A FIELD AND LABORATORY STUDY OF POLYSACCHARIDES IN FRACTURING TREATMENTS

DR. JAMES FRECK
JOHN GOTTSCHLING
BJ-Hughes Inc.

ABSTRACT

With the increased use of polysaccharides in fracturing treatments, subsequent problems have been encountered with inadequate polymer hydration, weak or over cross-linked fluid, formation of fish eyes, low viscosity and uncontrolled breakout. Problems have also occurred due to inadvertant contamination from water supplies and fracturing tanks. In field studies of the Lost Hills and South Belridge areas in Kern County, Calif., field conditions and operational procedures were found to constitute critical factors in successful dispersion and in ideal cross-linking of polysaccharides. A comparison of field fluids with laboratory fluids was conducted with special emphasis on the quality of field water and on the effects of pH and temperature on the viscosity and sand fall rate. Laboratory tests indicate that fluid mixed in the field can exhibit a more effective cross-linking structure, a more stable viscosity strength and a lower sand fall rate if more control is exercised in the determination of pH range, in the selection of buffers and in the choice of treating water. Attention to these factors, as pointed out in this paper, can reduce lost time, save expense and increase well performance.

INTRODUCTION

For 25 years, polysaccharide hydrocolloids have been successfully used to create gels and cross-linked fluids for fracturing treatments. In the Bakersfield area of southern California, polysaccharides have been used for over a year with continued success. The early fracturing fluids using polysaccharide hydrocolloids lacked certain performance characteristics which limited their applications. Improved performance was obtained by applying experience gained in the field plus continued investigations in the laboratory. The early deficiencies have been largely corrected by using improved polysaccharides which exhibit less residue and less sensitivity to salts. As a result, the most current fluids show improved viscosity, better stability at higher temperatures and more effective cross-linking ability.

One of the first steps in developing a gelled fracturing fluid is to obtain a more precise definition of the effects that pH, temperature and water quality have on the cross-linking of the polysaccharide hydrocolloid used. Such a definition would serve to assist in better controlling the fluid properties and, subsequently, the job performance. Also, the definition would explain some of the problems that can occur with viscosity and would provide new approaches to their solutions.

Initial studies of the roles that pH and temperature play in the effective use of polysaccharide hydrocolloids were part of a continuing effort to develop better fracturing fluids. The data presented in this paper can thus be used as a guideline for solving field problems as well as for developing products.

LABORATORY STUDIES

The polysaccharide hydrocolloid fluid chosen for laboratory testing was a 40-pound hydroxypropyl (HP) guar system which was cross-linked with an organic cross-linker. Representative of one of the most widely used fluids in the Bakersfield area, this system is designed for temperatures from 80°F to 220°F. It can be mixed with fresh water or with water containing sodium chloride (NaCl), calcium chloride ($CaCl_2$) or potassium chloride (KCl). The system can be batch mixed or continuous mixed. Upon breakout, there is less than 3 percent solid residue.

Three samples of the testing fluid were prepared at pH values of 6, 7 and 8. First, the 40-pound guar gel was dispersed in water containing 2 percent KCl, and then the fluid was adjusted with buffer to the pH values indicated above. For each pH value, the temperature was held successively at 40°F, 75°F, 90°F and 110°F before the cross-linker was added. In all but one instance, formation of the thickened gel occurred within 30 seconds. The exception was the fluid with a pH value of 6 at 40°F which required three to four minutes to form a thickened gel.

The cross-linking effect which produces a gelled fluid occurs when the hydroxyl groups on the HP guar and the cross-linking agent come in contact with each other. The rate and extent of this cross-linking reaction are affected by pH and temperature. The cross-linking reaction results in the formation of larger and larger molecules until three-dimensional structures are formed as is illustrated in Fig. 1.

Data collected in the laboratory on pH and temperature are shown in Figs. 2-9. The data indicates that at 75°F and at 90°F, higher viscosities and greater heat stabilities are attained at pH values of 6, 7 and 8. At these pH values, the initial viscosity and heat stability are lower at 110°F than at 90°F. In summary, the data shows that more stable viscosities for a 40-pound HP guar in 2 percent KCl occur when the system is cross-linked at a pH range from 7 to 8 and at temperatures from 75°F to 90°F (Table I).

In addition to pH and temperature, iron salts can also affect a polysaccharide hydrocolloid system. The effect of iron salts on viscosity is dramatic as can be seen in Fig. 9. From 40 to 70 percent loss of viscosity can be expected in the presence of 30 parts per million (ppm) ferrous iron (Fe^{+2}) salts. The iron salts can reduce the HP guar viscosity by at least three mechanisms:

(1) Formation of cross-linked gels when ferric iron (Fe^{+3}) comes into contact with the hydroxyl groups.

(2) Interference by Fe^{+3} and Fe^{+2} with organic cross-linker.

(3) Formation of a redox potential which catalyzes the oxidation of the carbohydrate chain (polymer backbone) through a free radical mechanism.

The final area of study involved the problem of bacterial contamination and its effect on fluid viscosity. This problem is particularly troublesome during warmer times of the year when high temperatures promote rapid bacterial growth. In laboratory tests, the gelled solution initially appeared satisfactory prior to cross-linking, but within one to two hours, the viscosity was drastically reduced as is shown in Fig. 10. Since tests of the water revealed no abnormalities in pH, temperature or metallic salt content, the only possibility left was bacterial contamination.

In its sealed container, the HP guar shows excellent stability. However, bacterial contamination can occur when solutions of the polymer are prepared. Like other polysaccharides, HP guar is subject to enzymatic degradation and loss of viscosity. While this property is utilized in designing breaker systems for fracturing fluids, it can lead to premature loss of viscosity if uncontrolled. Once bacterial degradation starts, the resulting enzymes can degrade the HP guar gels and cross-linked fluids long after the bacteria are killed.

One mechanism which can introduce bacterial contamination occurs during preparation of the solution. When surface or runoff water that contains enzymes are used to mix HP guar solutions, the resulting gel can break in one to two hours. Investigation has shown this process to be responsible for losses in viscosity.[1]

Another way that bacterial contamination is introduced involves the storage of gelled solutions in fracturing tanks. For instance, after a frac job is completed, a small amount of gel may ramain in the tank. If the tank sits idle for several days, conditions become perfect for bacterial growth. The bacteria feed on the polymer, and the warm temperatures assure rapid growth. When the tank is refilled with water for the next job, a biocide is added in addition to the polymer. Designed to kill all the organisms present, the biocide cannot inactivate the digestive enzymes previously produced by the bacteria. The result is rapid degradation of the new polymer solution.

