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Oil Soluble Copolymers for Versatile Synthetic and Oil-Base Drilling Fluids

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Abstract

The drilling fluids industry has evolved from the use of very crude mixtures of clay and water to complex fluid formulations based on sophisticated chemistry. Many of these changes have been the result of increasingly harsh downhole conditions and challenging environmental constraints. As a result, a large number of specialty products are now available to enhance the performance of drilling fluids. These products include additives to improve rheological and filtration control, well bore stability, bit performance, fluid stability, and environmental acceptability. However, most of these additives have limitations at high temperatures, and may cause excessive damage to producing formations.

The use of newly-developed chemical additives has been demonstrated to perform as rheological modifiers and as filtration control enhancement. These new high molecular weight oil-soluble copolymers for synthetic- and oil-base fluids are especially useful in fluid formulations requiring thermal stability under high temperature conditions.

This paper describes the laboratory and field evaluation of synthetic- and oil-base fluids formulated with copolymers. The copolymers have exceptional performance as rheological modifiers and as filtration control agents, in fluid densities ranging from 7.7-18.0 lb/gal (0.92-2.1 s.g.). The laboratory and field results demonstrate stable rheological properties, providing ideal hole cleaning, and high temperature and high-pressure filtration control. Drilling fluids containing these copolymers show little permeability damage to producing formations, allowing maximum oil and gas return permeability, at wellbore temperatures up to 400°F (204 °C).

Introduction

Thermally-stable drilling fluid systems, for use at temperatures higher than 300°F, are an important issue for HPHT applications in the drilling industry.

Oil-soluble copolymers have emerged as an alternative molecular group to maintain rheological properties and filtration control in drilling fluids at high temperatures. Copolymers are polymers with two different repeating monomers in their chain. The properties of copolymers are strongly influenced by the overall chemical composition and by the sequence of the monomer they contain. The exact sequence of monomer units along the chain can vary, depending upon the relative reactivity of each monomer during the copolymerization process.[1] Figure 1 illustrates the possible structures of copolymers containing A and B as repeating monomer units. Graft copolymers, such as styrene-butadiene (SBR), are oil-soluble molecules that could be used in drilling fluid as a rheological modifiers and/or filtration control.[2] Other copolymers that could act as rheological modifiers and filtration control agents are methacrylate/styrene and polyalkyl methacrylate.[3] An additional benefit reported for some copolymer applications is an increase in the lubricating properties of base oils.[4]

Several considerations are necessary for the appropriate selection of copolymers to obtain thermally-stable drilling fluids properties. These considerations include the copolymerization processes, monomer combinations, and the resulting molecular weight. The type and concentration of copolymer may change in various base fluids, especially under high temperature environments.

A laboratory study was performed in order to understand the influence of copolymers on the performance of drilling fluids with elevated temperature.

This paper describes the evaluation of synthetic-based and oil-based drilling fluids having polyalkyl methacrylate (PAMA) or SBR copolymers. The results established that the copolymer molecules used in this study maintain rheological and filtration control properties of the drilling fluids at high temperature. Evidence was also show that this copolymer approach will reduce the potential for excessive barite sag.

Association of copolymers in solution

Copolymers have an interesting tendency to display diverse ordered morphologies, such as lamellar, cylinders, spheres, and bicontinuous minimal-surface microestructures. These ordered morphologies exhibit rheological and other properties that differ from those of the disordered or random state.[5, 6]

Copolymer chemistry has been available for many years. The various morphologies exhibited by copolymers composed of two chemically distinct monomers have been extensively studied during the last decade. Because numerous industrial applicationhave benefited from the ordered morphologies generated by copolymers, research continues in the effort to better understand complex copolymer molecules.[7, 8]

The selection of a suitable solvent for a copolymer molecule is very important. Correct solvent selection will result in the creation of polymeric assemblies, such as micelles. It is also possible to create nanoscale materials which result from the polymeric assemblies in the final systems.

The stability of different copolymer morphologies results from an interplay between contact between chemically-different blocks, or enthalpic, and the chain-stretching, entropic, contributions to the system free energy. This can be described in terms of a diagram of the tendency for block segregation vs the copolymer composition (xN vs f)[5], where x is the Flory-Huggins interaction parameter, and N is proportional to molecular weight.

