Figure 16: Sample 3:1 - 07 at -20°F HB Viscometer

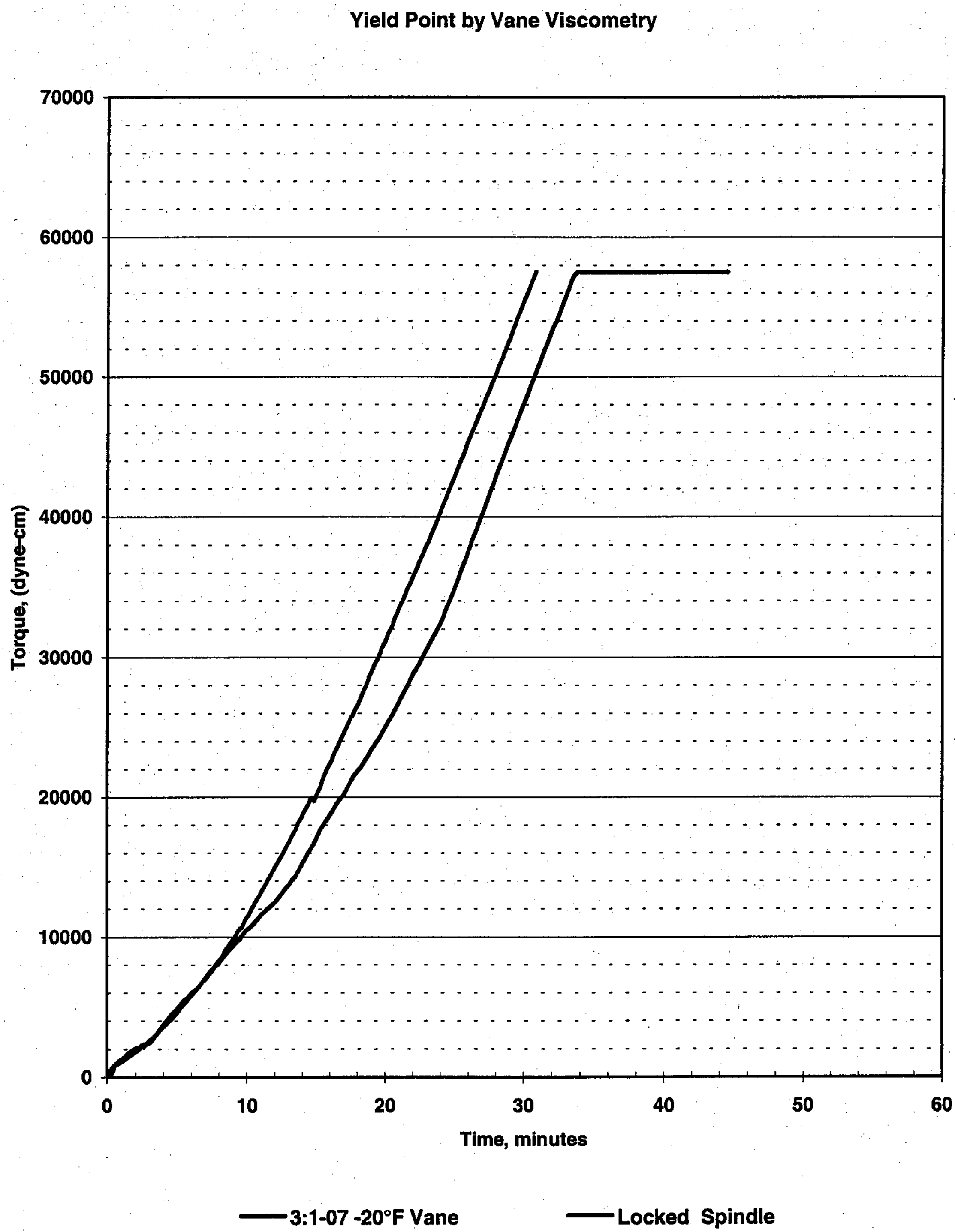


Figure 17: Sample 3:1 - 08 at -20°F HB Viscometer

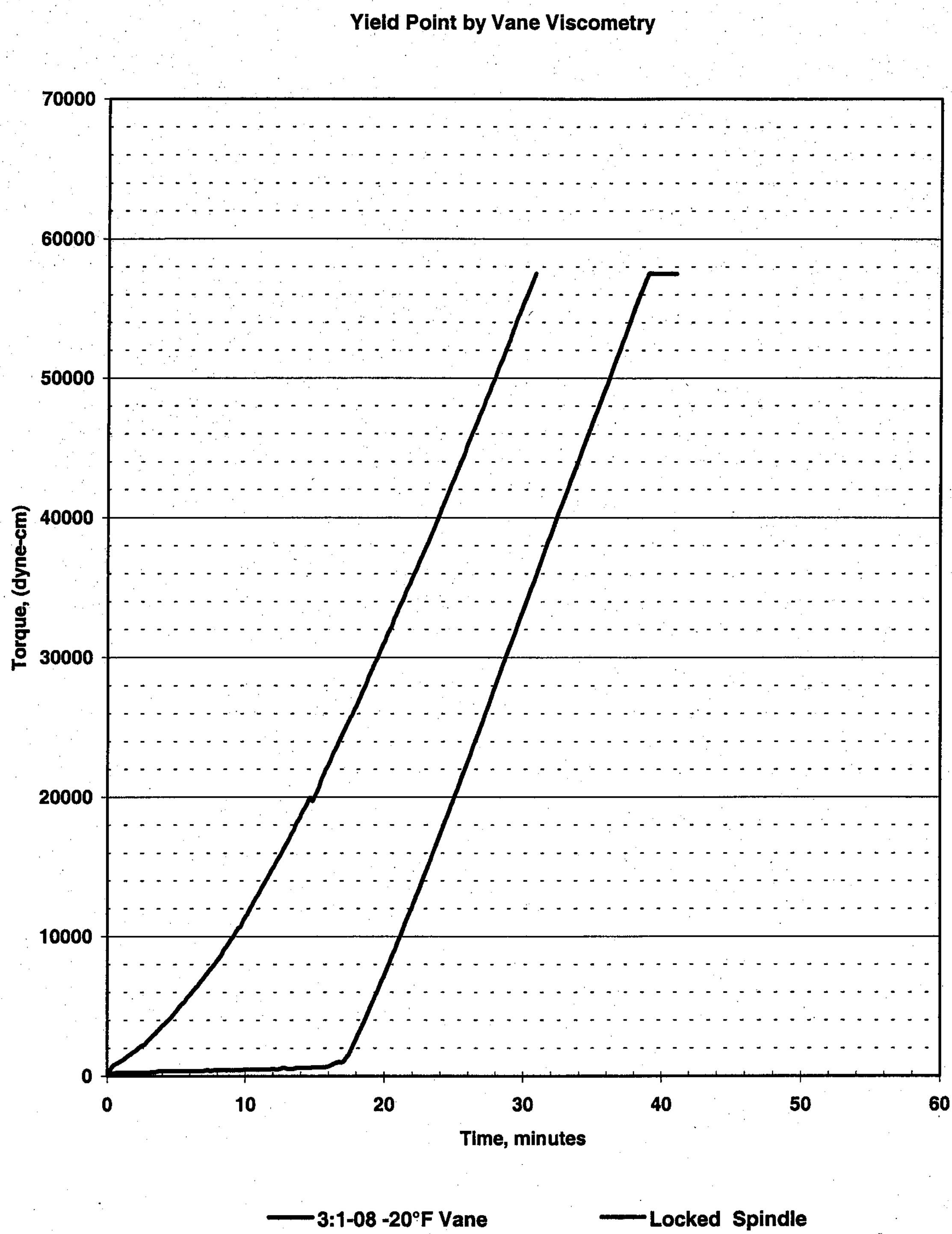


Figure 18: Sample 4:1 - 01 at 20°F RV Viscometer

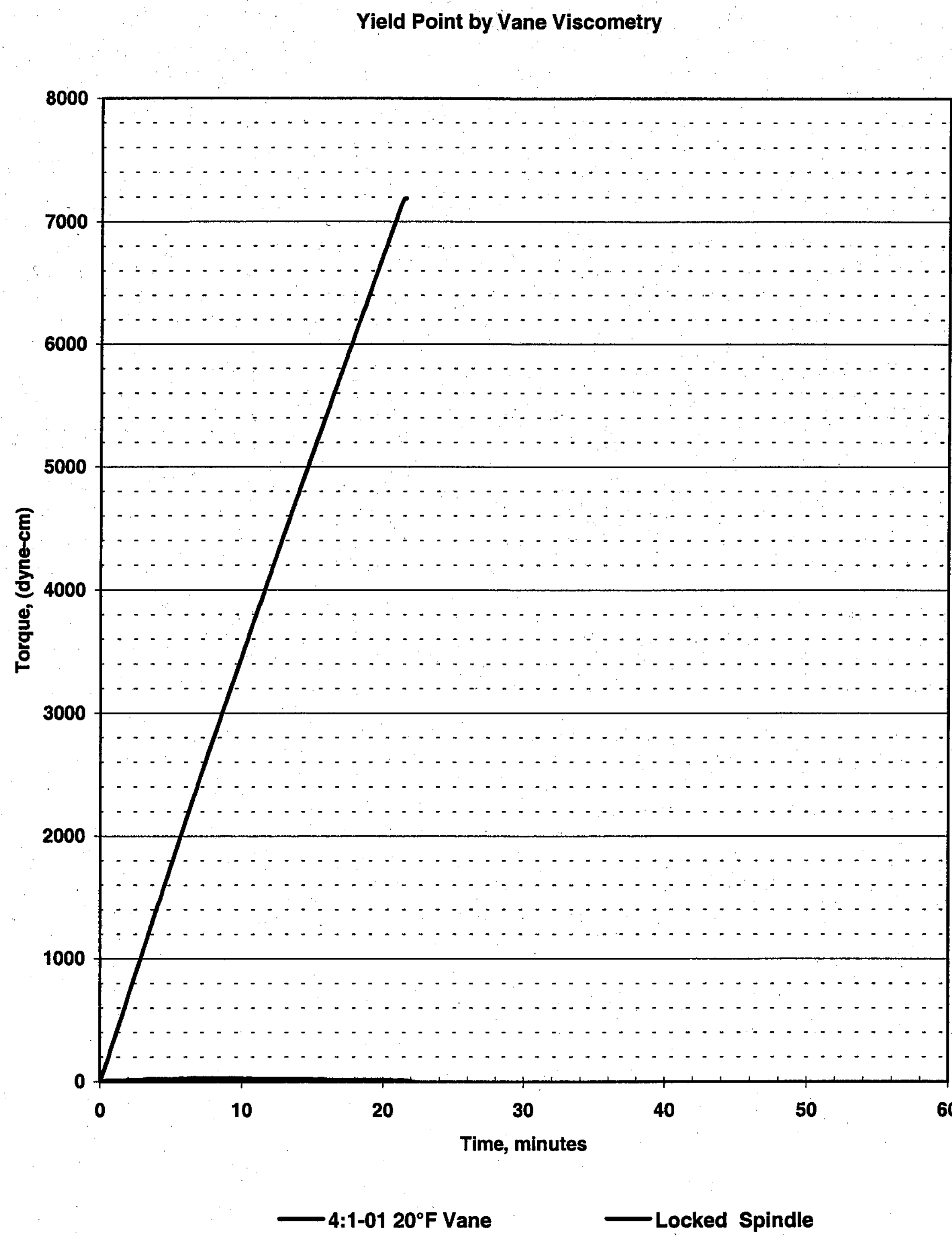


Figure 19: Sample 4:1 - 02 at 20°F RV Viscometer