To combat bacterial contamination, frac tanks should be dumped, cleaned and refilled. At this point, the water can be gelled immediately before the job commences. In addition, the pH of the water can be lowered to inactivate the enzymes and then readjusted to assure desirable viscosity qualities.

FIELD APPLICATIONS

With a review of laboratory data and field experience, several conclusions can be drawn for field applications. First, pH and temperature have an interactive effect on the cross-linking reaction of the HP guar system. As would be expected, higher temperatures, up to a certain point, result in higher viscosities. As stated previously, the best condition for cross-linking is at a pH value of 8 and at temperatures from $90^{\circ}F$ to $100^{\circ}F$. However, optimum conditions are not always possible in respect to temperature. In fact, cross-linked viscosity can remain a problem at lower temperatures.

However, further investigations have shown that by reformulating the organic cross-linker, viscosity variations experienced at extreme temperatures and at some pH values can be overcome. Such alterations must be done on an individual job basis. The data in Table II shows the results of cross-linking a 50-pound HP guar fluid at $100^{\circ}F$ using different organic cross-linkers. The gel contained 2 percent KCl buffered at pH 7 and was cross-linked at the indicated temperature. The results are the average of three tests. This data shows the control that is possible when the selection of cross-linkers is based on the temperature of the fluid at the time of cross-linking.

Second, iron salts in the water can pose a serious problem to viscosity. To lessen the effects of iron salts on viscosity, the design of fracturing fluids which can tolerate high concentrations of Fe^{+2} are needed. For instance, the 40-pound, HP guar cross-linked system used for testing is designed to tolerate up to 20 ppm Fe^{+2}. The presence of Fe^{+2} rarely occurs naturally in water over 20 ppm.

The problem can arise when the water comes into contact with iron, such as iron tanks, at a pH value of 7 or below.

Of the various mechanisms by which iron salts can affect viscosity, two reactions are postulated in Fig. 11.[2,3] They are (1) the formation of cross-linked gels when Fe^{+3} comes into contact with the hydroxyl groups and (2) the formation of a redox potential which catalyzes the oxidation of the carbohydrate chain through a free radical mechanism.

Finally, bacterial contamination can also be a problem. Here, as with the iron salts, the problem can be prevented by being aware of how contamination occurs. If the tanks are cleaned thoroughly after each job, no medium for bacterial growth will be present, and thus, contamination will be eliminated.

CONCLUSIONS

In summation, a 40-pound cross-linked HP guar system designed to meet field requirements in Kern County, Calif., has been successfully used to improve well productivity. Extensive laboratory testing done during the product development stages and subsequent field testing has shown this system to be a consistently good performer. Awareness of the mechanisms that can negatively alter fluid viscosity, such as pH, temperature, iron salts and bacteria, will assist the industry in its continued effort to insure consistent job successes.

REFERENCES

1. McElfresh, P. "Examination of Mixing Water Used In A Frac Job," internal report, BJ-Hughes Inc. (1979).

2. Carlherg, B.L. "Water Quality for Trouble-Free Injection," Petroleum Engineer International, 92-98, 101 (August 1980).

3. Cotton, F. Albert, and Wilkinson, Geoffrey. Advanced Inorganic Chemistry. New York: John Wiley & Sons, 851-853, 857-861 (1980).

ADDITIONAL REFERENCES

Andrianov, K.A. Metalorganic Polymers. New York: Interscience Publishers (1965).

E.I. du Pont de Nemours & Co. (Inc.). Versatile Tyzor Organic Titanates. Wilmington, Delaware: E.I. du Pont de Nemours & Co. (Inc.).

Lagally, Paul, and Lagally, Herta. "Atomistic Approach to the Crosslinking of Cellulose Fibers and Their Reaction with Fillers," TAPPI 39 (November 1956).

McDaniel, Robert R.; Houx, Mel R.; and Barringer, David K. "A New Generation of Solid-Free Fracturing Fluids," paper SPE 5641 presented at SPE 50th Annual Fall Meeting, Dallas, Texas (Sept. 28-Oct. 1, 1975).

ACKNOWLEDGEMENTS

The authors of this paper wish to express their thanks to BJ-Hughes Inc. for its cooperation, assistance and permission in presenting this paper.

HO · (HP Guar) · HO + XL + HO · (HP Guar) · OH ⟶

HO · (HP Guar) · O · XL · O · (HP Guar) · OH ⟶

Reaction continues to a 3-dimensional structure.

