

Effect of Pressure on the Performance of Poly(ethylene-vinyl acetate) as Wax Deposition Inhibitors by Calorimetric Method

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ABSTRACT: Chemical inhibition is one of the traditional methods used by the petroleum industry to prevent or correct the problems caused by the formation of organic deposits. In this work, three samples of poly(ethylene-co-vinyl acetate)s (EVAs) were added at different concentrations to three different Brazilian crude oils, and their effect on the wax appearance temperature (WAT) and crystallization enthalpy of the oils was evaluated as a function of increasing pressure and the type of saturation gas, using high-pressure microcalorimetry (HP μ DSC). The results show that different copolymer compositions present dissimilar performance in reducing WAT, and, in some cases, an optimum concentration was observed. When rising pressure, a positive influ-

ence on the WAT is observed, but the performance of organic deposition inhibitors that are ineffective at atmospheric pressure is not enhanced at higher pressures. On the other hand, additives able to modify the crystallization kinetics of waxes at atmospheric pressure show a synergy when evaluated in the presence of light fractions and under high pressures. HP μ DSC analysis is an important tool to optimize the additive concentration to be used in oil fields. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: wax crystallization; wax appearance temperature; organic deposition inhibitors; high-pressure microcalorimetry; poly(ethylene-co-vinyl acetate)

INTRODUCTION

Organic deposition in petroleum production can be caused by asphaltenes, paraffins, or both.^{1–3} Problems related to the crystallization and deposition of waxes are encountered in all areas of oil production, for example, reducing production or even blocking lines and equipment. The problems caused by precipitation of waxes, such as decreased flow rate, reduce the efficiency of operations and bring added costs for control and correction of wax deposition.⁴

The traditional methods used in the oil industry to prevent and correct these problems are^{5–9}: chemical inhibition, electrical and chemical heating of production lines, mechanical scraping, and insulation of lines.

Chemical additives act by modifying the structure of the wax crystals and impeding their growth and agglomeration. Polymers are extensively used in

petroleum production,^{1,3,10–14} and the typical wax deposition inhibitors are polyacrylates, polymethacrylates, and ethylene-vinyl acetate copolymers (EVA), among others.^{7–9,15,16} No inhibitor is universally effective, and so there is a need for laboratory tests to select the best ones, considering their compatibility with the materials of the injection system and stability under the pressure and temperature conditions in the field.¹⁷

The cost of using chemical additives increases excessively in deepwater operations and thus is one of the determining factors in the economic feasibility of offshore production.¹⁸ Therefore, it is important to evaluate the risk factors as accurately as possible, such as wax deposition that can adversely affect oil production economics. Furthermore, the laboratory tests must be conducted under conditions close to the real ones in the field. The wax appearance temperature (WAT) value measured depends on many factors, among them the composition of the oil, its thermal history, pressure, the measurement technique, and cooling rate.¹⁹ High-pressure microcalorimetry (HP μ DSC) has been used by many researchers to assess the influence of pressure on the wax crystallization temperature and enthalpy of pure crude oils and oils mixed with wax deposition

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inhibitors.^{16,20,21} In this work, Brazilian crude oils were mixed with organic deposition inhibitors and evaluated by the variation of the WAT as a function of pressure reduction and type of saturation gas.

EXPERIMENTAL

Materials

Three crude oil samples (named Crude Oil A, Crude Oil C, and Crude Oil D) were supplied by Petrobras. The main characteristics of these samples, including size and size distribution of the paraffin fraction, were presented in a previous work.²¹ The samples were analyzed according to the procedure described in another previous paper.²²

In this work, we used three EVA samples with varied proportion of ethylene/vinyl acetate. EVA copolymers were chosen, because they have the potential to act as wax deposition inhibitors, as observed in previous works.^{7,8} The sample called Inhibitor X is an EVA copolymer containing about 25% of vinyl acetate and was supplied by Politeno S.A., Brazil. The sample called Inhibitor Y is the same EVA copolymer used as Inhibitor X, but this sample was chemically modified by introducing 16% of hydrocarbon side chains containing 16 carbon atoms.²³ The third, called Inhibitor Z, is an EVA copolymer containing about 35% of vinyl acetate and was supplied by Schlumberger, Brazil.