The micellization of a specific copolymer in organic solvents is highly-dependent on temperature and concentration. The structures formed by copolymers such as SBR in the types of non-polar base fluids used in oil-based mud (OBM) and and synthetic-based mud (SBM) are characterized by high stability at high temperatures.

Testing Protocol

The performance of SBR and polyalkyl methacrylate copolymers was evaluated in synthetic-based mud and oil-based mud for a range of density between 7.7 and 18 lb/gal. The effects of molecular weight and copolymer concentration were studied in formulations after being hot-rolled at 150°F, as well as at temperatures up to 400°F.

Copolymer effectiveness was analyzed by rheological characterization of the fluid formulations using a Fann 35 viscometer and a Rheometrics SR5000 rheometer with a couette geometry.[9] HPHT filtration was also measured, as fluid loss control is a secondary function of the copolymers evaluated.

To verify the evaluated copolymers would work synergistically with organophilic clay to provide optimized viscoelastic properties and the control of barite sag under low-shear conditions, differential density between the top and bottom mud fractions was measured after static aging.

Results and Discussion

Influence of copolymer molecular weight

To evaluate the effect of various PAMA copolymer molecular weights, evaluations were conductd in in a 12.5 lb/gal, 85/15 SWR formulation. This formulation also contained 10 lb/bbl of an emulsifier, 3 lb/bbl of an organophilic clay and 3 lb/bbl of the copolymer under evaluation.

Test results obtained using PAMA copolymers with molecular weights between 100,000 and 450,000 g/mole are shown in Table 1. A fluid formulation was evaluated without the presence of a copolymer, for reference purposes

Test results indicated that rheological properties increase with copolymer molecular weight. There was a very small effect on the formulation with 100,000 g/mol polyalkyl methacrylate, when compared to the fluid without copolymer. The similar properties at 150 and 300°F indicate that there is virtually no temperature effect in the evaluated range.

It was additionally indicated in these tests that the PAMA copolymer also increases the viscoelastic properties of the fluid. Figures 2 and 3 illustrate the characterization of the drilling fluid's viscoelastic properties, as measured with a Rheometrics SR5000 rheometer. Figure 2 indicates that the 12 lb/gal, 85/15 formulation, with PAMA copolymer, forms a 3-dimensional, linked gel network by virtue of the elastic modulus (G') dominating over the entire frequency region. The only way that G' can dominate the entire frequency region is if network is present. The fluid formulation of Figure 3 is not characterized by such a network, as demonstrated be the elastic and viscous moduli (G' and G") convergence at low frequencies. This fluid also shows that the gel viscosity begins exhibiting Newtonian behavior at low frequencies, further indicating lack of rheological structure.

The sample with copolymer having a molecular weight of 100,000 g/mole did not exhibit good filtration control. However, the test samples containing copolymers with molecular weights between 200,000 and 450,000 produced good fluid loss control.

These test results with polyalkyl methacrylate copolymers, in a synthetic invert emulsion system, indicate that a minimum molecular weight of 200,000 is required to obtain acceptable filtration control and rheological properties.

Effect of copolymer on fluid loss reduction and rheology properties

The rheological properties measured at 120°F and HTHP filtration of fluid formulations with densities between 7.7 and 18 ppg, evaluated after hot-rolling at high temperatures are shown in Tables 2 and 3. Table 2 shows that a very simple OBM formulation, containing only organophilic clay, emulsifier, lime, and the SBR copolymer, maintains the initial rheological properties after being hot-rolled at 400°F. Also, a noticeable reduction in fluid loss was observed when compared with the same formulation without the copolymer. These results demonstrate the versatility of the SBR copolymer and its ability to provide thermal stability in the OBM formulations evaluated between 180 and 400°F.

This copolymer application can be made to a broad range of base fluids, including mineral, diesel and synthetic base oils. As shown in Table 3, the thermal stability ehibited by this type of copolymer in invert emulsions results in good rheological properties and HPHT filtration control, after being hot rolled at 400°F. This is the consequence of the synergistic effects between organophilic clay and SBR copolymersr.

