Ellenburger formation which has low permeability. When fracture-treating highly permeable formations, it may be necessary to include other fluid-loss additives.

Breakdown of Gelled PROD Fluids

Solutions of PROD gel will break down when exposed to excessive amounts of crosslinking chemicals, or when prepared in hard brines (60,000 ppm TDS), and when subjected to high temperatures of 300-350°F for extended periods of time. The rate of breakdown can be controlled through changes of one or a combination of the aforementioned variables.

Laboratory tests have shown that a gelled solution containing 40 lb PROD polymer, 12 lb sodium hydrosulfite, and 12 lb sodium dichromate per 1000 gal. tap water would break down in 12 hours when exposed to temperatures of 300-350°F. The resulting solution contained a small amount of residue and had a viscosity approximately equal to that of water. It was concluded that PROD gels would break down overnight when used in the Ellenburger formation in the Gomez Field, permitting rapid clean-up of the well.

Additional Favorable Characteristics

There are several favorable and unevaluated characteristics of PROD gels as a fracturing fluid. As it leaks off through pores, a filtering action occurs that removes a large quantity of gel particles from the fluid and concentrates the gelled polymer along the face of the formation at the pore openings. The net result is the formation of a less permeable and more viscous gel along the face of the formation.

A controlled amount of leak-off of the PROD solution into the pores is desired because it reduces the transfer of heat from the formation to the fluid moving down the fracture. The much higher concentration of PROD gel in the pore openings creates an additional insulation effect behind the thermal barrier zone, reducing the rate of heat-up of the fracturing fluid even further. It can be hypothesized that PROD gel would remain cooler, more viscous and more efficient in moving down a fracture than other frac fluids which exhibit no wall-building effect.

COMPETITIVE POSITION OF GELLED PROD FLUIDS

PROD gel appears to have the characteristics necessary for an efficient fracturing fluid for use at high temperatures; and a comparison with the commercially available fluids reveals that comparable viscosities can be developed with PROD gel at less cost. Figure 4 shows the apparent viscosities for a range of temperatures up to 300°F for various fracturing fluids. PROD gel at concentrations of 40 lb/1000 gal. gives viscosities up to 300°F that are equivalent or higher than those of the other fracturing fluids at polymer concentrations of 80-110 lb/1000 gal.

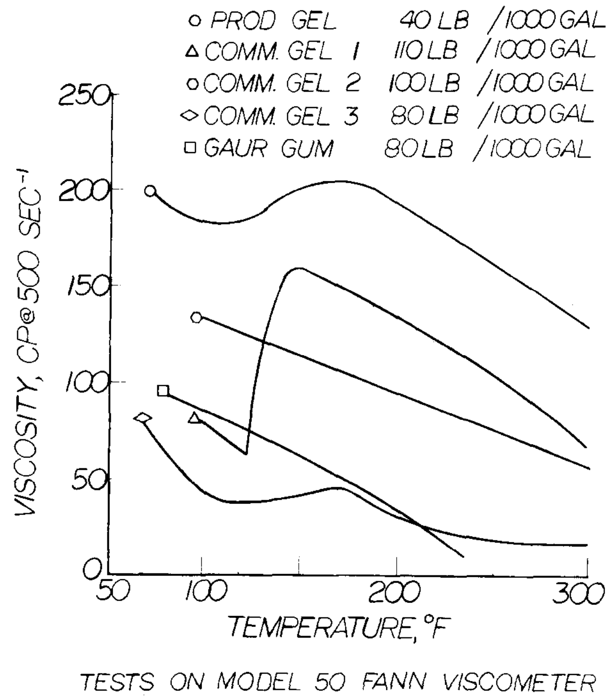

FIG. 4—VISCOSITIES OF HIGH TEMPERATURE FRACTURING FLUID

FIELD-TESTING GELLED PROD FLUID AS A PAD IN THE GOMEZ FIELD

Fracture-Acidizing Treatment of Gas Well

PROD gel was field-tested in a fracture-acidizing treatment of the gas well in the Gomez Field. Prior to the treatment the well produced about 6 MMCF/D at maximum capacity even though its allowable was about 20 MMCF/D. Therefore, the objective of the treatment was to raise the producing capacity to 20 MMCF/D from 6 MMCF/D.