The following blends of standard gases were used: Standard Gas Blend 1 was composed of nitrogen (0.5%), carbon dioxide (0.4%), methane (86.94%), ethane (10%), propane (2%), isobutene (0.05%), *n*-butane (0.04%), isopentane (0.03%), *n*-pentane (0.02%), and *n*-hexane (0.02%); Standard Gas Blend 2 was composed of nitrogen (0.56%), carbon dioxide (0.62%), methane (66.62%), ethane (13.91%), propane (1.33%), isobutene (2.82%), *n*-butane (4.08%), isopentane (0.03%), and *n*-pentane (0.03%). White Martins, Brazil, supplied all the gases.

Methods

Calorimetry

The HP μ DSC tests were performed in a Setaram μ DSC VII apparatus, using two 500- μ L Hastelloy cells: one for the sample and the other for reference. The operating and analytic conditions were established in a previous work.²² After pretreatment of the sample with heating at 80°C for 1 h, the testing program consisted of heating from 30 to 80°C at a rate of 1°C/min, an isotherm at 80°C for 180 min (saturation time), cooling from 80°C to -10°C at a rate of 1°C/min, another isotherm at -10°C for 15 min, and finally heating from -10 to 30°C at 1°C/min. The sample's weight was about 100 mg, and N₂ at 1.5 bar

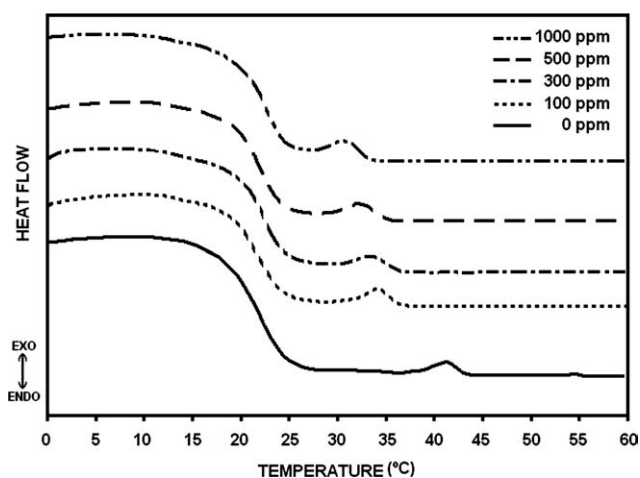


Figure 1 μ DSC curves as a function of temperature for Crude Oil A with different concentrations of inhibitor X.

was used as carrier gas. The cooling fluid was recirculated at a flow of 100 L/h and $\Delta T < 0.1^\circ\text{C}/\text{min}$, at a temperature of 5°C. Undecane was used in the reference cell at atmospheric pressure.

RESULTS AND DISCUSSION

The effect of pressure on the behavior of waxes in the presence of the polymeric organic deposition inhibitors was evaluated in two steps. First, μ DSC tests were performed on Crude Oils A, C, and D with and without addition of each inhibitor, at a pressure of 1.01 bar (1 atm). Each of the copolymer samples was added to the oils at concentrations of 100, 300, 500, and 1000 ppm. Then, the same samples (crude oils and additives) were tested at pressures of 50, 100, and 150 bar.

The aim of the test at 1.01 bar was to study the inhibitors' effect at atmospheric pressure to compare the results with subsequent tests under high pressure as well as to select just two additives for the tests under varying pressure and type of saturation gas. The action mechanism of EVA as inhibitor is already known. The hydrocarbon segments interact with the wax, and the vinyl group changes the crystal structure, so that the crystals do not agglomerate. That is, the wax crystallizes but does not form large solid deposits.^{2,7,8}

Figure 1 shows the μ DSC curves for Crude Oil A containing different concentrations of inhibitor X. As discussed in a previous work,²¹ two crystallization events occur: (1) WAT, at a higher temperature, corresponding to crystallization of the waxes with higher molar masses and (2) a second crystallization event at lower temperatures, corresponding to the crystallization of waxes with lower molar masses. In this case, the WAT decreased with increasing inhibitor concentration.

