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The effect of additives on the properties of crude oil

TIMUR CHIS[1,3*], RENATA RĂDULESCU[2]
[1] Ovidius University, Constanta, Romania
[2] Oil and Gas University, Ploiesti, Romania
[3]Technical Science Academy of Romania, Bucuresti, Romania

Abstract. Crude oil extracted in Romania has different pompability characteristics, depending on their formation period (they can be asphalt or paraffin). One method of improving pompability is that in which various additives are used to reduce the freezing point and/or viscosity. These mixture additives may be polymers or other chemical agents. The role of the additives is to reduce the precipitation of the paraffin crystals in the solution by keeping the paraffin molecules as separate entities. This reduces the cohesive forces between the crystals and the adhesion forces between the paraffin crystals and other surfaces. The vast majority of modifiers proposed as oil depressants are macromolecular compounds.
The purpose of this article is to analyze the effect of additives on the property of crude oil.

Keywords: oil, aditives, parafine, pompabilitate, congelare, vascositate.

1. Introduction

Nowadays, oil fuels provide 85% of the energy consumption needed by the world's population.
Petroleum is a fossil product that is used to distill and obtain fossil fuels. But oil fields have oil reserves that have formed over millions of years and under different conditions of temperature, catalysts and pressure.
That's why the American Petroleum Institute has classified crude oil into four categories based on the specific gravity expressed in API degrees. [1].

$$\text{API specific gravity} = (141.5/\text{specific specific gravity})-131.5 \quad (1)$$

The API crude oil classes are:

*Correspondence address: timur.chis@gmail.com

- Light crude oil with API> 31.1.
- Average crude oil with API between 22.3 and 31.1.
- Heavy crude oil with AP less than 22.3.
- Very heavy crude oil with API less than 10.

Heavy and very heavy crude oil is not pumpable due to its high viscosity, but it is very cost-effective in terms of price and especially for obtaining bitumen.
The viscosity of paraffinic crude oil remains low, up to a certain temperature, slightly higher than the freezing temperature, after which, when the temperature decreases, it suddenly increases to very high values.
In the case of oily crude oil, the variation in viscosity with temperature is less pronounced.
At normal pumping temperatures (20°C - 70°C), however, their viscosity is higher than that of paraffinic oils.
The explanation for this behavior lies in the fact that paraffin oils contain a high percentage of low viscosity white products but also paraffin.
As long as the paraffin remains in solution, the viscosity of the crude oil is determined only by the viscosity of the components and their relative proportions.
So, during this period, the viscosity of paraffin oil will be lower and will increase slowly when the temperature drops.
When the paraffin begins to come out of the solution, as a result of cooling, the presence of paraffin crystals produces a rapid increase in viscosity.
As the number of crystals increases, so does the viscosity, which reaches very high values until the oil freezes.
On the other hand, oily crude oil, containing higher proportions of black, viscous products, will have, even at high temperatures, a higher viscosity than a paraffin oil. This viscosity will increase continuously and slowly as the temperature drops.

That is why several viscosity reduction solutions have been tried, namely:
a. Use of diluents [2,3,4],
b. Use of lubricants [5,6,7],
c. Heated transport of crude oil,
d. Modification of its composition with the help of additives.

From the point of view of the use of the viscosity reduction technique with additives, several techniques have been developed, namely the use of viscosity reducing agents, the use of chemical agents and the use of emulsifiers.
In the transport of crude oil in our country, in order to ensure the transport of viscous or freezable crude oil, it is necessary to create mixtures by:
a. Dilution with low viscosity products to reduce the viscosity of asphalt crude oil,
b. Dilution with products with a low freezing point, which reduces the freezing point of paraffinic crude oil.
If these products are not present in oil fields, or to not affect the quality of crude oil and therefore refining products (because for diluting crude oil is usually used diesel

or non-compliant gasoline or other crude oil with different properties-mixtures blend type) it is necessary to create oil additives.

The purpose of transporting crude oil treated with additives is to reduce the freezing temperature and viscosity.

The mechanism of their action is not well known to date. Additive molecules are thought to be adsorbed on the surface of paraffin crystals preventing the formation of spatial networks of resistant paraffin crystals.

For this process to be effective, the oil must be heated to the temperature that melts the paraffin crystals and then mixed with additives.