The measurement of rheology at HPHT conditions has demonstrated the stability of these fluids at high temperatures. As shown in Figure 4, the rheological profile of a 17 lb/gal drilling fluid formulation is enhanced with the addition of copolymer. When evaluated on a Fann Model 75 viscometer, from 150 to 390°F, with pressures between 8,000 and 13,500 psi a positive trend is evident. The properties follow a trend with increasing temperature, without a corresponding change in the slope of the curve, as occurs in the measurements with the drilling fluid formulation without the copolymer additive.

Effect of copolymer concentration

In order to determine the adequate copolymer concentration, drilling fluid formulations, with various concentrations of selected PAMA copolymers, were tested. This optimization helped to define additive concentrationst to compliment the solids-suspending characteristics of the organophilic clay for preventing barite sag, or, sedimentation.

Table 4 shows the results obtained in a 12.5 lb/gal formulation with 4 lb/bbl organophilic clay, and 10 lb/bbl emulsifier. The fluid formulations exhibit an increase in rheological properties with increasing copolymer concentration, from 1 to 3 lb/bbl. However, all samples had rheological properties in the acceptable range for drilling applications.

The results show a reduction of free oil and differential density (sag), as the PAMA copolymer concentration increases. In high temperature testing, organophilic clay alone cannot minimize sedimentation to desireable levels. After increasing the organophilic clay from 4 to 5 lb/bbl, in the formulation without PAMA copolymer, a differential specific gravity of 0.30 and 90 mL of free oil were measured.

Effect of drilling contaminants on formulation with copolymers

A contamination study, incorporating various solids, and seawater dilution, was performed in a 12.5 lb/gal, 85/15 SWR formulation. This formulation contained 10 lb/bbl emulsifier, 3 lb/bbl organophilic clay and 4 lb/bbl PAMA copolymer. As shown in Table 5, the results of these tests indicate the system is extremely stable to contaminants such as highly-reactive bentonite and seawater, having HPHT fluid loss values less than one mL. Also, when increasing the density from 12.5 to 14.5 lb/gal rheological and filtration control properties were not negativelt affected. It was also evident in these tests that the system as formulated is resistant to the sedimentation of barite after exposure to extended static aging conditions at elevated temperatures.

Return permeability

A series of return permeability tests were performed using Berea sandstone and field cores.The tests were carried out at various temperatures in a range between 180 and 300°F, with overbalance between 500 and 1000 psi and crude oil supplied by field operators. Table 6 summarizes the results of this testing.

With the 7.7 lb/gal formulation and heavy crude oil, with ab API gravity of 12°, the return of permeability was 93%. Two additional formulations, a (14.5 lb/gal all-oil based and 13 lb/gal invert emulsion, were evaluated at 300°F, using a light crude oil. The results from these tests indicated a 100% permeability return afterflow back.

The observed break-out pressure required to remove the filter cake, which was less than 10 psi in all the tests performed, was another very promising observed result. These test results indicate a high probability of minimal damage to the formation.

Field applications

Numerous well containing either the PAMA or SBR copolymers have been drilled to date.[10] Performance results reported by operators include good cuttings transport and hole cleaning, minimal non productive time and operations problems, such as partial drilling fluid losses and stuck pipe. Also highlighted has been the reduction of drilling time, increased hydrocarbon production and the reduction of the total drilling cost.

A weakness of the application of SBR is the physical characteristics of the dry copolymer. The copolymer has a "solid crumb" texture, with a low initial solubility in base fluids. This slow solubility results in additional time during the the mud preparation stage. For maintenance of the drilling fluid, a concentrated SBR copolymer solution is pre-mixed in base fluid and added directly to the circulating fluid during the drilling operations.

Conclusions

Copolymers of polyalkyl methacrylate (PAMA) and styrene-butadiene (SBR) are useful for filtration control and rheological modification in synthetic and oil-based drilling fluids, including HPHT drilling applications.

Synthetic and oil-based fluids formulated with high molecular weight SBR or PAMA copolymers show excellent thermal stability and fluid loss control at temperatures up to 400°F. However, 400°F is not necessarily the upper limit of thermal stability.

Fluids formulated with SBR or PAMA copolymers are very stable in the presence of drilling contaminants.

Return of permeability test results, with fluids formulated with SBR or PAMA copolymers, indicate minimal expectation of formation damage to the reservoirs.