TABLE I
Wax Appearance Temperature (WAT), Second Crystallization Event, and Enthalpy of Crystallization of Crude Oil A (Pure and with Additives), at Atmospheric Pressure

Additive	Conc. (ppm)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min							
				35°C	30°C	25°C	20°C	15°C	10°C	4°C	0°C
–	–	44.6	26.7	0.16	0.26	0.54	1.86	3.98	6.29	9.04	10.78
X	100	36.2	24.0	0.04	0.25	0.37	1.13	2.92	4.97	7.48	9.10
	300	36.3	25.1	0.03	0.26	0.44	1.39	3.29	5.45	8.14	9.89
	500	35.0	24.6	–	0.22	0.38	1.23	3.10	5.23	7.85	9.54
	1000	33.2	25.0	–	0.17	0.40	1.38	3.33	5.56	8.32	10.14
Y	100	37.0	25.5	0.07	0.28	0.47	1.43	0.35	5.56	8.26	10.01
	300	36.8	25.5	0.07	0.32	0.53	1.51	3.43	5.64	8.32	10.07
	500	36.0	25.3	0.04	0.30	0.50	1.44	3.36	5.58	8.34	10.15
	1000	35.3	25.4	0.01	0.29	0.50	1.47	3.40	5.66	8.42	10.24
Z	100	40.0	24.7	0.16	0.28	0.47	1.48	3.47	5.67	8.36	10.13
	300	–	21.6	–	–	–	0.36	2.40	4.55	7.18	8.89
	500	–	26.0	–	–	0.10	0.96	2.88	4.90	8.02	9.78
	1000	36.0	23.2	–	0.23	0.44	1.09	3.11	5.47	8.26	10.10

Tables I–III summarize the results of the WAT, second crystallization event, and enthalpy of crystallization for, respectively, Crude Oils A, C, and D, without and with addition of different types of copolymer.

The results obtained for Crude Oil A (Table I) containing Inhibitors X and Y showed that the highest reductions in the WAT attained were $\sim 11^\circ\text{C}$ for Inhibitor X and $\sim 9^\circ\text{C}$ for Inhibitor Y, at a concentration of 1000 ppm, after already having reached relatively lower WAT values ($\Delta \sim 8^\circ\text{C}$) at a concentration of 100 ppm. There were no significant changes in the second crystallization event temperatures with both inhibitors. With Inhibitor Z in this crude oil at a concentration of 100 ppm, there was a small reduction of 4°C . However, at concentrations of 300 and 500 ppm, only the second crystallization event was observed, that is, the crystallization of higher

molar mass waxes was inhibited. The concentration of 1000 ppm was over-dosage, because the WAT increased for Crude oil A. The temperature of the second crystallization event fell more at a concentration of 300 ppm. At the other concentrations of Inhibitor Z, it was virtually unchanged. These results indicate that Inhibitor Z performed the best for Crude Oil A, and Inhibitors X and Y performed similarly.

The behavior observed for Inhibitor Z was similar to that commonly reported in the literature,⁷ showing that there is an optimum additive concentration, above which the additives can promote nucleation of the waxes and contribute to increase the agglomeration of the crystals.

The results are in agreement with those obtained before, which indicated the best EVA composition is about 30% vinyl acetate, because it is necessary for

TABLE II
Wax Appearance Temperature (WAT), Second Crystallization Event, and Enthalpy of Crystallization of Crude Oil C (Pure and with Additives), at Atmospheric Pressure