FIGURE 1—CROSS-LINKING REACTION OF HYDROXYL GROUPS ON THE HP GUAR AND OF THE CROSS-LINKING AGENT

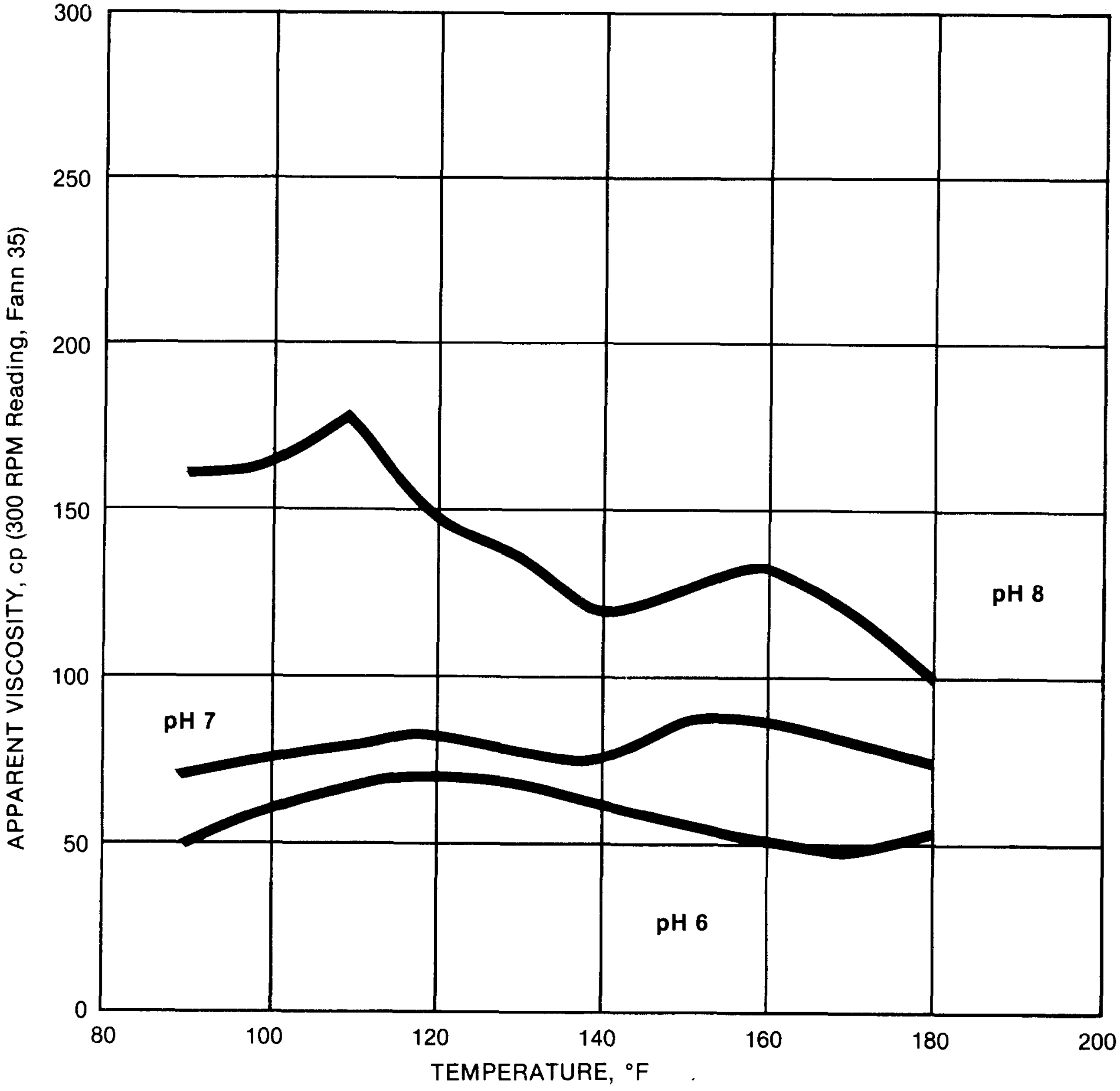


FIGURE 2—APPARENT VISCOSITY OF FLUID CROSS-LINKED AT 40°F VS TEMPERATURE