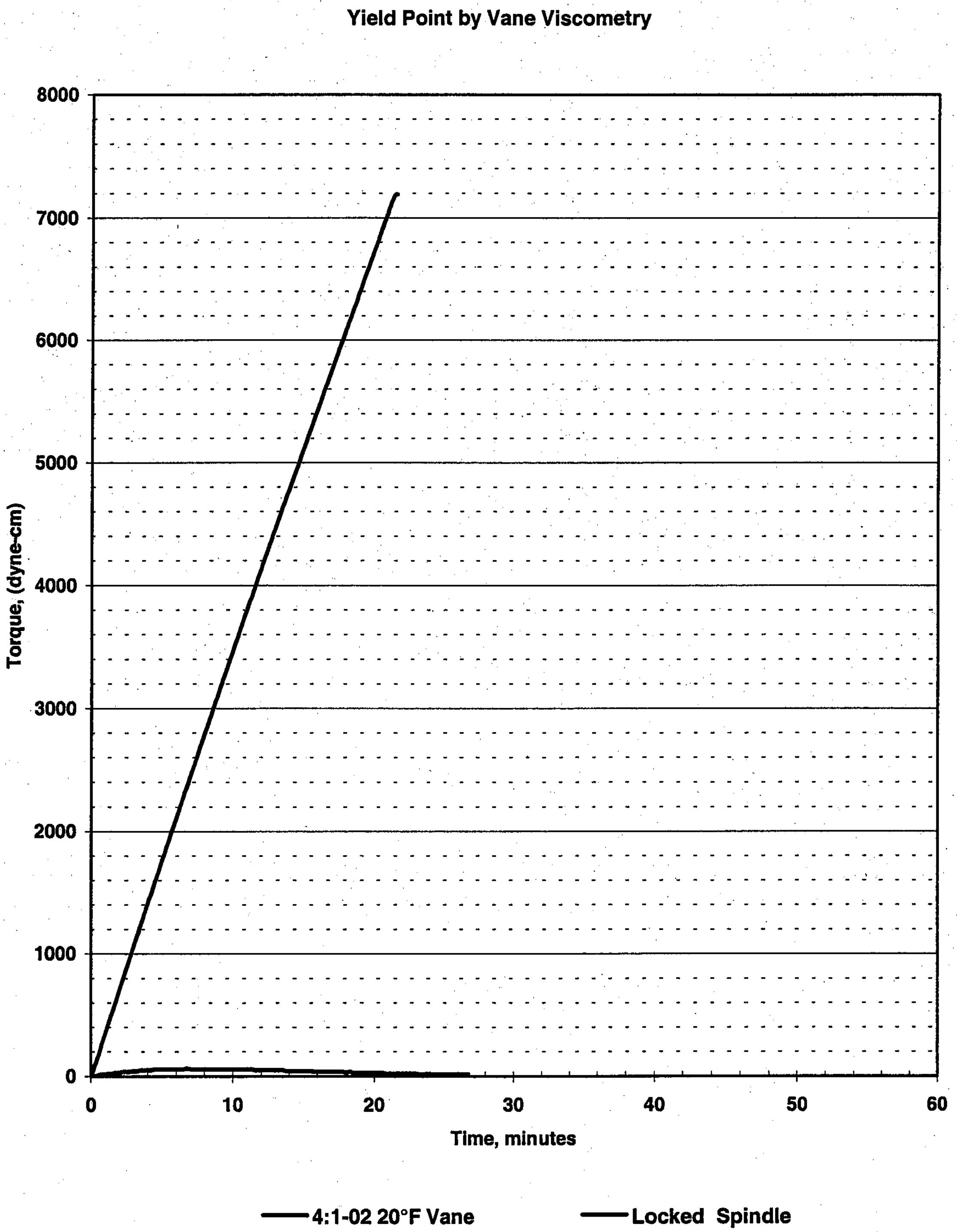


Figure 20: Sample 4:1 - 03 at 20°F RV Viscometer

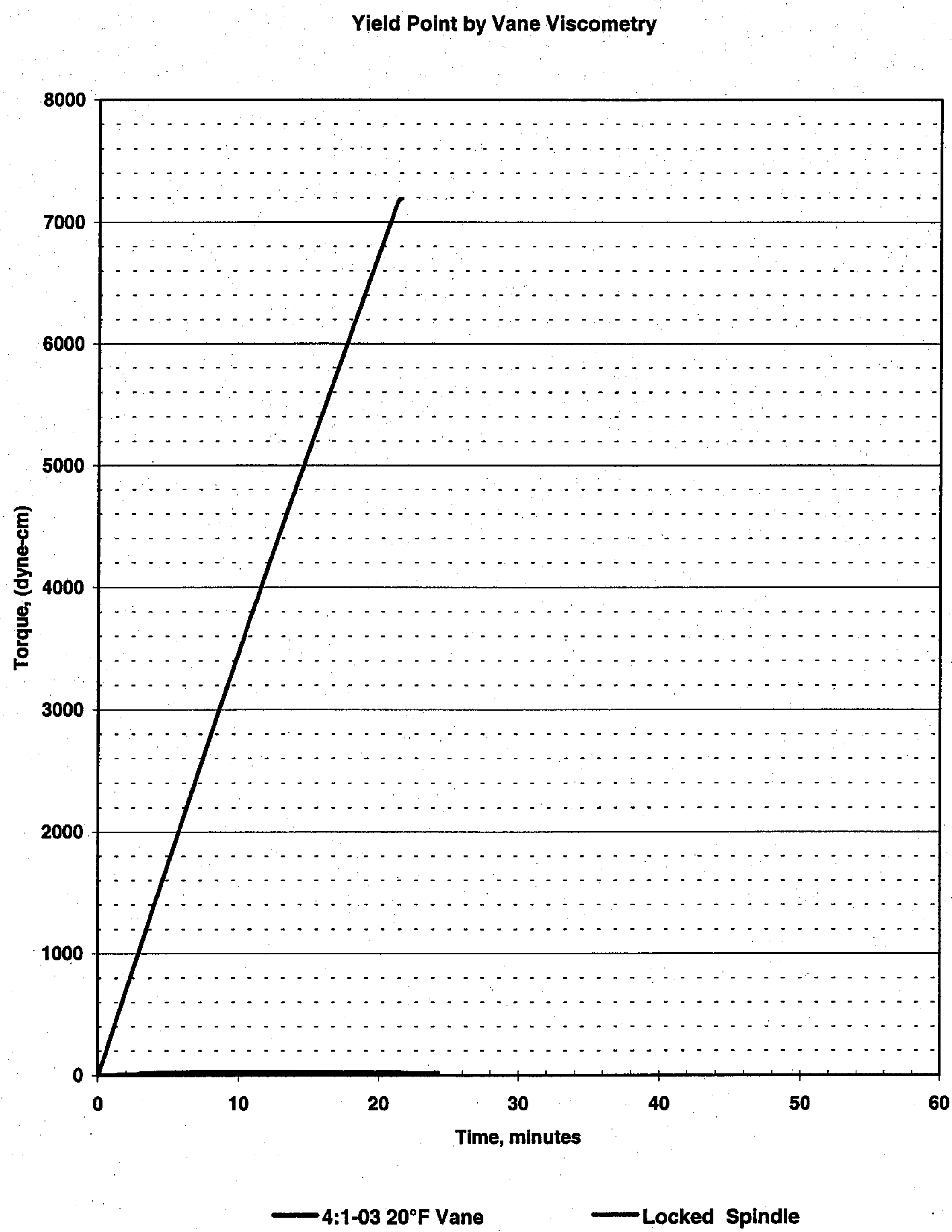


Figure 21: Sample 4:1 - 04 at 0°F LV Viscometer

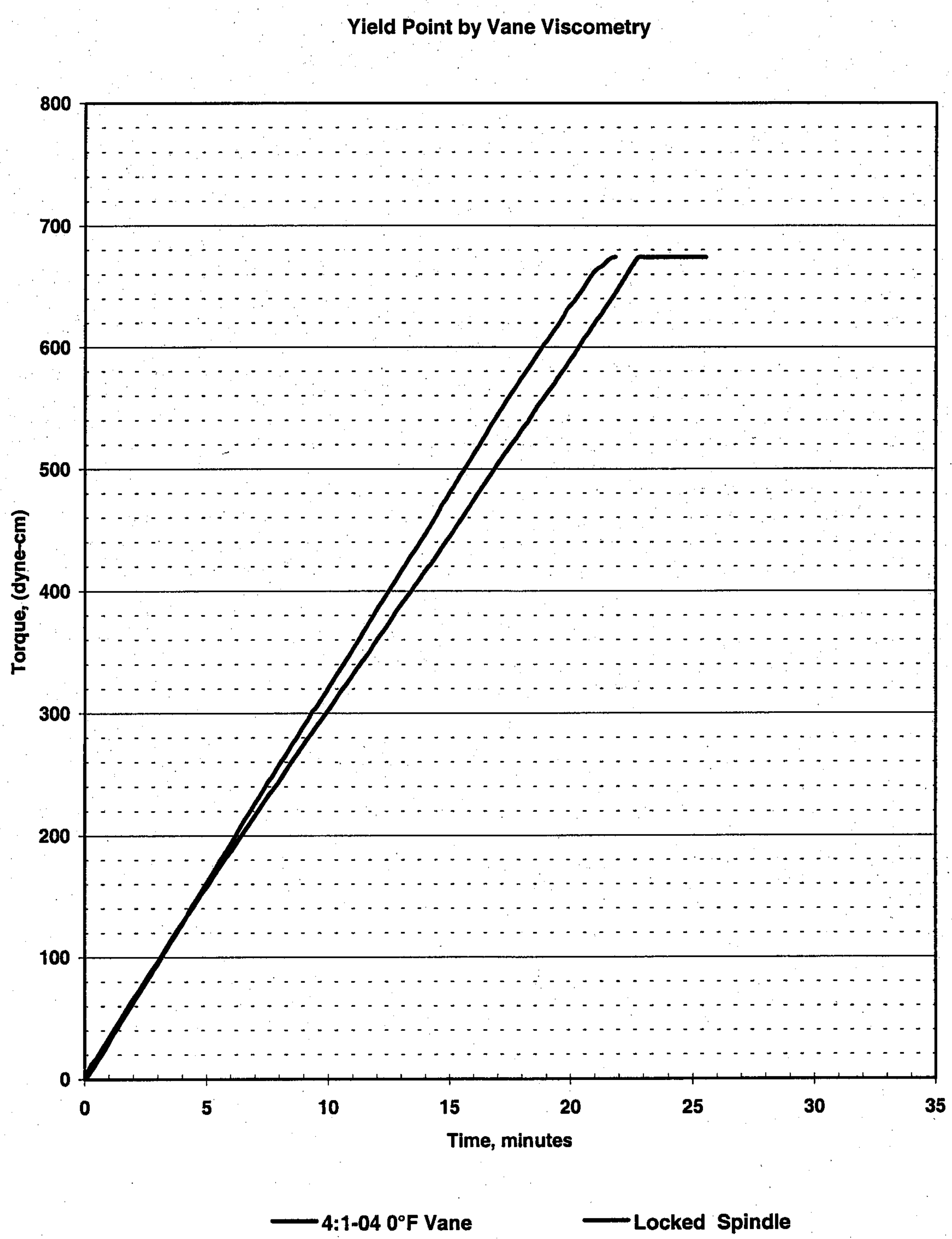


Figure 22: Sample 4:1 - 05 at 0°F   RV Viscometer

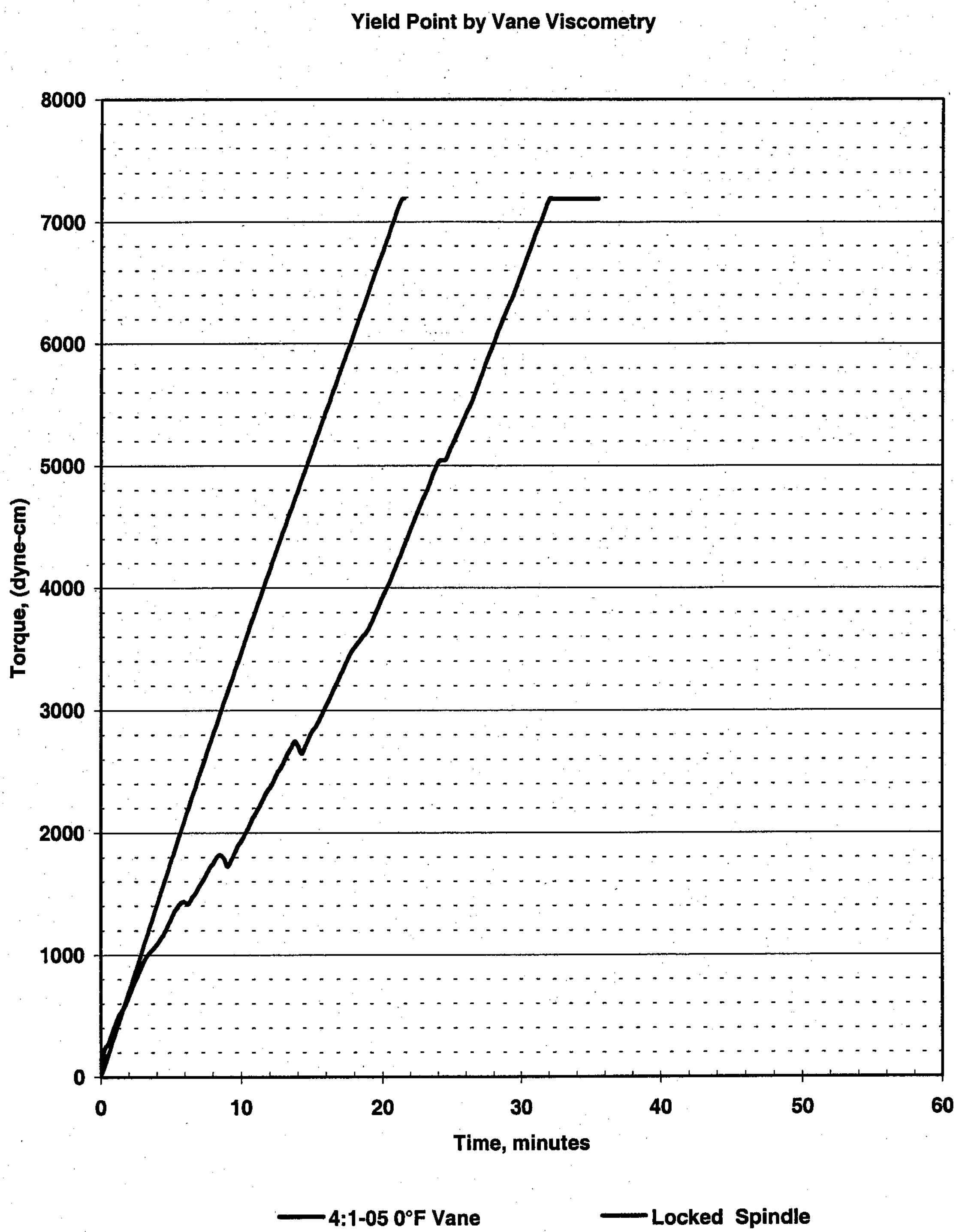


Figure 23: Sample 4:1 - 06 at 0°F HB Viscometer