Additive	Conc. (ppm)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min							
				35°C	30°C	25°C	20°C	15°C	10°C	4°C	0°C
–	–	44.2	22.5	0.31	0.39	0.51	0.78	1.91	3.40	5.14	6.22
X	100	38.2	21.0	0.17	0.33	0.39	0.54	1.66	3.22	5.03	6.15
	300	36.2	20.4	0.04	0.29	0.34	0.43	1.37	2.80	4.50	5.52
	500	36.8	21.0	0.06	0.32	0.39	0.53	1.63	3.16	4.91	6.00
	1000	34.3	21.2	–	0.22	0.38	0.56	1.80	3.32	5.06	6.14
Y	100	39.9	21.4	0.22	0.30	0.32	0.47	1.56	3.02	4.68	5.69
	300	38.4	21.4	0.19	0.32	0.37	0.54	1.62	3.12	4.84	5.92
	500	37.9	21.4	0.14	0.31	0.36	0.52	1.57	3.05	4.76	5.83
	1000	36.6	21.5	0.09	0.33	0.40	0.58	1.65	3.16	4.92	6.03
Z	100	40.0	20.4	0.25	0.32	0.38	0.50	1.51	2.97	4.62	5.70
	300	37.8	19.5	0.06	0.24	0.32	0.41	1.31	2.78	4.45	5.49
	500	37.3	18.8	0.04	0.21	0.32	0.39	1.15	2.66	4.38	5.46
	1000	–	18.3	–	–	–	–	0.93	2.51	4.27	5.33

TABLE III
Wax Appearance Temperature (WAT), second Crystallization Event, and Enthalpy of Crystallization of Crude Oil D (Pure and with Additives), at Atmospheric Pressure

Additive	Conc. (ppm)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min									
				40°C	35°C	30°C	25°C	20°C	15°C	10°C	4°C	0°C	
–	–	62.5	42.5	5.54	10.42	17.34	23.86	29.43	34.16	38.09	42.09	44.36	
X	100	62.4	42.7	5.67	10.54	17.54	24.14	29.79	34.52	38.48	42.37	44.58	
	300	61.6	42.0	5.32	9.78	16.73	23.38	29.08	33.78	37.62	41.32	43.28	
	500	62.4	42.8	6.00	11.08	18.10	24.76	30.44	35.18	39.16	43.17	45.46	
	1000	61.6	42.3	5.60	10.37	17.44	24.18	29.88	34.61	38.51	42.26	44.30	
Y	100	58.3	40.0	4.53	7.64	14.53	21.82	28.11	33.31	37.57	41.75	44.10	
	300	58.2	39.8	4.20	7.10	13.76	20.73	26.65	31.45	35.28	38.90	40.82	
	500	61.4	42.2	5.59	10.41	17.36	24.01	29.70	34.47	38.49	42.49	44.75	
	1000	61.5	42.4	5.77	10.81	17.84	24.49	30.18	34.94	38.96	42.97	45.23	
Z	100	62.1	42.3	5.49	10.13	17.10	23.73	29.39	34.11	38.02	41.82	43.48	
	300	61.7	41.9	5.26	9.62	16.52	23.23	28.93	33.65	37.54	41.29	43.32	
	500	61.6	41.8	5.20	9.47	16.35	23.00	28.72	33.44	37.33	41.11	43.15	
	1000	61.6	42.3	5.53	10.27	17.31	24.00	29.64	34.31	38.14	41.80	43.78	

the additive to present a balance between hydrocarbon chains and polar groups.^{2,7,8}

Table II shows that Inhibitor X reduced the WAT of Crude Oil C, at a concentration of 100 ppm, by nearly 6°C. This reduction reached 10°C at a concentration of 1000 ppm. Neither Inhibitor X nor Y produced any changes in the temperature of the second crystallization event, which corresponds to paraffins with lower molar mass. Inhibitor Z had a similar effect as the previous ones up to a concentration of 500 ppm. However, at a concentration of 1000 ppm, it was no longer possible to detect the first crystallization event (WAT), but only the second one. With respect to the performance of the additives, the results obtained with this crude oil were very similar to those obtained with Crude Oil A, that is, Inhibitor Z performed best.

The waxes of Crude Oil D (Table III) were not sensitive to the addition of the inhibitors chosen for testing in this work. There was no change in the crystallization temperatures with the addition of Inhibitors X and Y at all the concentrations evaluated. The greatest crystallization temperature reductions attained did not exceed 4°C, with Inhibitor Y at concentrations of 100 and 300 ppm.