A description of the treatment which totaled 424,000 gal. is shown in Table 3. Injection rates were 25-54 BPM (considered to be extremely high) over a 5-1/2 hour pumping period. Two stages of gelled PROD of 100,000 and 50,000 gal. were used as pads ahead of slugs of 20% hydrochloric acid. Each 1000 gal. of the PROD gel contained 40 lb PROD polymer which was mixed in fresh water from the city of Fort Stockton about 44 hours before starting the treatment; 12 lb sodium dichromate that was mixed into the PROD solution 30 hours prior to the job; and 78 lb sodium thiosulfate that was added "on-the-fly" during the treatment. The temperature of the PROD-dichromate solution was maintained at 130°F with hot-oil units prior to the treatment. Samples of PROD gel obtained during the job exhibited viscosities equal to those observed in the laboratory.

TABLE 3—FRACTURE-ACIDIZING TREATMENT - GOMEZ FIELD

Volume Injected and Treatment Sequence	
Stage 1	2,000 Gal. 15% nonemulsified acid
	80,000 Gal. preflush
	100,000 Gal. PROD gel as a pad*
	50,000 Gal. 20% retarded HCl
	50,000 Gal. overflush
	Ball Drop: Ten - 7/8-in. OD ballsealers
Stage 2	2,000 Gal. 15% nonemulsified acid
	40,000 Gal. preflush
	50,000 Gal. PROD gel as a pad*
	25,000 Gal. 20% retarded HCl
	25,000 Gal. overflush
	Total Volume = 424,000 Gal.

*Pad fluid was prepared by mixing PROD polymer in fresh water 44 hours prior to treatment and then adding the sodium dichromate followed by circulation of the mixing tanks. The sodium thiosulfate was added "on-the-fly" by a blender as the pad fluid was being pumped into the well. Gelation of the pad fluid began following the addition of the sodium thiosulfate.

Results from Treating the Well

A favorable response in pressure and pumping rate was observed during the treatment. A significant break in injection pressures from 9400 to 7600 psi was observed when the acid "hit" the formation following the PROD gel in the first stage. The reduction in pressure permitted an increase in the injection rate from 35 to 54 BPM. There was an apparent change in the fracture gradient equivalent to an overall pressure change approximating 2000 psi. One interpretation of this response is that the treatment broke into a weaker part of the Ellenburger formation.

CONCLUSIONS

Although only a limited amount of laboratory field information has been obtained, PROD gel does appear to have the necessary favorable characteristics required for a high-temperature fracturing fluid. It also offers a lower-cost viscous fluid which can be used in stimulating deep wells where high temperatures above 250°F are encountered. It can be pumped at pressure losses (due to friction) that are less than those for water; but gelling can be timed to provide viscosities of more than 100 cp when flowing into a fracture. On the basis of equal viscosity, PROD gels offer a price advantage over other high-temperature fracturing fluids.

Solutions of PROD gels would be applicable as a viscous fracturing fluid in the following situations:

1. When viscosities of 100 cp or more are needed in fractures at high temperatures of 250-300°F.
2. When it is necessary to create wide fractures with high flow capacities. It should be especially useful where mechanical limitations necessitate the use of low injection rates.
3. When injection rates must be limited to reduce fracture heights and to avoid fracturing into undesirable zones, such as bottom water or gas caps over an oil column, but, at the same time wide fractures must be created.
4. When it is necessary to fracture soft formations and place high concentrations (2-6 lb/1000 gal.) of large 8 to 12 mesh size proppants into formations with temperatures above 250°F.