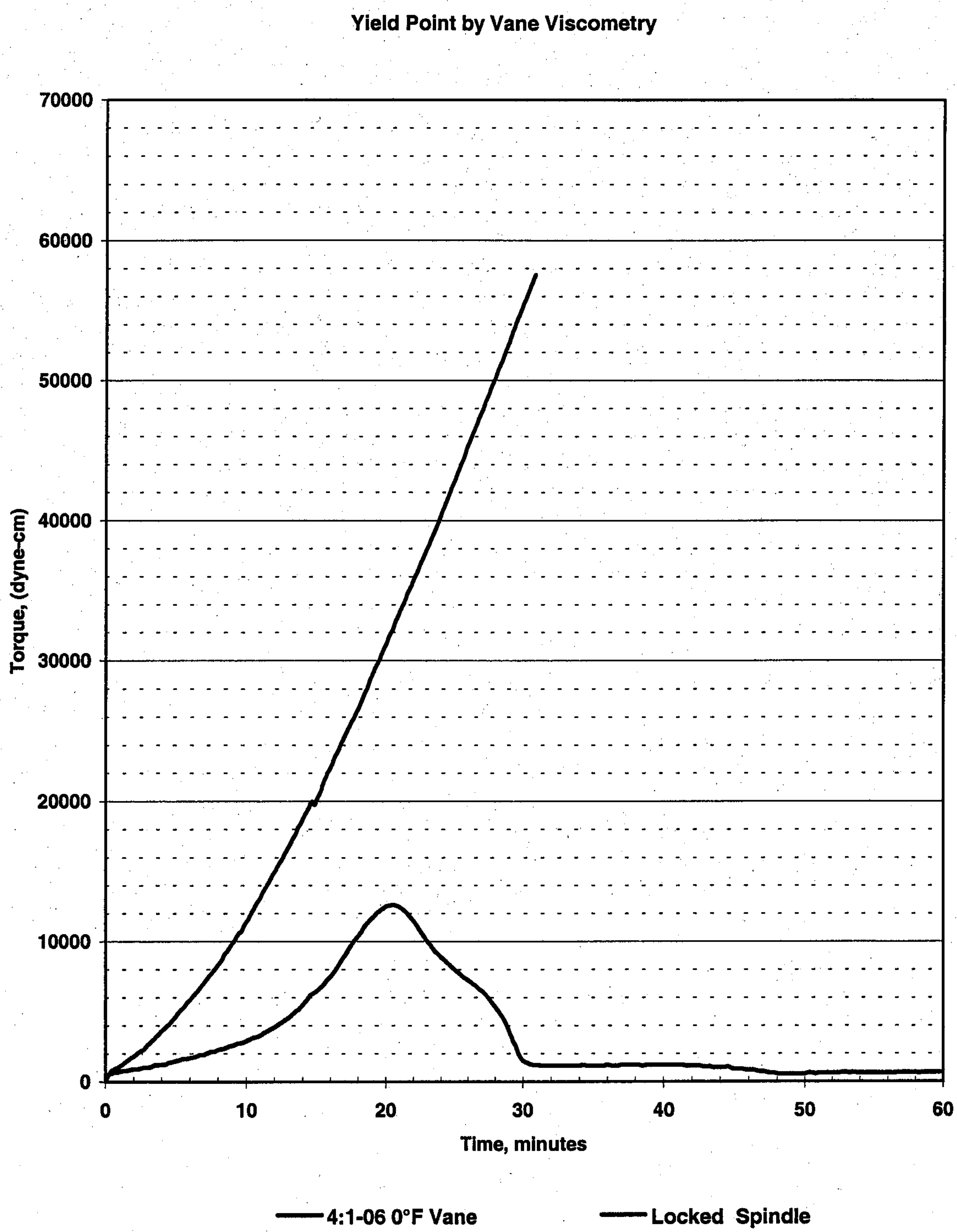


Figure 24: Sample 4:1 - 07 at 0°F HB Viscometer

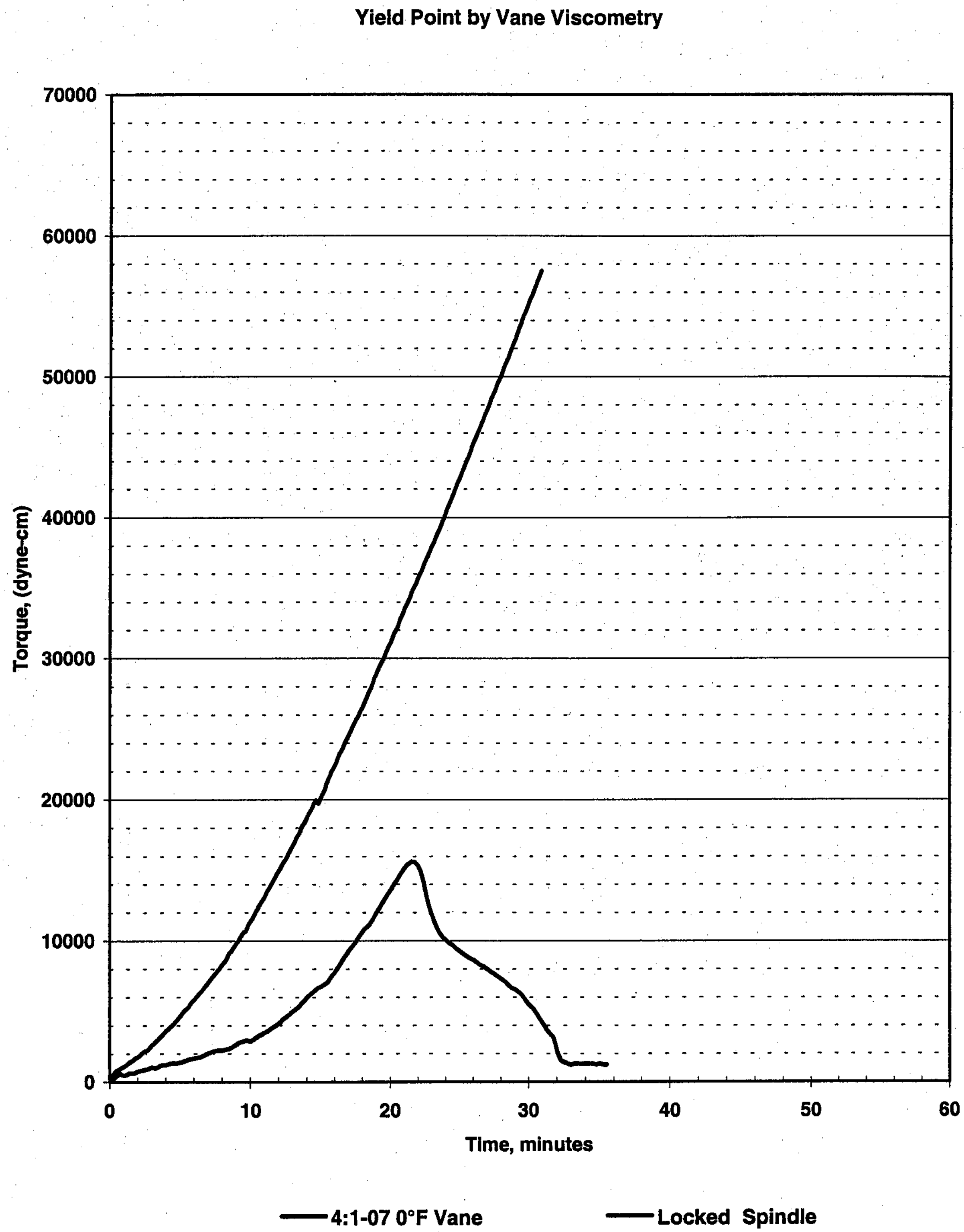
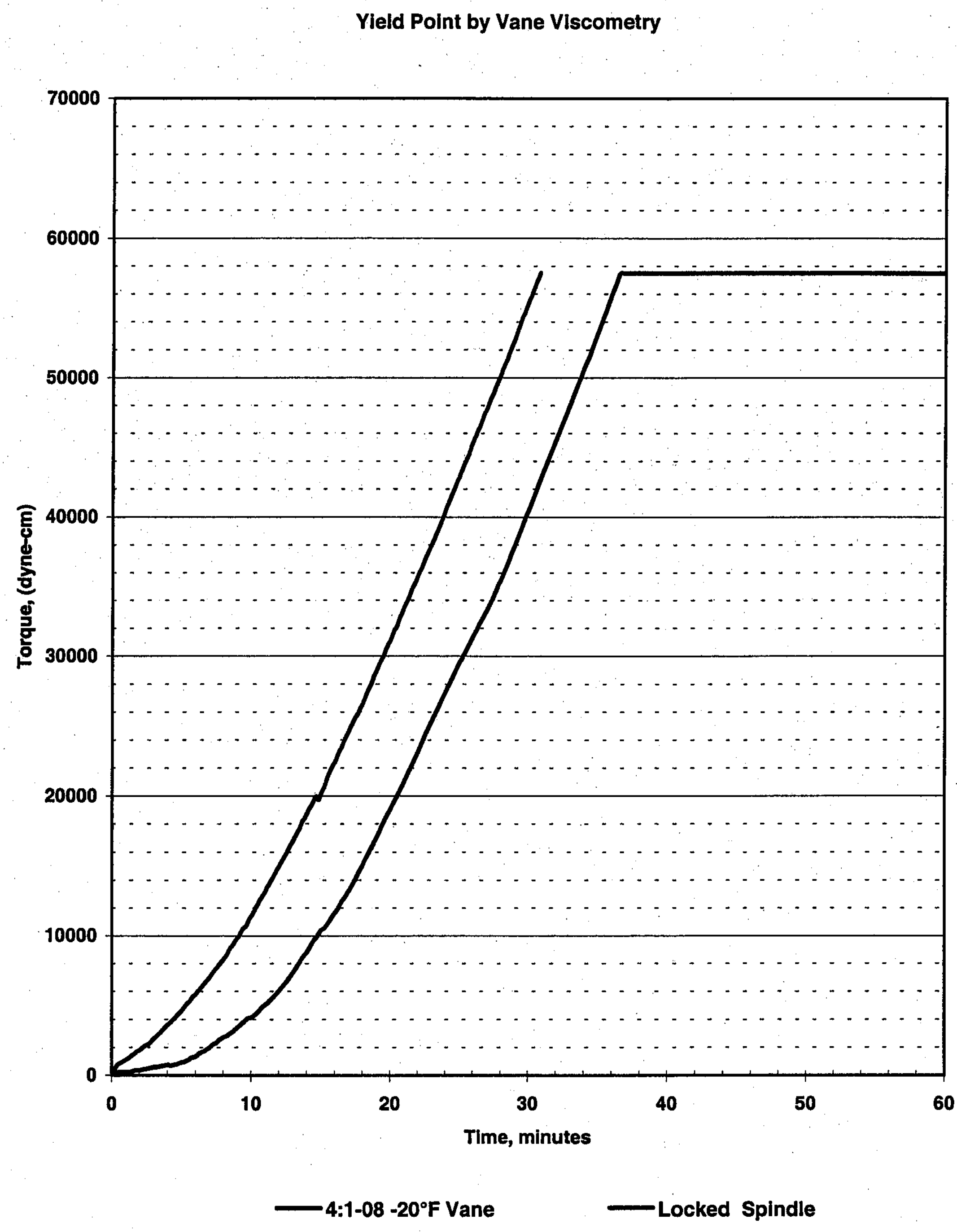


Figure 25: Sample 4:1 - 08 at -20°F   HB Viscometer



Appendix A

Vane Viscometer - Yield Stress Data For GTL & Crude Oil Blends

100% GTL #2

3:1 Ratio Blend

25% GTL #2 + 75%TAPS Crude Oil at PS-1

4:1 Ratio Blend

20% GTL #2 + 80%TAPS Crude Oil at PS-1

Appendix B

Standard Laboratory Procedure

(SLP-307)

"Crude Oil Yield Stress Value Determination By Vane Viscometry"

Subject: Crude Oil Yield Point Determination by Vane Viscometry	Document No: SLP-307
Date: July 31, 2000	Revision 3

Prepared by: Neal Magri
Applicable to: Westport Technology Center International

Technical Review by: Bayram Kalpakci	Date: July 31, 2000
Safety Review by: Robert Jaros	Date: July 31, 2000
Quality Assurance Review: John Shillinglaw	Date: July 31, 2000

Scope: This test method describes the use of the Brookfield viscometer for the determination of the yield stress value of crude oils.