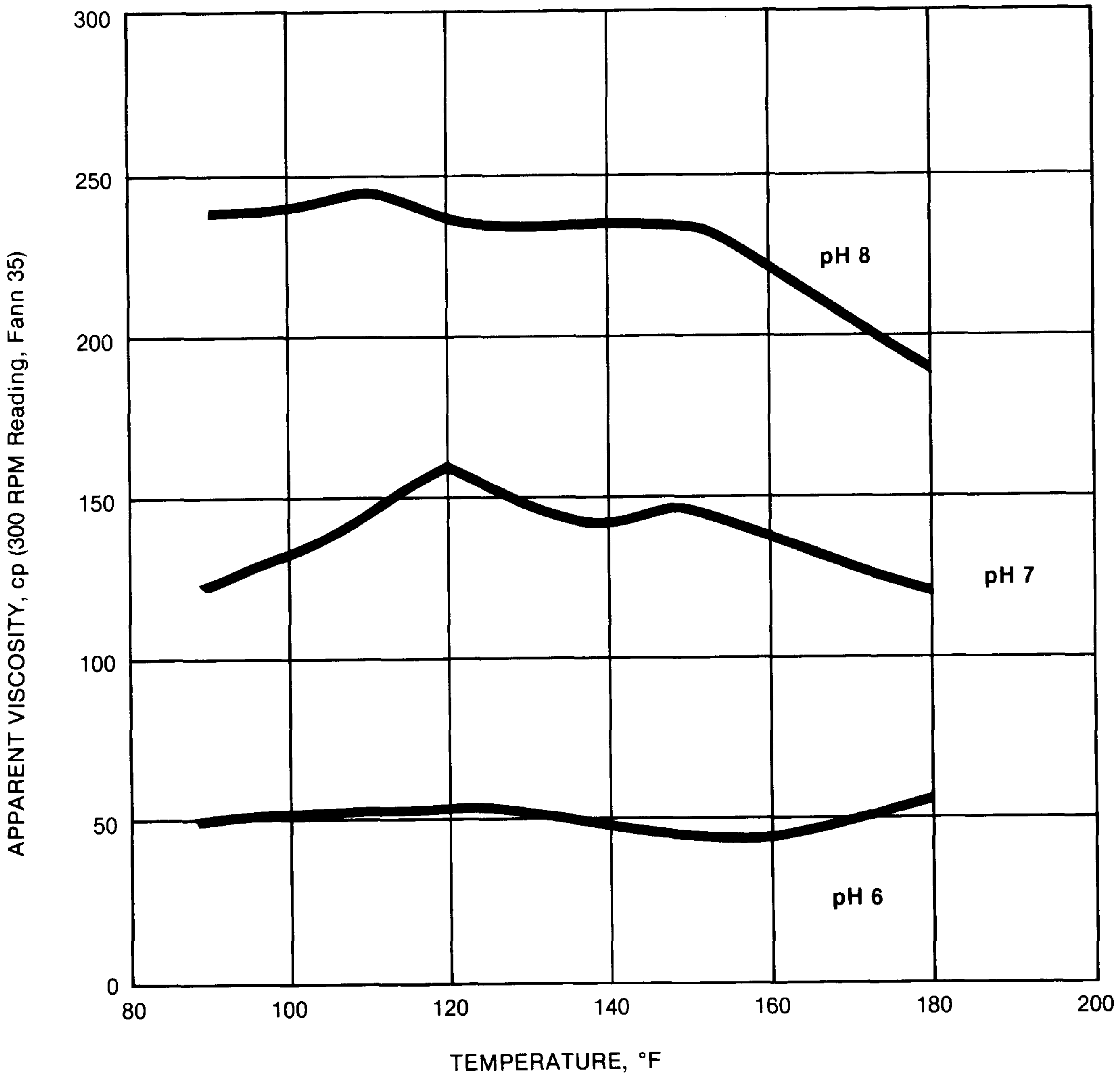


FIGURE 3—APPARENT VISCOSITY OF FLUID CROSS-LINKED AT 75°F VS. TEMPERATURE

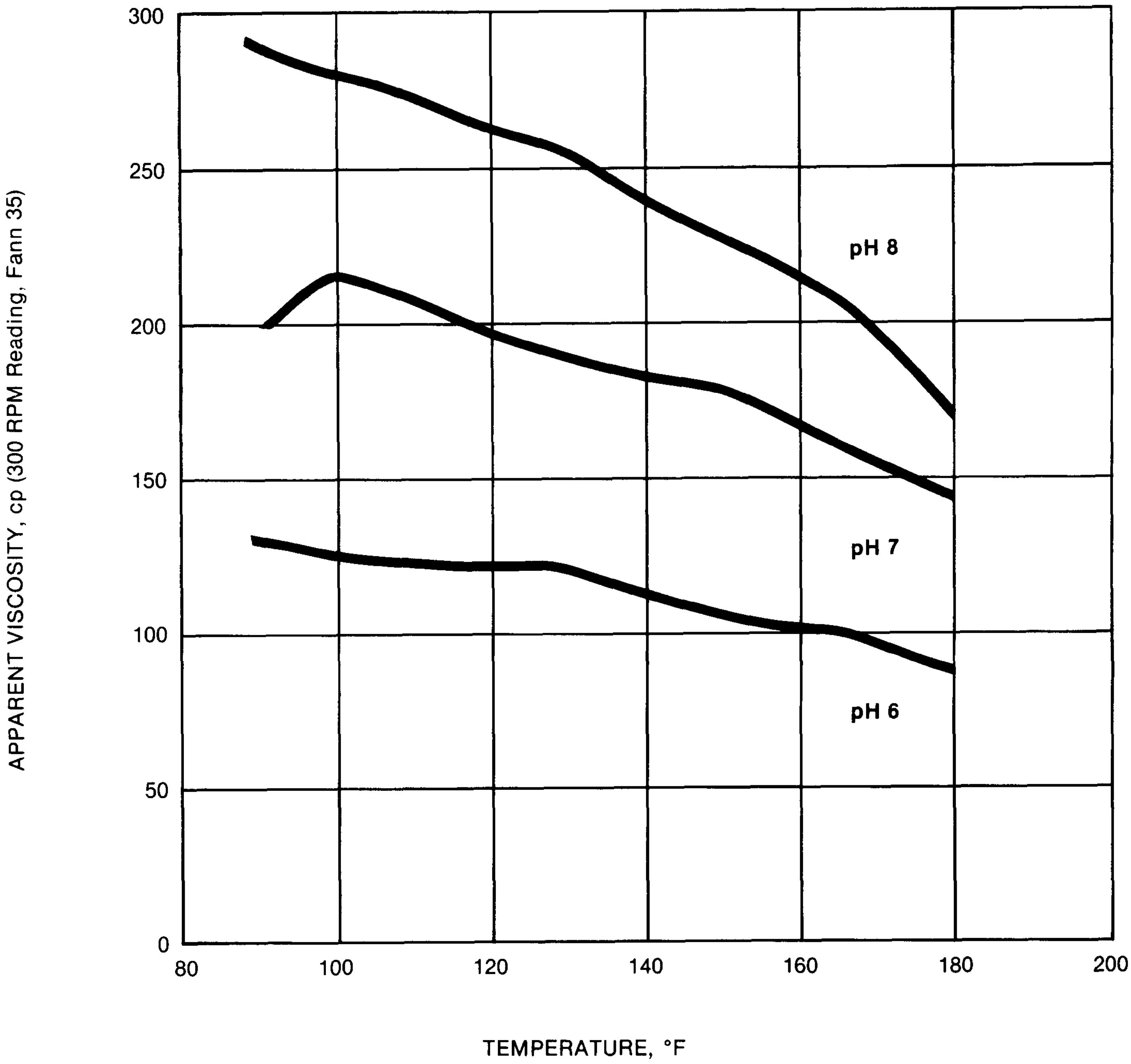