Overall, the set of results for all the additives tested in all the crude oils showed that different additives performed differently in each type of oil.^{2,9,23–25} This behavior means that there is a need for previous tests of a family of additives in the particular type of petroleum to be treated in each production field. To date, no relation has been established between any characteristic of the additive and petroleum. We could not establish any correlation between the results obtained in this work regarding the performance of the systems with the data obtained in a previous work²¹ on the characteriza-

tion of crude oils (composition and/or size and size distribution of waxes). It is possible that the relation does not involve only one parameter of the polymer and one of the oil, but instead a set of parameters in each case, requiring more complex studies of the variations in these parameters to try to establish useful correlations.

The reductions in the enthalpy of crystallization values evidenced a change in the crystallization kinetics for paraffins caused by the inhibitor's action, mainly for Crude Oils A and C, which had higher WAT reductions. The crystallization enthalpies are related to the solubilization of the waxes in the oil, whether by the action of the polymeric inhibitors or the action of the pressure imposed by the light fractions. In both cases, when there was a change in the crystallization kinetics, this modification could be clearly perceived in the variation in the crystallization enthalpy. The results here also made it clear that this variation can be more easily perceived at temperatures near the crystallization temperature.

The results obtained in this step of the work showed that Inhibitors X and Z at a concentration of 1000 ppm in general caused the greatest reductions in the crystallization temperatures and thus were most efficient at inhibiting wax deposition. Therefore, we chose these for the μ DSC experiments under pressure.

We determined the crystallization temperatures of the crude oils mixed with the inhibitors at pressures of 50, 100, and 150 bar, corresponding to the pressures found in production lines, using Gas Blend 2 for Crude Oils A, C, and D and Gas Blend 1 only for Crude Oil D. The choice of the gas mixtures to be used in each analysis was based on similarity to the natural gases found in each crude oil. The only exception was Crude Oil D, which was analyzed

TABLE IV
Wax Appearance Temperature (WAT), Second Crystallization Event, and Enthalpy of Crystallization of Crude Oil A with Additive, Under Pressure with Gas Blend 2 (GB-2)

Additive	Conc. (ppm)	P (bar)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min							
					35°C	30°C	25°C	20°C	15°C	10°C	4°C	0°C
-	-	1.01	44.6	26.7	0.16	0.26	0.54	1.86	3.98	6.29	9.04	10.78
		50	36.3	20.9	0.04	0.12	0.14	0.30	1.31	3.17	5.70	7.42
		100	27.5	14.7	-	-	0.05	0.14	0.18	1.04	3.70	5.74
		150	26.6	15.2	-	-	0.02	0.12	0.28	1.34	3.89	5.44
		1000	33.2	25.0	-	0.17	0.40	1.38	3.33	5.56	8.32	10.14
X	1000	50	26.6	19.8	-	-	0.04	0.37	1.13	2.85	5.18	6.68
		100	17.0	-	-	-	-	0.23	0.94	2.76	4.26	
		150	9.9	-	-	-	-	-	-	1.21	2.36	
Z	1000	1.01	36.0	23.2	-	0.23	0.44	1.09	3.11	5.47	8.26	10.10
		50	32.3	18.8	-	0.06	0.25	0.44	1.24	3.36	6.10	7.92
		100	17.0	-	-	-	-	-	0.19	0.86	3.15	5.11
		150	17.9	-	-	-	-	-	0.16	0.74	2.14	3.16

with both gas mixtures. The two inhibitors were used in solutions of 5% by mass in aromatic solvents at a concentration of 1000 ppm. The results are shown in Tables IV–7.

The results in Table IV, referring to the evaluations of Crude Oil A mixed with 1000 ppm of Inhibitors X and Z, show that the samples' crystallization temperatures fell sharply when pressurized with Gas Blend 2. Up to a pressure of 50 bar, the reductions did not exceed 7°C. For higher pressures, of 100 and 150 bar, only one crystallization event was detected, and the greatest reductions in the crystallization temperatures occurred with the sample with Inhibitor X. The results also show that for samples with additives, the enthalpies of crystallization during cooling were always lower than those obtained from the same oil without the additive under the same conditions. These reductions reached nearly 76% for Inhibitor X, at a temperature of 0°C, and 69% for Inhibitor Z at the same temperature. These results show that the presence of light fractions

enhances the performance of the additives, as expected from the results obtained for the oil without additives. Besides this, we also observed that the effect of the light fractions is similar for the two types of additives, because their differences in performance remained the same.