Safety Precautions: Approved safety glasses with side shield and protective clothing must be worn at all times in the laboratory. Protective gloves are required to be worn when handling crude oil and solvents. Keep away heat, sparks and open flame. Use only with adequate ventilation, (i.e. sampling performed within a fume hood if possible). Avoid contact with skin, eyes and clothing. Avoid breathing mist or vapor. Keep containers closed. Open containers with caution.

Important: Crude oil and container will be hot after the initial heating during the beneficiation process. Handle and dispose of syringes and needles properly. Empty containers may contain toxic, flammable/combustible or explosive residue or vapors. Do not cut, grind, drill, weld, reuse or dispose containers unless adequate precautions are taken against these hazards. Observe ALL PRECAUTIONARY LABELING.

Hazard: **CRUDE OIL**, Vapors may be harmful. Possible aspiration hazard if swallowed, can enter lungs and cause damage. May be irritating to the skin, eyes and respiratory tract. May release toxic hydrogen sulfide vapors. Skin cancer hazard based on tests with laboratory animals. Contains **BENZENE**—a cancer hazard. Extremely flammable liquid. Vapor may cause flash fire.

Reference Documents: ASTM D2983 Standard Test Method for Low-Temperature Viscosity of Automotive Fluid Lubricants; Westport Standard Procedure SLP-305 Rheological Properties of Crude Oils by Rotational Viscometer; Brookfield Digital Viscometer Model DV-II+ Version 2.0, Operating Instructions, Manual No. M/92-161-F1193; Brookfield WinGather Software, Operating Instructions, Manual No. M/95-320-C398; Operations and Programming Manual for Sigma Systems M26-C3 Environmental Chamber with Programmable Temperature Controller / Model CC-3. Dzuy, N.Q., Boger, D.V., "Yield Stress Measurement for Concentrated Suspensions", J. Rheology, 27 (4), 321-9 (1983).

Table of Contents

Summary of Test Method

This test method consists of determining the yield stress value of a crude oil by measuring the torque on a spindle, using a Brookfield viscometer, rotating at 0.01 rpm in the material. The spindle to be used consists of four rectangular vanes dimensioned (0.75"w x 2.25"h) and oriented at 90 degree increments around the central axis. The sample cup is dimensioned (1.5" id x 4.0"h). Vertical orientation of vanes within the sample cup is dimensioned (1.00" from top and 0.75" from bottom). The crude oil is initially heated to 150°F to destroy all temperature and shear histories and then cooled to 90°F at which stress value it is loaded into the cup apparatus. The cup apparatus holds the vanes rigidly during cooling and aging and prevents loss of light ends through evaporation. After loading into the cup apparatus the sample is cooled in an environmental chamber at a controlled rate to -20°F. The cooling rate mimics the expected rate of cooling of the pipeline oil in the case of shut-in.

Samples are withdrawn from the environmental chamber at 10 test temperatures (approximately 80, 65, 50, 40, 20, 10, 0, -10, -15 and -20°F) and transferred to a refrigerated circulator that maintains the sample at test temperature. The spindle is attached to the Brookfield viscometer before the spindle clamping mechanism is released. The clamping mechanism is released and the viscometer is started at 0.01 rpm and torque as a function of time is measured, at least until a maximum reading is obtained. The maximum torque obtained is divided by a vane parameter constant K to obtain the yield stress. The constant K is calculated based on the dimensions of the vanes. (K=36.19 cm^3, for a Vane with D=0.75 inch (1.905 cm) and H=2.25 inch (5.715 cm))

Significance and Use

The test method is used for determining the yield stress value of a cooled crude oil, with or without aging. This determination will be made with vane spindles, which extend horizontally through a sample, minimizing the impact of slippage at the spindle wall. The method will determine the minimum amount of torque necessary to initiate oil movement at low shear, and subsequent viscosity of the fluid after initiation of flow. These data can be directly used in modeling of crude oil behavior in pipelines, during start-up conditions.

Equipment Required

- Certified rotational-type viscometers capable of a minimum rotational speed of 0.01 rpm such as: the Brookfield Viscometer, Model LV DVII+, RV DVII+ or HB DVII+ having the capability of 20 speeds when programmed accordingly.
- Thermometer, Fluke digital thermometer which has been certified to ±0.3°C from –40°C to 100°C and ±2.0°C from –50°C to –100°C, using standards traceable to the National Institute of Standards and Technology or the National Physical Laboratory or using natural physical constants or ratio calibration techniques.
- Westport vane viscometry cup apparatus and vane spindle for the Brookfield viscometer.
- 100 ml glass syringe, and syringe needle equipped with valve.
- Sigma System M26-CC3 environmental chamber, equipped with a liquid nitrogen supply for cooling.
- Temperature controlled refrigerated circulator bath, such as a Julabo FP-50 series.

PROCEDURES

A. Calibration of Apparatus

Calibration as it is normally understood, carrying out an experimental measurement with a standard material, in the same manner as for the unknown sample, does not apply to vane viscometry; there are no standards. However, as received, from the factory the Brookfield viscometers are certified to give accurate speed and percent torque readings, and it is these two measurements which are critical to vane viscometry.

Tests of consistent viscometer response will be carried out as verification that the viscometer is in good working order. Testing will be carried out for each viscometer when used in each experimental set (an experimental set entails the testing of all samples cooled in one set in an environmental chamber, generally a population size of 24).

1.0 Procedure

1.1 Level the Brookfield viscometer, and the plastic bracket to hold the vane apparatus using the spirit levels attached to them.

1.2 Take an empty vane apparatus, with the top removed but with the spindle locked, and place the apparatus in the refrigerated circulator, temperature is not critical at this step.

1.3 The vane apparatus is held in place by a plastic bracket; make certain the apparatus is placed as far to the right as possible and as far towards the back of the bath as possible.

1.4 Tighten the clamp that holds the vane apparatus in the bracket.

1.5 Attach the alignment rod to the Brookfield viscometer. Move the Brookfield viscometer vertically and horizontally until the alignment rod fits into the top of the vane spindle (without lateral motion).

1.6 Remove the alignment rod and screw on the S hook attachment to the Brookfield viscometer.

1.7 Loosen the clamp that holds the vane apparatus in the bracket.

1.8 Attach the vane spindle to the Brookfield viscometer as shown in Figure 1.

1.9 Raise the Brookfield viscometer until all slack is taken out of the connections to the vane spindle but the vane spindle is not lifted off its plastic support bracket.

1.10 Rotate the vane apparatus until the torque reading is less than 0.05%. It is best not to start with negative torque readings as these are not recorded by the WinGather program.

1.11 Tighten bracket that holds the vane apparatus in place, using the knob in the top right corner of the bracket.

1.12 Start the WinGather program for timed torque readings. Time between readings will be 10 seconds for a speed of 0.01 rpm.

> As the Brookfield software does not recognize the vane spindle, spindle input is not necessary. Time, torque and temperature readings, which are independent of spindle, are the only data that will be used.