Acknowledgements

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Nomenclature

SWR = Synthetic base/water ratio
OBM = Oil base mud
EWR = Ester/water ratio
SWR = Synthetic/water ratio
M_W *= Molecular weight*
PAMA = polyalkyl methacrylate copolymers
SBR = Styrene-butadiene rubber copolymer
HPHT = High pressure high temperature
PV = Plastic viscosity
YP = Yield Point
10-sec gel = API 10 second gel strength
10-min gel = API 10 minute gel strength
F = Temperature, oFahrenheit
x = Flory-Huggins parameter
N = index proportional to molecular weight
f = copolymer composition

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Si Metric Convertion Factors

ft x 3.048	E -01 = m
psi x 6.894 575	E +03 = pa
cP x 1.08	E -03 = Pa.s
mL x 1.0	E -06 = m^3
mD x 9.869 233	E -16 = m^2
lbf/100 ft^2 x 0.478 803	E +00 = Pa
lb/gal x 1.198 264	E +02 = kg/m^3
lb/bbl x 2.853 019	E +00 = kg/m^3
Microns x 1.0*	E -06 = m
°F (°F-32)/1.8	= °C
°A 141.5/(131.5 +°API)	= g/cm^3

Table 1 Invert emulsions fluids formulated with poly-alkyl methacrylate (PAMA) copolymers

	Without copolymers	PAMA 1	PAMA 2	PAMA 3
Copolymers, lb/bbl	-	3	3	3
Average MW	-	450.000	200.000	100.000
Properties at 120°F (after hot-rolled at 150°F)				
Plastic Viscosity, cP	22	38	31	24
Yield Point, lbf/100 ft^2	12	29	25	13
3-rpm reading	7	13	12	8
10-sec gels, lbf/100 ft^2	8	13	13	9
10-min gels, lbf/100 ft^2	9	20	17	11
Electric Stability, Volts	2000	2000	2000	2000
Properties at 120°F (after hot-rolled at 300°F)				
Plastic Viscosity, cP	19	41	33	24
Yield Point, lbf/100 ft^2	12	29	25	12
3-rpm reading	6	12	12	9
10-sec gels, lbf/100 ft^2	7	13	12	9
10-min gels, lbf/100 ft^2	10	19	16	11
Electric Stability, Volts	1644	1557	1543	1611
HPHT filtrate @ 300°F, mL/30 min	7	3.8	4.2	10.6

Table 2 OBM formulated with SBR copolymer for high-temperature applications

Additives	**OBM without SBR 14 lb/gal**		**OBM with SBR copolymer**							
			7.7 lb/gal		**14 lb/gal**		**12 lb/gal**		**18 lb/gal**	
Oil base, bbl	0.72		0.91		0.72		0.79		0.58	
Organophilic clay, lb/bbl	6		12		6		12		2.5	
Emulsifier, lb/bbl	6		6		6		6		6	
Lime, lb/bbl	4		1		4		6		4	
SBR copolymer, lb/bbl	-		4		3		3		2.5	
Densifier, lb/bbl	364		51		364		255		577	
Properties	Initial	HR @ 350°F	Initial	HR @ 180°F	Initial	HR @ 350°F	Initial	HR @ 350°F	Initial	HR @ 400°F
PV, cp at 120°F	15	15	16	17	35	37	32	37	70	66
YP, lb/100 ft^2	5	1	5	6	18	17	14	14	10	11
6-rpm reading	3	1	4	4	8	9	6	6	5	6
10-sec gel, lb/100 ft^2	4	1	3	5	8	10	6	7	5	9
10-min gel, lb/100 ft^2	7	2	4	6	8	10	8	9	11	18
HPHT Filtrate, mL/30 min	-	21	-	2.2	-	5	-	5	-	8