Also with respect to Crude Oil A, it can be concluded that the effects of the additive and the light fractions are synergetic in relation to reduction of the WAT, because the effect of only the light fractions (Gas Blend 2 at 150 bar) led to a reduction of ~ 18°C (Table II), the effect of only Inhibitor X (1000 ppm) led to a reduction of ~ 11°C (Table I), and the effect of pressure (150 bar) and Inhibitor X (Table IV) together led to a reduction of 34.7°C. However, we did not observe this synergetic effect in all the systems tested.

For Crude Oil C (Table V), the reductions of the WAT values of the samples with inhibitors were around 52% under a pressure of 150 bar for Inhibitor X and 56% for Inhibitor Z at the same pressure.

TABLE V
Wax Appearance Temperature (WAT), Second Crystallization Event, and Enthalpy of Crystallization of Crude Oil C with Additive, Under Pressure with Gas Blend 2 (GB-2)

Additive	Conc. (ppm)	P (bar)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min							
					30°C	25°C	20°C	15°C	10°C	7°C	4°C	0°C
-	-	1.01	44.3	22.5	0.39	0.51	0.78	1.91	3.40	-	5.14	6.22
		50	40.1	19.0	0.31	0.42	0.59	0.83	1.37	-	2.82	4.86
		100	28.7	13.7	-	-	0.29	0.54	0.81	-	1.43	3.46
		150	26.7	13.9	-	-	0.15	0.59	0.79	-	1.29	2.87
X	1000	1.01	34.3	21.2	0.22	0.38	0.56	1.80	3.32	-	5.06	6.14
		50	28.0	17.3	-	0.15	0.51	1.05	2.66	3.73	4.82	6.24
		100	14.7	-	-	-	-	-	0.61	1.24	2.11	3.39
		150	16.6	-	-	-	-	0.11	0.73	1.35	2.13	3.18
Z	1000	1.01	18.3	-	-	-	-	0.93	2.51	-	4.27	5.33
		50	18.4	-	-	-	-	0.96	2.53	3.46	4.31	5.39
		100	8.4	-	-	-	-	-	-	0.44	1.22	2.98
		150	8.1	-	-	-	-	-	-	0.29	1.56	3.06

TABLE VI
Wax Appearance Temperature (WAT), Second Crystallization Event, and Enthalpy of Crystallization of Crude Oil D with Additive, Under Pressure with Gas Blend 2 (GB-2)

Additive	Conc. (ppm)	P (bar)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min							
					50°C	40°C	30°C	20°C	15°C	10°C	4°C	0°C
-	-	1.01	62.5	42.5	-	5.54	17.34	29.43	34.16	38.09	42.09	44.36
		50	58.3	39.0	2.19	4.07	11.43	24.21	29.43	33.98	38.51	41.04
		100	49.4	31.8	-	2.73	5.14	14.73	22.02	29.28	37.56	42.78
		150	49.9	32.0	-	2.78	5.05	14.90	21.63	27.28	32.67	35.46
X	1000	1.01	61.6	42.3	-	5.60	17.44	29.88	34.61	38.51	42.26	44.30
		50	57.9	39.0	2.30	4.27	11.74	24.94	30.60	35.47	40.50	43.44
		100	53.3	34.8	0.25	2.47	6.28	15.82	22.14	28.29	35.59	40.63
		150	49.1	34.0	-	2.62	6.90	17.64	24.02	29.65	35.31	38.37
Z	1000	1.01	61.6	42.3	2.96	5.53	17.31	29.64	34.31	38.14	41.80	43.78
		50	55.0	36.2	1.70	3.52	8.00	20.40	26.33	31.39	36.40	39.17
		100	51.4	33.2	0.84	2.67	5.22	15.17	21.87	28.31	35.77	40.58
		150	48.8	31.8	-	3.09	5.97	16.18	23.28	29.56	35.63	38.81