> The WinGather program is Version 1.1 from Brookfield Engineering Laboratories, Inc., located at 11 Commerce Blvd., Middleboro, MA 02346. See referenced manual for further WinGather information. The manual and a copy of the software will be archived at Westport Technology Center.

1.13 Start the Brookfield motor with the locked spindle mechanism in place.

1.14 Continue the test run until the torque reading goes off scale.
1.15 Save the WinGather data file and record the data file name.

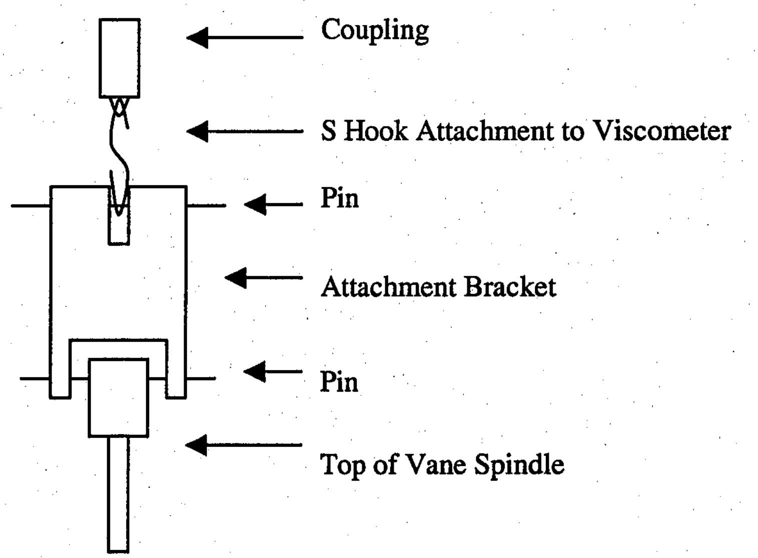


Figure 1. Attachment of Vane Apparatus to Viscometer

2.0 Acceptable Calibration

Differences in torque versus time measurements will include variations in viscometer speed and torque measurement. For purposes of measuring yield stress, variances in viscometer speed are not critical. Speed is important however for determining slippage of the sample at the yield stress value. A torque versus time run will be acceptable if it varies no more than 10% of the maximum torque of the viscometer, at any stress value in the experimental run.

B. Verification of Cooling Rate

1.0 Data Recording

Temperatures will be measured by the environmental chamber thermocouple and recorded by a YEW Model 3088 Hybrid Recorder (chart recorder). The chart recorder will print time and temperature at 0:00 and 12:00 each day, in addition to a continuous trace of the temperature. This temperature recording procedure has been verified against a certified Fluke thermometer and found to be within ±1°F. The temperature recording of the environmental chamber and Yew recorder will be re-verified each time the Fluke digital thermocouple meters are re-certified.

1.1 At the end of each vane experimental run, when all samples originally placed in the environmental chamber have been tested or disposed of, remove the chart recorded paper from the recorder. This data is to be saved, and archived with other items for this test method, such as laboratory notebooks.
1.2 The chart recording should be inspected to ascertain if there are any significant anomalies, such as rapid, transitory increases or decreases in temperature.
1.3 Printed temperatures from the chart recorder should be recorded and contrasted with target temperatures as part of final reporting.

Table 1. Times and Target Temperatures

Day (24 hrs)	Target Temperature (°F)
0	90
2.5	70
5.0	50
7.5	35
10	20
12.5	10
15	0
17.5	-10
21	-20

C. Preparation of Sample

The solubility of paraffins in crude oil decreases with decreasing temperature. As an oil cools past its wax appearance temperature, regardless of the rate at which the oil was cooled, significant amounts of paraffin may precipitate. However, the rheological properties of the precipitated wax are highly dependent upon the shear and temperature history of the oil above and below the wax appearance temperature. The initial step in determining yield stress of an oil is to heat the sample to 150°F and hold the oil at that temperature for at least 2 hours, to destroy all temperature and shear histories. It is important to make certain the oil container is tightly closed during this initial conditioning, as loss of light ends through evaporation may significantly increase yield stress.

Following the initial heating of the oil, allow the oil to cool to 90°F in a Sigma environmental chamber. At this stress value the oil containers, the vane apparatuses and the 100-ml glass syringe for oil transfer are thermally equilibrated in the environmental chamber at 90°F. Allow at least an hour for all materials to reach temperature.

D. Loading of Vane Apparatus

A 100-ml glass syringe equipped with needle and valve is used to load the oil sample into the vane apparatus.

1. Take the syringe, one sample bottle (120-ml) and one vane apparatus out of the environmental chamber that is set at 95°F to 100°F.
2. Remove the plunger from the syringe, invert the syringe and close the needle valve.
3. Pour 100 ml of crude oil into the syringe and replace the plunger.
4. Turn the syringe upright, open the needle valve and expel the gas bubble.
5. The syringe should contain at least 95 ml of oil but no more than 98 ml. If necessary add more oil or expel some of the oil into a waste container.
6. Inject the oil sample through the loading port of the vane apparatus.
7. Set the top-sealing chamber of the cup apparatus in place and place the vane apparatus back into the environmental chamber.
8. Place a Styrofoam block on top of the vane between the vane and environmental chamber roof, to hold the top down.
9. Repeat steps 1-8 until all samples have been loaded.

E. Controlled Cooling and Aging of Samples in Environmental Chambers

The environmental chamber's programmable temperature controller allows up to 100 program steps. Each step has 5 sub-steps (0-4). To program ramp and soak functions select a step, and input setting specific parameters in the corresponding sub-steps.

The sub-step parameters and ranges are as follows:

0	+/- TTT.T	Set stress value temperature displayed to the nearest 0.1°C (+200 to –100°C)
1	HH.MM	Ramp time hours (00-99), minutes (00-59)
2	HH.MM	Hold time hours (00-99), minutes (00-59)
3	NNN	Next step (00-99, 100=end)
4	P	Active temperature control probe (1 or 2)

As described in section B cooling will be carried out in 8 steps with a final hold time of 99 hours to allow for aging if required.

F. Measurement of Yield Stress

1. If an approximation of the yield stress for the sample under test conditions is not available make the initial measurement with the Brookfield RV viscometer. Prior measurements, at warmer temperatures, will dictate selection of appropriate Brookfield viscometer for future testing, at colder temperatures.
2. Level the Brookfield viscometer, and the plastic bracket to hold the vane apparatus using the spirit levels attached to them.
3. If the viscometer has not been previously aligned during calibration do so following steps 1.2 through 1.7 in section A.
4. Equilibrate the Brookfield temperature bath at –2°F below test temperature, as the test sample will be warmer than the bath temperature due to heat picked up from the top of the vane apparatus.

5. Remove a vane apparatus from the environmental chamber along with the insulated container of ethylene glycol. Place the vane apparatus in the insulated container.

Important: Even though the vane spindle is locked in position all movements of the vane apparatus should be made as gently as possible to reduce the possibility of disrupting wax networks present.

6. Gently carry the vane apparatus to the Brookfield viscometer.
7. Remove the top of the vane apparatus.
8. Place the apparatus in the refrigerated circulator at temperature. Move the apparatus as far to the right and toward the back of the bracket as possible.
9. Pin the vane apparatus spindle to the Brookfield spindle as shown in Figure 1.
10. Adjust the height of the viscometer so that all slack is taken out of attachments but the vane apparatus is not lifted from the plastic bracket
11. Rotate the vane apparatus so that the torque reading is as close to zero percent as possible.
12. Tighten the knob that holds the vane apparatus in place.

Important: At this stress value the vane spindle will be released from its locking mechanism. Careful handling of the apparatus from this stress value onward is especially critical to avoid uncontrolled breakdown of any wax networks formed.