Table 3 SBM formulated with SBR copolymer for high-temperature applications

Additives	Fluid Density		
	12 lb/gal	14 lb/gal	16 lb/gal
Synthetic base, bbl	0.49	0.44	0.40
Organophilic clay, lb/bbl	3	2	1.5
Emulsifier, lb/bbl	22	22	22
Wetting agent, lb/bbl	0.5	0.5	0.5
25% $CaCl_2$, bbl	90.5	66	43.5
Lime, lb/bbl	2	2	2
SBR copolymer, lb/bbl	4	4	4
Barite, lb/bbl	231	345	458
SWR	75/25	80/20	85/15
Properties (after hot-rolled at 400°F)			
Plastic viscosity, cP at 150°F	29	35	45
Yield point, lb/100 ft^2	14	10	10
6-rpm reading			
10-sec gel, lb/100 ft^2	7	6	6
10-min gel, lb/100 ft^2	10	9	9
HPHT Filtrate,@ 350°F, ml/30 min	8	7	7

Table 4 Effect of copolymer concentration on SBM formulations

Properties at 120°F (after aging at 300°F)	Concentration of PAMA 2			Formulation without copolymer
	1 lb/bbl	2 lb/bbl	3 lb/bbl	
Plastic Viscosity, cP	23	28	36	21
Yield Point, lbf/100 sq ft	17	25	30	27
3-rpm reading	10	12	16	15
10-sec gels, lbf/100 ft^2	11	13	15	13
10-min gels, lbf/100 ft^2	13	14	20	16
Electric Stability, Volts	1529	1531	1604	1461
Barite sag measured after static aged at 300 °F				
SG top-SG bottom	0.31	0.20	0.16	0.65
Free oil, mL	78	62	14	128

Table 5 Effect of contaminant on 85/15 invert emulsion formulated with 4 lb/bbl PAMA 1

Properties	Base	Synthetic Seawater	MIL-GEL NT	Weight up
		10%	35 lb/bbl	12.5 to 14.5 lb/gal
Plastic viscosity, cP	29	27	39	34
Yield point, lbf/100 ft^2	8	18	16	15
6-rpm reading	5	8	6	7
10-min gel, lbf/100 ft^2	10	11	7	10
HTHP filtrate @300°F, mL/30 min	0.8	0.8	0.8	2.2
48-hours static aged:				
Free oil, mL	7	-	-	-
Barite Sag (delta SG)	0.21			

Table 6 Return of permeability tests

Properties	Fluid density formulations, lb/gal		
	7.7	13	14.5
Formation	Icotea	Naricual	Naricual
Test temperature, °F	180	300	300
Overbalance pressure, psi	500	500	500
Initial Permeability, md	23	11	5
Final Permeability, md	22	11	5
% of return of permeability	93	100	100

Figure 1. Structures of copolymers containing A Y B repeating monomers

RANDOM
-A-A-B-A-B-A-B-B-A-B-A-A-B-A-A-B-

ALTERNATING
-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-

ABA-TRIBLOCK
-A-A-A-A-B-B-B-B-B-B-B-B-A-A-A-A

GRAFT

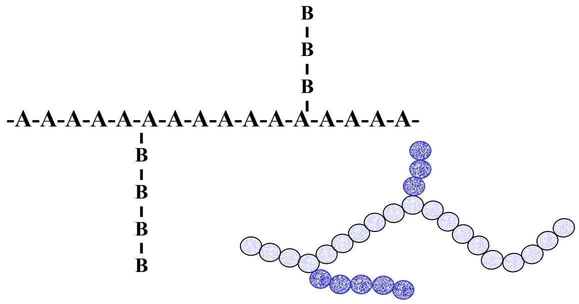

Figure 2 Viscoelastic Properties for 12.5 lb/gal, 85:15 SWR fluids with 2 lb/bbl of PAMA copolymer