FIGURE 4—APPARENT VISCOSITY OF FLUID CROSS-LINKED AT 90°F VS. TEMPERATURE

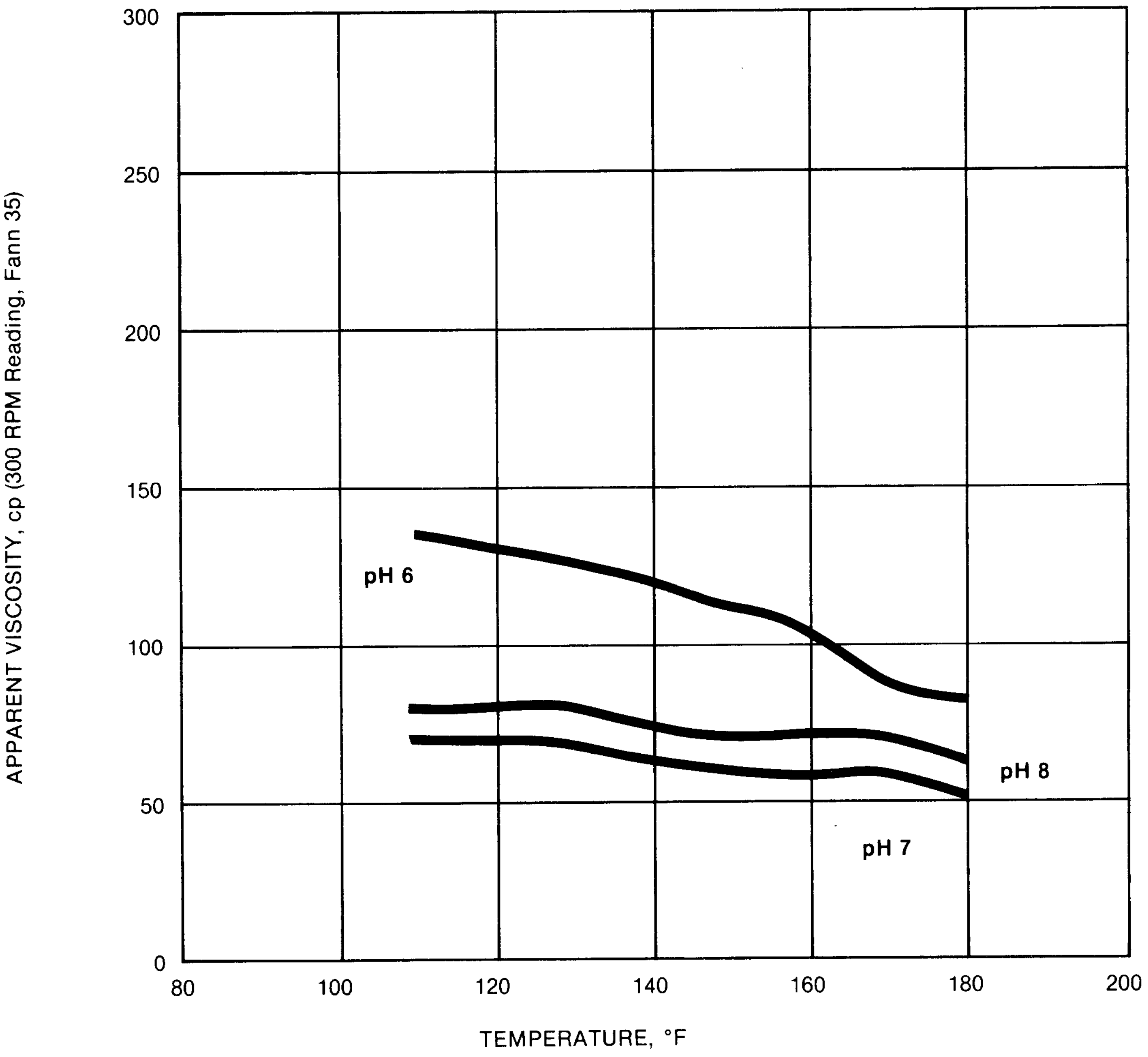


FIGURE 5—APPARENT VISCOSITY OF FLUID CROSS-LINKED AT 110°F VS. TEMPERATURE