These reductions were always greater than those obtained for pure Crude Oil C, under the same pressure conditions.²¹ The crystallization enthalpy curves as a function of cooling showed the same effect observed for pure crude oils,²¹ that is, the reductions were only noted at pressures above 50 bar for all the samples tested. At pressures of 100 and 150 bar, for both inhibitors, the variations in the crystallization enthalpies with changing temperature behaved similarly, as can be seen if graphs are plotted.

For Crude Oil D (Table VI), the reductions obtained under pressurization with Gas Blend 2, for the samples mixed with Inhibitors X and Z, were about 20% until a pressure of 150 bar. This behavior is similar to that obtained under pressure for pure Crude Oil D with the same Gas Blend, showing that the inhibitors did not have any effect on the behavior of the waxes in this oil. In other words, higher pressures did not enhance the performance of the additives considered inefficient in the tests at atmospheric pressure. This result shows that pressure affects the behavior of the waxes but not the behavior of the additive itself. We believe the mechanism behind the effect of the light fractions is that they improve the solubility of the waxes, which in turn are more

affected by the action of the inhibitors that are capable of modifying the crystallization kinetics of these paraffins. For additives that are not able to modify the crystallization kinetics of the paraffins of a certain crude oil at atmospheric pressure, increased pressure will not improve their performance.

The results for Crude Oil D (Table VII), mixed with 1000 ppm of Inhibitor Z, obtained with pressurization of the sample with Gas Blend 1, show that the reductions of the crystallization temperatures of this crude oil were very small in comparison with the results obtained in a previous work²¹ for a pure sample pressurized with the same gas mixture. This shows that the inhibitors had no action even in tests under reduced pressure. These results agree with the discussion presented for Crude Oil D with Gas Blend 2.

CONCLUSIONS

The main conclusions obtained in this work are that the behaviors observed for dead crude oils are very similar to those that occur in samples of oils saturated with gases. Inhibitors that are not efficient under atmospheric pressure also have no action in

TABLE VII
Wax Appearance Temperature (WAT), Second Crystallization Event, and Enthalpy of Crystallization of Crude Oil D with Additive, Under Pressure with Gas Blend 1 (GB-1)

Additive	Conc. (ppm)	P (bar)	WAT (°C)	Second cryst. (°C)	Enthalpy of crystallization (J/g) at 1°C/min							
					50°C	40°C	30°C	20°C	15°C	10°C	4°C	0°C
-	-	1.01	62.5	42.5	2.01	5.54	17.34	29.43	34.16	38.09	42.09	44.36
		50	60.1	40.8	2.62	5.09	14.97	28.74	34.56	39.63	44.88	47.90
		100	56.6	37.8	2.09	4.11	10.35	24.11	30.46	36.08	42.08	45.74
		150	55.3	36.7	1.89	3.64	8.72	22.59	29.48	35.46	42.40	46.76
Z	1000	1.01	61.6	42.3	2.96	5.53	17.31	29.64	34.31	38.14	41.80	43.78
		50	58.6	39.8	1.99	3.42	12.13	23.41	27.28	30.07	32.26	33.12
		100	56.0	37.9	1.74	3.32	9.83	22.49	27.40	31.27	34.77	36.58
		150	53.8	36.4	1.56	3.50	8.86	22.94	29.26	34.74	40.47	43.97

preventing organic deposits under pressurized conditions. However, inhibitors that show good efficiency in modifying the crystallization kinetics of waxes in petroleum at atmospheric pressure also show a synergetic effect through the action of pressure and additive. The use of high-pressure microcalorimetry allows choosing wax deposition inhibitors for each type of crude oil and quantifying the degree of inhibition for each of the pressure and temperature conditions found during flow in the field, besides identifying the ideal concentrations for their use, thus avoiding unnecessary treatment costs to prevent organic deposition caused by waxes.

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