Macromolecular compounds such as polymethyl acrylates, polyisobutylene, polymers of ethylene, propylene, which modify the precipitation of paraffin crystals in solution, can be used as additives, by one of the following mechanisms:

a. the modifier leaves the solution at a temperature slightly higher than the equilibrium temperature of the paraffin solution;

b. the modifier comes out of solution at an equilibrium temperature of the paraffin solution and co-crystallizes with paraffin;

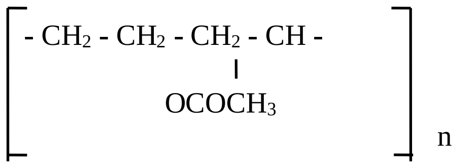
c. the modifier comes out of the solution at a temperature slightly lower than the equilibrium temperature of the paraffin solution and is absorbed on the paraffin crystals.

The modifier present in the solution, acting by one of the above mechanisms, tends to keep the paraffin molecules as separate entities, by reducing the cohesive forces between the crystals and the adhesion forces between the paraffin crystals and other surfaces [8,9].

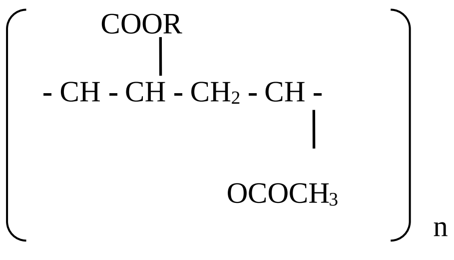
The vast majority of modifiers proposed as oil depressants are macromolecular compounds [10].

Of these, two groups stand out:

1. copolymers ethylene - vinyl acetate, with average molecular weights, relatively small, of 1000-10000, having the general structure:



2. copolymers of unsaturated esters with long alkyl chains.



There are also some depressants that limit paraffin deposits and others that slightly reduce the crystallization temperature.
Depending on the nature of the addition, it is recommended that it fall within the limits of 0.02 ... 20% by weight.
It seems that the efficiency of the additions is manifested only in turbulent motion.
In laminar regime they are not efficient and the cost is quite high.
For example, the use of PULSER polymer (p = 660 kg /m^3) used as an addition to Videle A3 crude oil by 2.66% reduced the viscosity from 1427 to 1088 cP, decreasing the pressure drop from 84 to 82 atm (for the summer period) so practically zero efficiency.

2. Analysis of depressant additives on the market

Depressing additives are used in the transport of crude oil to reduce their freezing points in order to ensure transport through pipelines.
A large number of additives have been produced for this purpose, most of which are low molecular weight copolymers such as copolymers of maleic, acrylic and methacrylic esters.
Most of these depressants have a disadvantage, namely they have a limited operating range (40-60°C) and the addition does not prevent the deposition of paraffin crystals on the walls of the pipes.
In Romania, three additives patented by patents RO 67487, RO 113057, RO 116550 were created.
In patent RO 67487 [7] was made a depressant additive for paraffin crude oil with a freezing temperature of about +20°C. This additive is obtained by copolymerizing vinyl acetate with fumarous diesters containing 20-22 carbon atoms in the alkyl chain.
RO 113057 [8] also uses copolymers of vinyl acetate with fumarous diesters with 20-22 carbon atoms in the alkyl chain, the additive obtained being useful in the transport of crude oil with a freezing point of +16, +20°C.
It is found that although the addition of crude oil ensures a proper reduction of the freezing point, over time paraffin deposits appear on the walls of the pipes, which requires frequent stops to remove them.
The formation of these deposits is due to the fact that the respective additives do not ensure a dispersion of the paraffin crystals in the crude oil mass which leads in time to their deposition.
The technical problem proposed in patent RO 116550 [9] is the development of an antidepressant additive composition which also has a dispersing action on the paraffin deposits on the walls of oil pipelines.
The process for obtaining the additive consists in subjecting a terpolymerization with vinyl acetate, at a temperature of 80-100°C, for 14-16 hours, in the presence of benzoyl peroxide, a mixture consisting of a fumarous diester, containing in percentages molar 4-6% C_{18} fumarate, 45-55%, C_{20}, 35-30%, C_{22} fumarate, 15-7%,

C_{24} fumarate, 1-2%, C_{26} fumarate and a fumaric monoester with the same number of carbon atoms in the alkyl chain.