13. Start the WinGather program for timed torque readings. Time between readings will be 10 seconds for a speed of 0.01 rpm.

As the Brookfield software does not recognize the vane spindle, spindle input is not necessary. Time, torque and temperature readings, which are independent of spindle, are the only data that will be used.

The WinGather program is Version 1.1 from Brookfield Engineering Laboratories, Inc., located at 11 Commerce Blvd., Middleboro, MA 02346. See referenced manual for further WinGather information. The manual and a copy of the software will be archived at Westport Technology Center.

14. Gently remove the locking pin from the vane apparatus.
15. Gently cut the band holding the locking clamps in place.
16. Gently separate the locking clamps slightly.
17. Start the Brookfield motor.
18. Continue the test run until a stable torque reading has been obtained or until the torque reading goes off-scale.

If maximum torque reading on the Brookfield RV is <9% of full scale (647 dyne-cm), repeat steps F1 through F18 with a new sample using the LV Brookfield viscometer.

If torque reading goes off-scale, it will be necessary to repeat steps F1 through F18 with the next strongest Brookfield viscometer (HB). If yield stress is beyond the full-scale capabilities of the Brookfield HB viscometer, stop testing and report accordingly.

19. Save the WinGather data file and record the data file name.
20. At test completion, insert certified Fluke thermocouple into vane apparatus and take a final sample temperature.
21. Repeat the test as stated:
    - Under test conditions where (possibly above the oil's WAT) observed torque readings are below 10% full scale on the LV viscometer (lowest torque spring viscometer) only test one sample.
    - If torque readings are above 10% full scale on the LV, then run a second sample for repeatability. If the two test results are not within 10%, run a third sample for precision purposes.
    - Three samples should always be tested at the lower temperatures if test samples are available. If necessary, for precision statements, repeat additional times.

G. Data Recording

Initiate Data Verification and Validation Checklists. Data recording, which will include quality assurance tests such as calibration and data checks, will be achieved using the enclosed vane viscometry data sheets.

Data Sheet 1 (DS1-307) includes recording of data when all the samples, for an entire tests, are prepared, transferred to their respective vane apparatuses, cooled to test temperature and aged.

The data to be recorded include:

- <u>Test Number</u>; Designate the test by number so that subsequent individual vane data sheets (DS2-307) can be traced to the parent data sheet. (i.e. IDC Test 1, Phase 1–Test 1…)
- <u>Sample Description</u>; Identification of sample (i.e. TAPS Mix, PBU, Kuparuk…)
- <u>Sample Benefication</u>; Record temperature treatment information for the samples before transfer to the vane apparatuses.
- <u>Transfer of Samples</u>; Record start and stop times for transfer of all samples from original bottles to vane apparatuses to environmental chambers.
- <u>Cooling/Aging of Sample</u>; Record temperature of environmental chamber when samples are first introduced, also record target temperature (normally –20°F) and the target period of time for cooling samples to that temperature (normally 21 days). Temperature/time measurements will be recorded by the Yew hybrid chart recorder.

Data are to be recorded for each individual sample withdrawn and tested from the environmental chambers on vane viscometry Data Sheet 2 (DS2-307). Record data including:

- <u>Test Number</u>; the same number as used on DS1-307, establishes tracking of DS2-307 sheets.
- <u>Sample Description</u>; Identification of sample (i.e. TAPS Mix, PBU, Kuparuk…)
- <u>Testing</u>; date and time of sample withdrawal, the temperature of the environmental chamber, the name of the WinGather data file where testing data is stored, the type of viscometer (LV, RV or HB) and the speed (rpm) at which the test was carried out (normally 0.01).

- Data Check; data for the vane testing will be recorded using the WinGather program. The data check section of the data sheet will be used for quality assurance of this WinGather data. During testing (at 5 to 10 minute intervals), record the percent full scale (torque) reading directly from the Brookfield viscometer display, and record the data stress value of the WinGather program where this data was recorded electronically.
- Maximum Torque; Record the observed highest percent full-scale reading (torque).
- Data Stress values of Maximum Torque; Record the approximate range of WinGather stress values during maximum torque (i.e. numbers 73-78).
- Final Oil Temperature; Record the sample temperature after completion of test.

H. Calculation and Interpretation of Results

The experimental test is designed to produce direct readings, temperature and %torque, as data.

Calculation of torque and yield stress.

1. Calculate torque readings from the percent of full-scale readings recorded by the WinGather software by multiplying the percent full-scale reading by 6.733 dyne-cm for the LVDV-II+ viscometer, or 71.87 dyne-cm for the RVDV-II+ viscometer, and 574.96 for the HBDV-II+ viscometer. Torque data may be interpreted by graphing the torque versus time readings obtained during testing. Determine a yield stress value from this data by observing where a maximum torque reading had been obtained, followed by a decrease in torque reading over time. Calculate the Yield Stress by the following equation;

$$\textbf{Yield Stress} = \textbf{Maximum Torque Obtained (dyne-cm)/ K (36.19 cm}^3\textbf{)}$$

I. Reporting

1. Report the following information:
   - 1.1 Completed and signed Data Verification and Validation Checklists,
   - 1.2 Date of test,
   - 1.3 Sample Identification,
   - 1.4 Cooling time for sample,
   - 1.5 Aging/testing temperature in degrees Fahrenheit (environmental chamber temp.),
   - 1.6 Final oil temperature at end of test (measured directly in cup),
   - 1.7 Viscometer speed,
   - 1.8 Maximum torque reading,
   - 1.9 Yield Strength versus Temperature,
   - 1.10 Locked Spindle Torque versus Time Curve,
   - 1.11 Time versus torque reading for each test will be reported graphically,
   - 1.12 Numerical data for the graph,
   - 1.13 Combined Plot of all Torque vs. Time Curves on one Log Scale Plot,
   - 1.14 When multiple oils are analyzed, plot all Yield Strength vs. Temperature curves on one Lop Scale Plot.

J. Precision

Precision – See Section A2 for precision during QC/QA calibration checks. Initial Demonstration of Capability for test resulted in the following;

Determinability (d) – Measurements are performed on individual oil samples, taken at selected temperatures, through a maximum shear condition which destroys any wax structure present. No attempt was made to duplicate measurements on the same oil sample within the test cell; the results would be misleading. Therefore, no statement of determinability can be made on.

Repeatability (r) - The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of this method, have a relative standard deviation at or below 15%.

Reproducibility (R) - The Brookfield viscometers are a very common apparatus for measuring rheological properties. However, with the Vane cup and spindle apparatus design and modifications for low temperature testing of the TAPS/COS samples, no statement of reproducibility by other independent laboratories can be made.

Data Sheet 1 for Vane Viscometry **Form: DS1-307**

Heating, Transfer, Cooling, and Aging for Sample Sets

Test Number:	
Sample Description:	

Sample Beneficiation				**Transfer of Samples**
Date:		Start Time:		Start Time:
Temp.:		Stop Time:		Stop Time:

Cooling/Aging of Samples			
Chamber Temp.:		Target Temp.:	
Ramp Start Time		Target Time:	

Sample Identification

Chamber 1		Chamber 2	
Vane No.	Sample ID	Vane No.	Sample ID

Analyst Signature:______________________________

Data Sheet 2 for Vane Viscometry Form: DS2-307

Withdrawal and Testing of Individual Samples

Test Number:	
Sample Description:	

Sample Testing

Withdrawal Date and Time:		Viscometer:	
Chamber Temp.:		Viscometer Speed:	
WinGather File Name:			

Data Check

WinGather Data Stress value Number	Percent Full Scale (Torque)		WinGather Data Stress value Number	Percent Full Scale (Torque)

Maximum Percent Full-Scale (Torque):	
Data Stress values of Maximum Torque:	
Final Oil Temperature:	

Analyst Signature:______________________