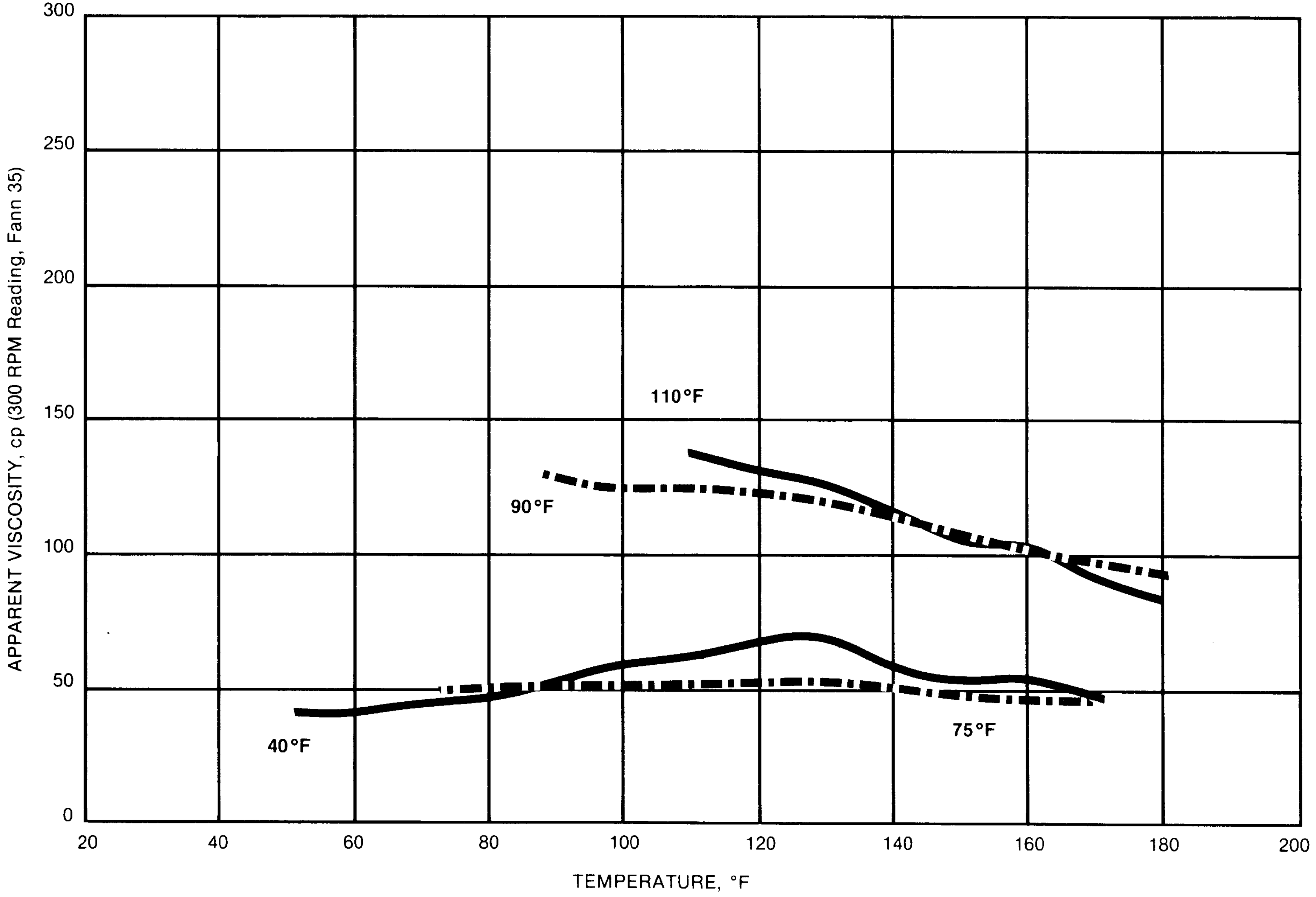


FIGURE 6—APPARENT VISCOSITY OF FLUID AT pH6
VS. TEMPERATURE

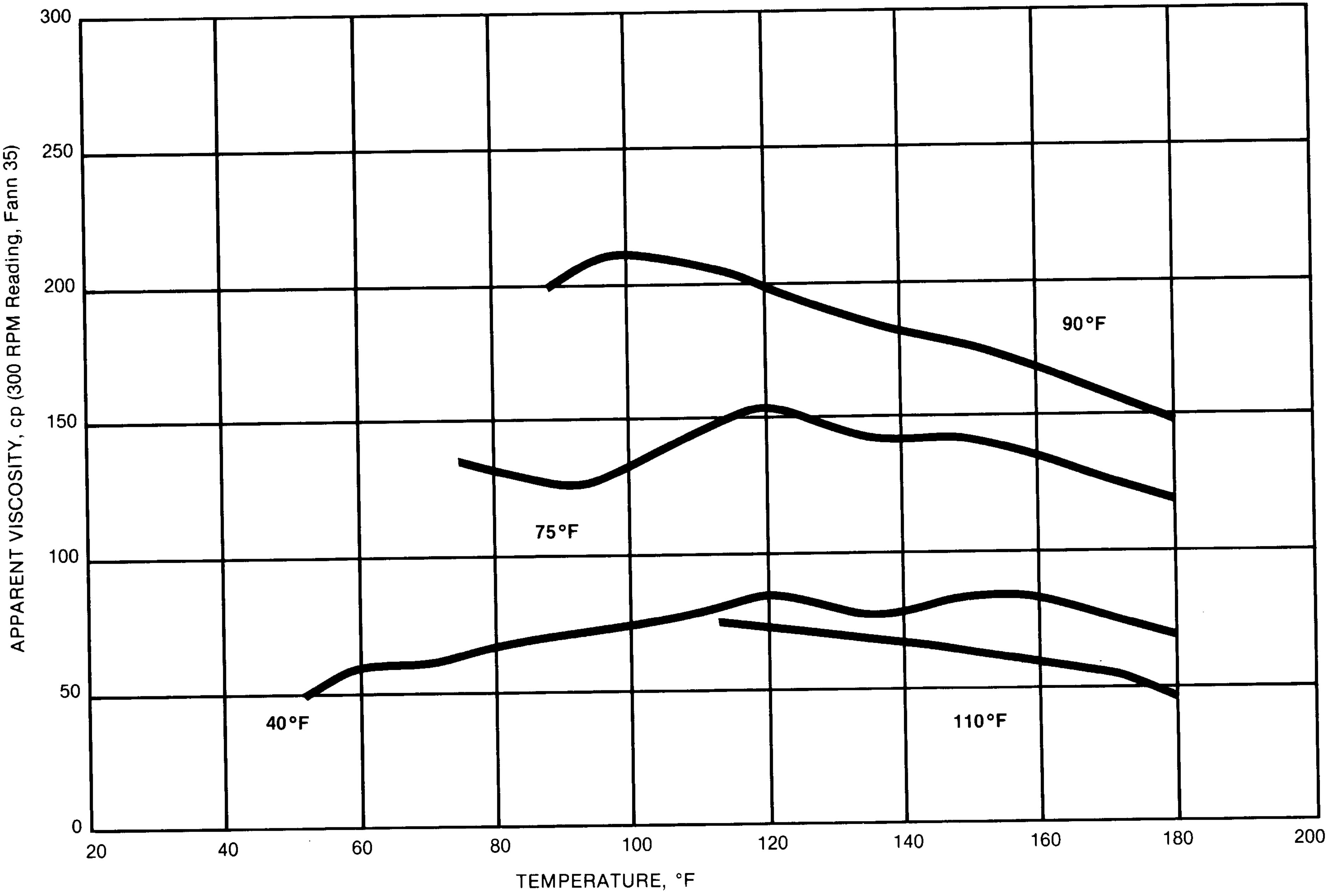


FIGURE 7—APPARENT VISCOSITY OF FLUID AT pH 7
VS. TEMPERATURE