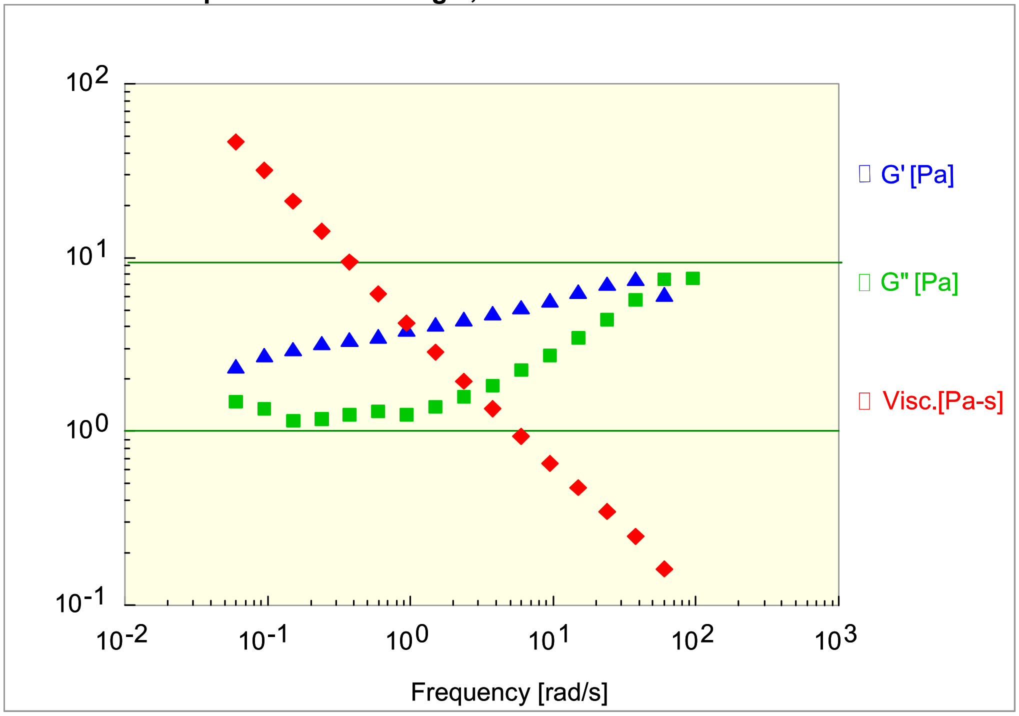

Figure 3 Viscoelastic Properties for 12.5 lb/gal, 85/15 SWR fluids without copolymer

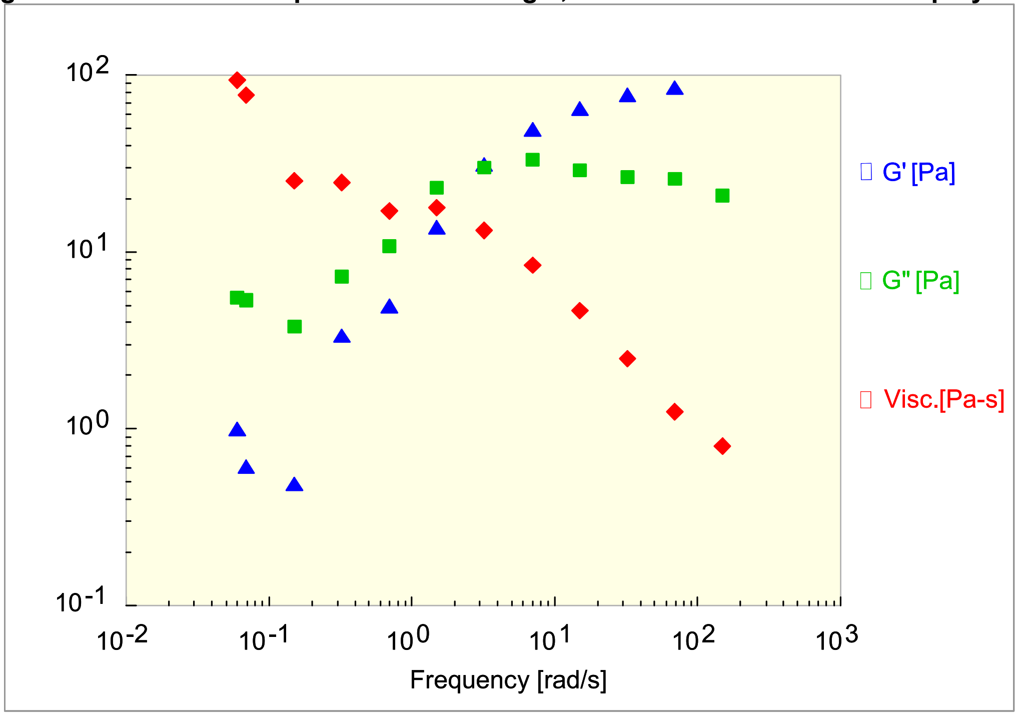

Figure 4 Rheological profile of a 17 ppg formulation evaluated from 140 to 400 °F