So this additive consists of a toluene solution containing 45-55% terpolymer resulting from the terpolymerization of 60-70% mol vinyl acetate with 35-25% mol fumaric diester with C_{18}-C_{26} alkyl chains and 5% mol fumaric monoster with the same number of carbon atoms in the alkyl chain, the remaining 55-45% being toluene.

Table 1. Data obtained from the use of depressants obtained according to patent RO 116550

Additive		Crude oil PETROMAR Freezing temperature °C					Crude oil Ukraine Freezing temperature °C
Type	Ppm	1	2	3	4	6	
		+6	+7	+9	+11	+17	+25
Ex.1	300	-4	-5	-4	-3	-3	
Ex.2	300	-7	-6	-5	-4	-5	
commercial	300	-9	-7	-5	-4	-7	
Ex.1	500						+16
Ex.1	1000						+19

It is observed that the additives made in Romania are compatible with the import type additives, but they are less used due to the lack of financing necessary for the industrial production.

That is why more expensive import additives are used but with a constant supply.

The dispersing efficacy of the additive according to RO 116550 was tested by a standard process called COLD FINGER TEST [10], which measures the amount of paraffin deposited on a cooled metal cylinder, imesed in the crude oil sample, the percentage of additive being 300 ppm.

Table 2. Data obtained from the COLD FINGER test on the use of depressants obtained according to patent RO 116550

Additives	The amount of paraffin deposited, g	% paraffin deposit reduction
No additive	1530	0
Commercial additive	925	39,5
Additive Example 1	532	65,3
Additive Example 2	428	72,02

3. Experimental model

To study the influence of additives on the rheological characteristics of crude oil, we created two additives.

Additives supplied from the import (Baker company) were also used.

The first additive made in the laboratory of Ovidius University consists of:

- 75 ml o, m, p-xylene with a content of C_8H_{10} 96%, Fe 0,00001 g, HCl 0,0004 acidity, evaporation resistance 0,001%, water 0,02, density 0,865
- 15 ml of liquid $C_4H_6O_2$ vinyl acetate, density 0.93, boiling point 73°C,

- 10 ml of 90% formic acid solution for the removal of biological structures,

The second additive consists of:
- 75 ml of well condensate, density 0.72,
- 15 ml of liquid $C_4H_6O_2$ vinyl acetate, density 0.93, boiling point 73°C,
- 10 ml of formic acid, for the removal of biological structures,

The components of each additive were mixed for one hour at 80°C, then cooled.
The additive was mixed with crude oil in various proportions.
It started with Petromar crude oil to which 25 ml of additive variant 1 or variant 2 and 75 ml of crude oil was added.

The analyzes performed were performed in accordance with the standards:

Table 3. Standards used for laboratory analyzes

Standard	Method used	Remarks
ASTM D1298 - 12b	Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Aerometer method
ASTM D445 – 12	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)	Engler viscometer
ASTM D5133 - 13	Standard Test Method for Low Temperature, Low Shear Rate, Viscosity/Temperature Dependence of Lubricating Oils Using a Temperature-Scanning Technique	Thermometer
	STAS oil distillation curve	

Table 4. Density of products used at 20°C

Density	value Kg/mc
Petromar	820
Additives 1	898
Additives 2	855,6

The first experiment consisted in determining the viscosity of PETROMAR crude oil when adding the two additives.
As can be seen, the viscosity decreases with the addition of the additive, the best being the condensate.
The second test was to determine the influence of the additive on the STAS processing curve.

Table 5. Viscosity of additive products at 20°C

Viscosity	Value, °E	Mixture type
Petromar	1,45	
Petromar+additive 1	1,19	25 ml additive 1 mixed with crude oil PETROMAR 75 ml.
Petromar+additive 2	0,72	25 ml additive 2 mixed with crude oil PETROMAR 75 ml.