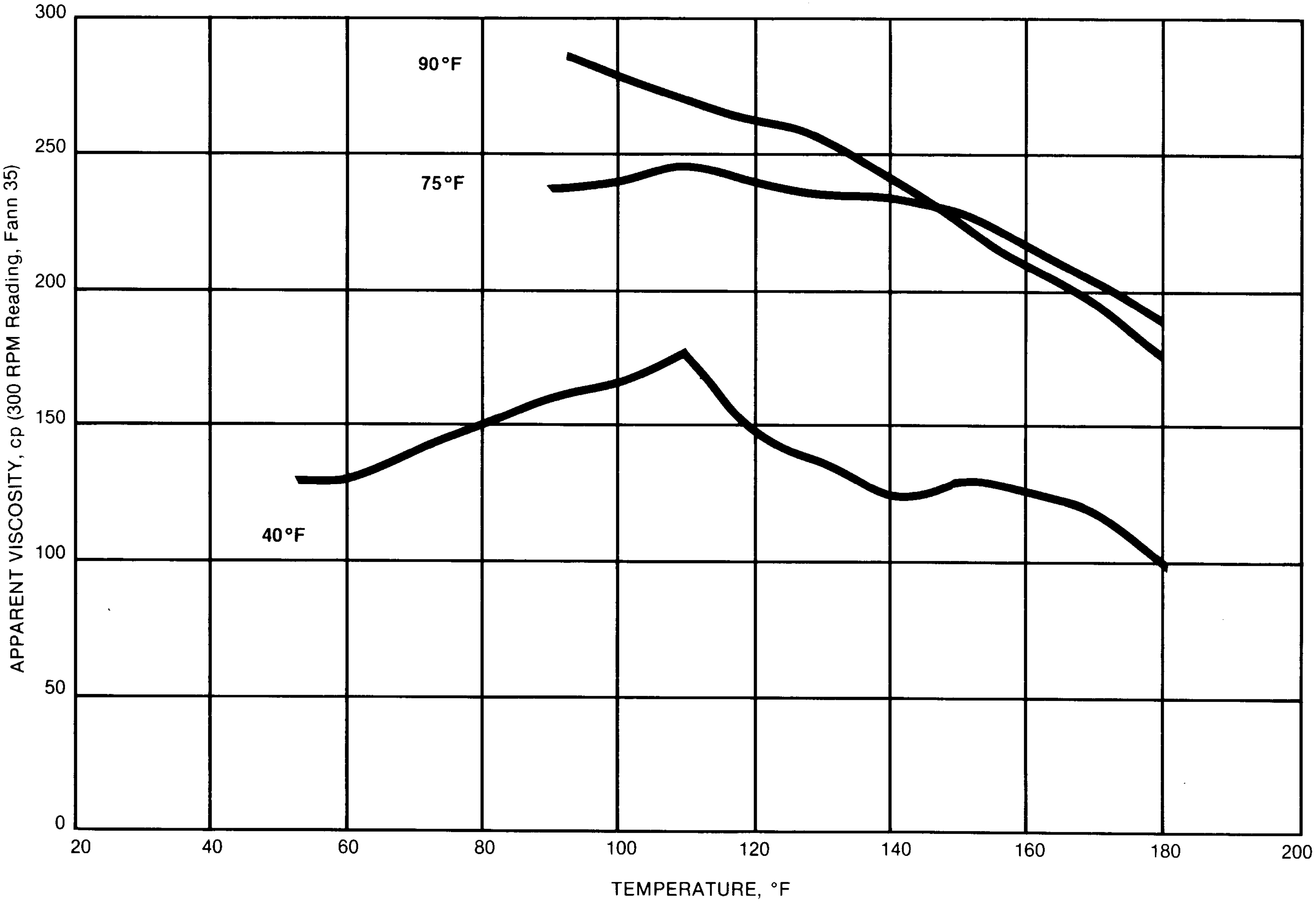


FIGURE 8—APPARENT VISCOSITY OF FLUID AT pH 8
VS. TEMPERATURE

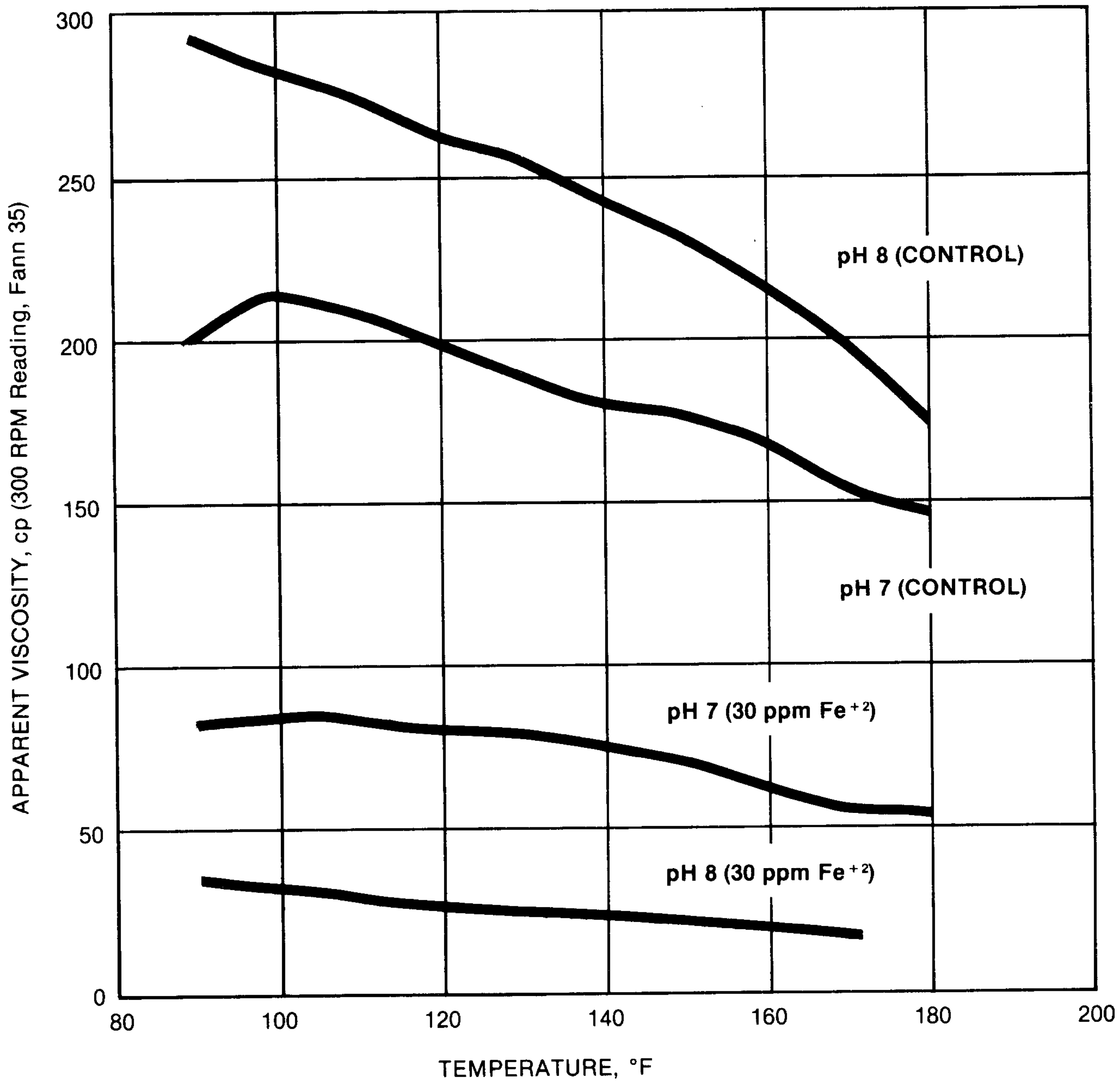
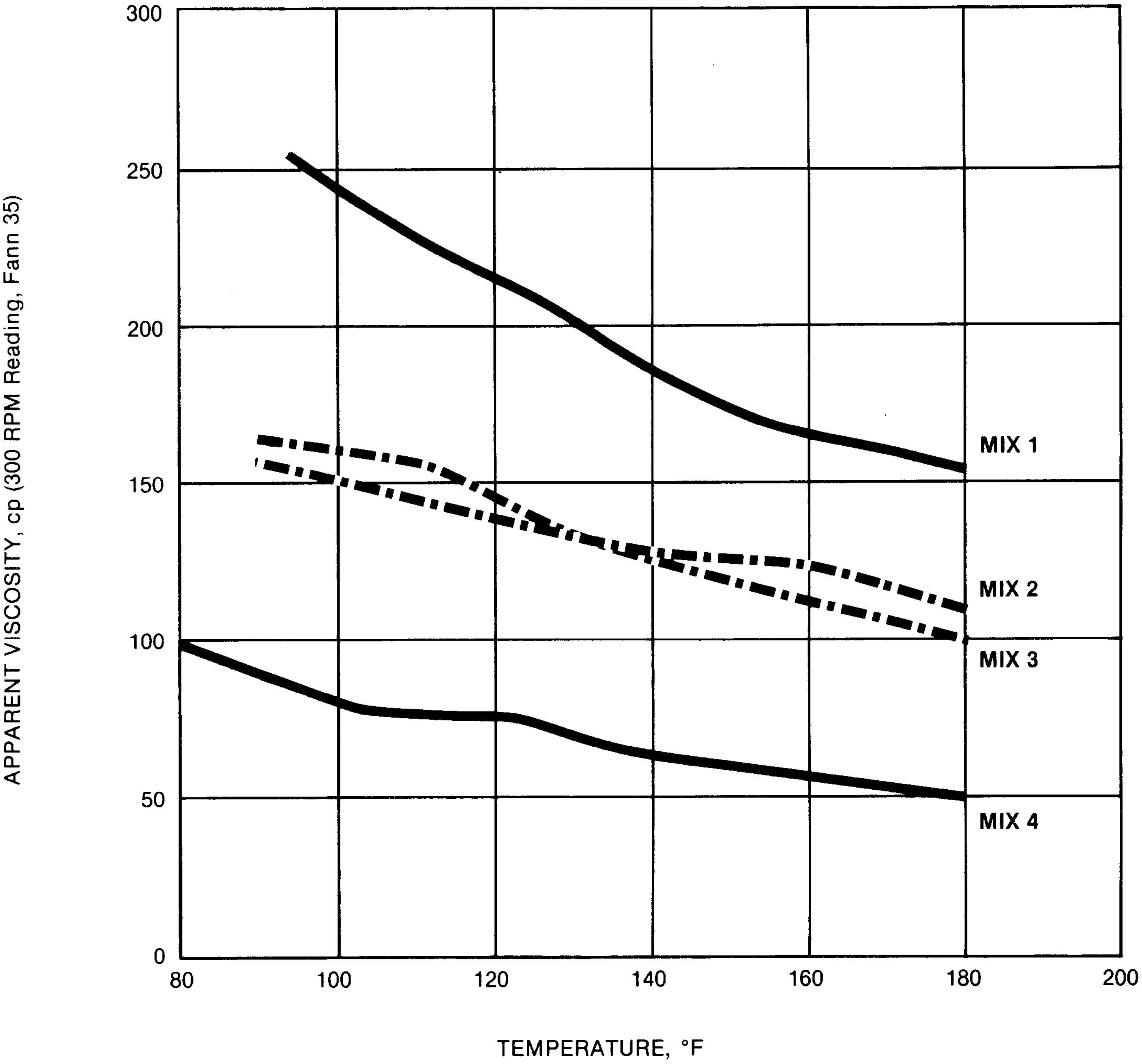