Table 6. STAS curve of distillation of additive products

Temperature value	PETROMAR crude oil	PETROMAR Crude Oil + Additive 1	PETROMAR Crude Oil + Additive 2
100 °C	15 ml	5 ml	12 ml
150 °C	31 ml	25 ml	25 ml
200 °C	41 ml	33 ml	31 ml
260 °C	49 ml	45 ml	40 ml
270 °C	56 ml	50 ml	45 ml

It is observed that the presence of the additive does not influence the distillation curve, but the addition of xylene and condensate influences the distillation curve, especially the condensate which leads to an increase in the amount of distilled product at 100 ° C.

I also did research on Dudești crude oil.

Table 7. Characteristics of crude oil used to determine the freezing point

Parameters	**DUDEŞTI**
Density d_4^{20} [kg/m^3]	844
freezing temperature $t_{freezing}$ [°C]	+27
% paraffin	7,45
viscosity at 20°C, CP	144

Table 8. Influence of additives on Dudești crude oil

Nr. crt.	**Crude oil type**	**Total volume**	**Depressant type**	**Depressing volume**	**Freezing temp**
-	-	**(ml)**	-	**(ml)**	**(°C)**
1.	Dudeşti oil witness test	100	-	-	26 - iniţială
2.	Dudeşti oil witness test	100	Additiv 1	10	13
3.	Dudeşti oil witness test	100	Additiv 1	15	11
4.	Dudeşti oil witness test	100	Additiv 2	10	18
5.	Dudeşti oil witness test	100	Additiv 2	15	16

The crude oil was treated with additive at 40 ° C.

Was used Dudești crude oil with high freezing temperature, in order to be able to more easily observe the temperature reduction and to easily determine the freezing temperature (close to that of the environment).

This table shows the following:

1. the freezing temperature decreases from 26 to 11 ° C, by 15 ° C, using depressant additive 1, and decreases by 14 ° C (26-16) ° C using depressant additive 2;
2. their action is not lost in time (verification was done after 48 hours);
3. additives influence the STAS distillation curve, slowing down the distillation rate.

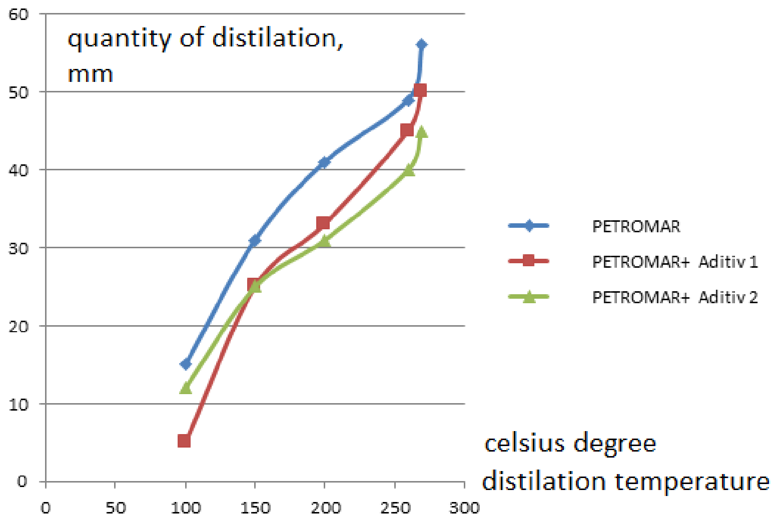


Fig. 1. Influence of additives on the oil distillation curve.

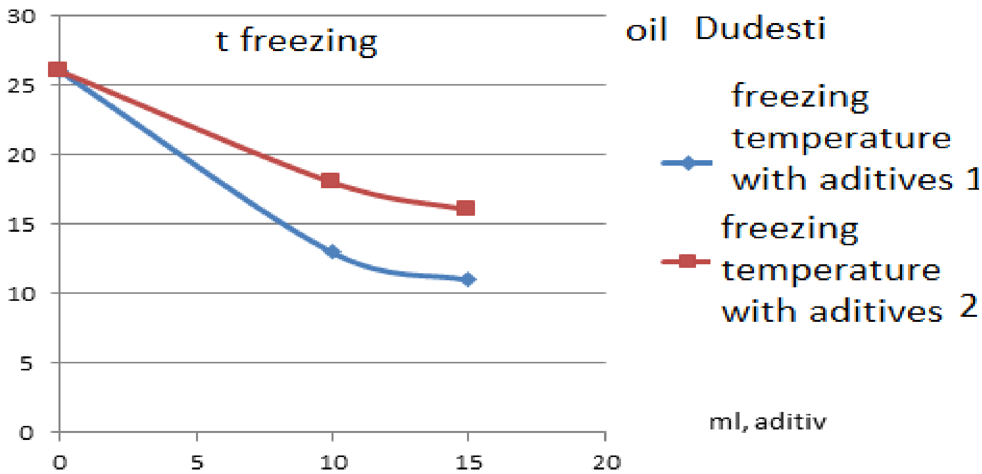


Fig. 2. Influence of additives on the freezing point of Dudești crude oil.