FIGURE 9—APPARENT VISCOSITY OF FLUID CROSS-LINKED AT 90°F VS. TEMPERATURE



MIX 1 = 50-pound HP guar, cross-linked system incubated for eight days at 95°F.

MIX 2 = 40-pound HP guar, cross-linked system using 10 percent of MIX 1.

MIX 3 = MIX 2 incubated for 12 hours at 95°F.

MIX 4 = MIX 1 inoculated with dust and incubated for 12 hours at 95°F.

FIGURE 10—APPARENT VISCOSITY OF FLUID CROSS-LINKED AT 40°F VS. TEMPERATURE

(1) The formation of cross-linked gels when Fe^{+3} comes into contact with the hydroxyl groups:

$Fe + 2H^{+} \xrightarrow{pH>7} Fe^{+2} + H_2$

$Fe^{+2} + 0_2 \longrightarrow Fe^{+3}$

Fe^{+3} + HP Guar $\xrightarrow{H+}$ complex formation reaction with hydroxyls (OH) of HP Guar.

(2) The formation of a redox potential which catalyzes the oxidation of the carbohydrate chain through a free radical mechanism:

$2Fe^{+2} + 1/2\ 0_2 \longrightarrow 2Fe^{+3} + H_20$

$Fe^{+2} + 0_2 \longrightarrow Fe0_2^{+2}$

$Fe0_2^{+2} + Fe(H_20)^{+2} \longrightarrow Fe\ (00H)^{+2} + Fe\ (0H)^{+2}$

(hydroperoxy ion)

$Fe\ (00H)^{+2} \longrightarrow Fe^{+3} + HO_2^{-}$ (free radical) attacks polymer chain and also oxidizes ferrous iron to ferric iron.

FIGURE 11—SUGGESTED MECHANISMS BY WHICH IRON SALTS CAN EFFECT VISCOSITY

TABLE 1—APPARENT VISCOSITY VS. TEMPERATURE

Temperature Of Gel When Cross-Linked	pH Value of Gel	Apparent Viscosity, cp (300 RPM Reading, Fann 35)			
		Initial Viscosity	Viscosity at 130°F	Viscosity at 160°F	Viscosity at 170°F
40°F	6	41	67	54	47
	7	48	75	84	78
	8	127	138	133	120
75°F	6	50	53	45	48
	7	130	145	135	126
	8	240	235	218	206
90°F	6	123	119	101	98
	7	215	189	168	155
	8	280	255	213	198
110°F	6	134	126	105	88
	7	96	69	57	57
	8	78	78	---	67

TABLE 2—APPARENT VISCOSITY WITH VARIOUS ORGANIC CROSS-LINKERS

Organic Cross-linkers	Temperature Of Gel When Cross-linked	Apparent Viscosity, cp (Fann 35 Reading)	
		300 RPM	600 RPM
Type A	75°F	300+	300+
Type A	100°F	106	135
Type B	100°F	300+	300+
Type C	100°F	115	140
Type A (at double the initial concentration)	100°F	155	193
Type A + 40% Type B	100°F	300+	300+