4. Mathematical modelling of the oil additive process

In order to observe the equation of variation of the freezing point with the amount of additive introduced in the crude oil, for the Dudești type crude oil with the initial freezing temperature 40°C [11,12].

A Baker additive, commercially called Baker, was used. The crude oil was treated with additive at 40 °C.

Table 9. Test results with different doses of Baker depressant la t_{treat} = 40°C

Nr. crt.	Depressant dose Ppm	Freezing temperature ° C performed after treatment
1.	400	+10
2.	600	+8
3.	800	+7
4.	1000	+6
5.	1200	+5

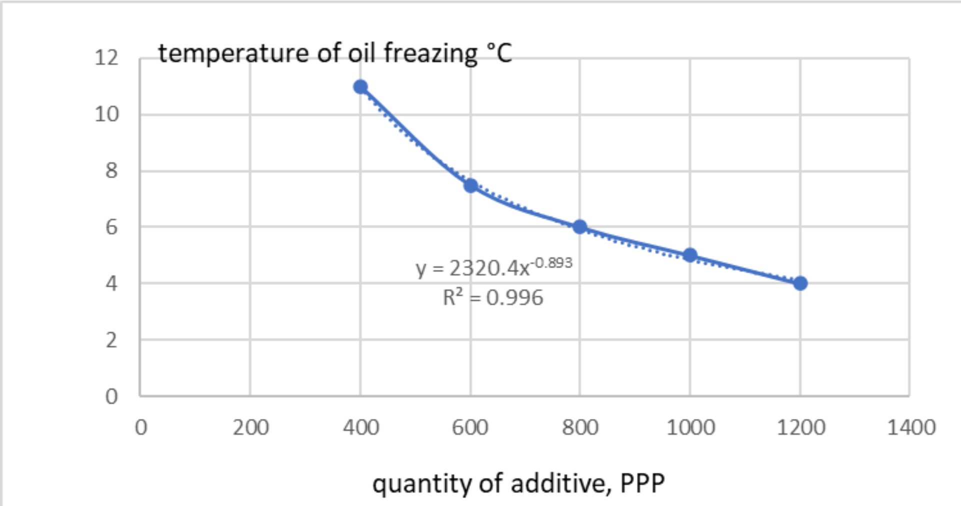


Fig. 3. Variation of freezing temperature with the dose of depressant in Dudești crude oil.

5. Conclusions

In this paper we presented two polymers made in the laboratory of Ovid University and an additive imported from Baker.
The additives made in the laboratory highlighted the following:
1. the freezing temperature decreases from 26 to 11°C, by 15°C, using depressant additive 1, and decreases by 14°C (26-16)°C using depressant additive 2;
2. their action is not lost in time (verification was done after 48 hours);
3. additives influence the STAS distillation curve, slowing down the distillation rate.

The additive supplied by Baker has also been shown to be highly effective:
- is the best depressant (efficiency: 85.71%) which decreased the freezing point from (+28 to + 4°C), at a dose of 1200 ppm and t = 40°C.
- the higher the dose, the higher the efficiency, from the point of view of the intended purpose (decrease of the freezing point), but not from the economic point of view.

Our comments on oil additives are as follows:
a. the additives made in Romania are of the polymeric type, easy to make but without success because they cannot be made industrially,

b. Import additives are of better quality but have high acquisition costs,
c. the additives influence the distillation curve, by the presence of additives in the additive (paraxylene and condensate),
d. the least squares equation shows an exponential dependence between the freezing temperature and the amount of depressant,
e. the role of the additive is to modify the structure of the paraffins, but it is necessary to add the additive at a temperature above the starting limit of the formation of the crystalline paraffin structure (above the freezing point).

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