“DEPRAN” R&D LLP

111116 Moscow, Aviamotornaya st. 6
Phone/ fax: +7(495)796-97-82
E-mail: info@depran.ru, depran@mail.ru
Web: www.depran.ru

RHEOLOGICAL POUR POINT DEPRESSANTS DMN

Moscow 2013

Introduction

Pour point depressants

The main purpose for application of rheological pout point depressants (PPD) is improvement of low temperature properties of crude oil and heavy oil products, decrease of their dynamic viscosity during transportation. Besides that, some of PPD, including ours, slow down and/or prevent asphaltenes, tar and paraffin waxes (ATP) sludge formation inside pipelines while ensuring non-interruptive crude-oil transportation. In general the application of PPD facilitates rate of flow, decrease pressure inside the transfer lines and shorten drainage time of tank cars and tankers due to more efficient and complete drainage of crude oil.

The special feature of our PPD is their susceptibility to composition and physicochemical properties of crude oil and oil products. As a consequence it is important to apply PPD correctly; otherwise the desired results will not be achieved. The key factors that greatly affect PPD performance are: auxiliary solvent(s), crude oil temperature and temperature of PPD, as well as the mixing process of PPD with crude oil. We strongly recommend preliminary lab testing during which we can formulate PPD and technical solution suitable for particular crude oil.

ATP Inhibitor

It is well established that content of tar and paraffin waxes in crude oil increases as oilfield aging. This is due to that on earlier stages of production activity an extraction of more mobile, light fraction of crude oil occurs. Further, when applying secondary methods of production activity the extraction of heavier fraction of crude oil occurs. One of the important problems at the production activity is removal of waxes from oil well equipment. Wax build-up leads to decrease of flow area of transfer lines and also affects working parts of pumps. As a result the rate of yield decreases and the frequency of necessary repairs increases. Technological process of crude oil collection and transportation is accompanied by corrosion of inner surfaces of transfer lines. This is related with high mineralization of oil-well products, corrosive activity of water, extracted simultaneously with crude oil, presence of atmosphere oxygen and other factors. As water content in the products of oil well extraction increases the corrosion of transfer lines increases even more and often leads to the outbreak of pipelines. It's well known that such outbreak of transfer lines can lead to ecological catastrophe. Partial replacement of the transfer line can't guarantee against the possibility of future outbreaks at different spots of transfer line. The replacement of whole transfer line even 10-20 km in length requires substantial investments. In most cases methods of chemical protection of transfer lines are most cost effective. To prevent the corrosion of inner surfaces of pipelines water and oil soluble inhibitors are used. Our additive NHTI allows to improve rheological properties of crude oil: decrease paraffin wax deposits on the surfaces of oil well equipment and increase timeframe between required purging of oil wells. Quantitative estimation of wax deposition is conducted using cold-finger method.

Below you will find some information regarding our additives based on the information we gathered for the past 20 years.

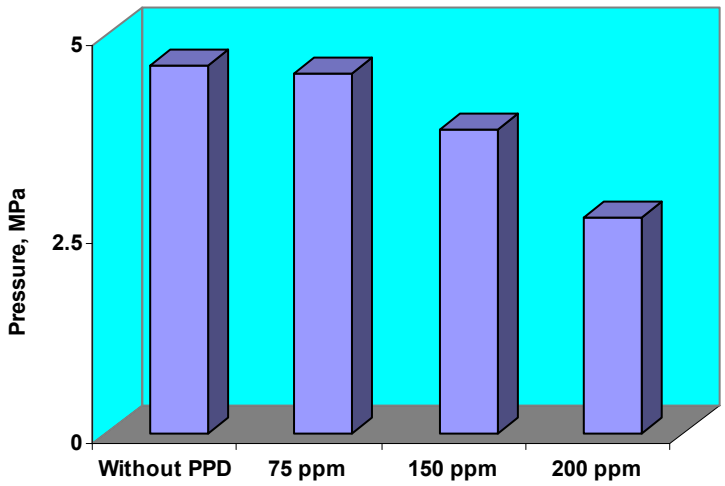
Figure 5. "Cold finger" test of crude oil without and with PPD.

The amount of paraffin wax deposition on the steel plates, mg. Left to right:
1. Crude oil without PPD
2. Crude oil with 500ppm of PPD
3. Crude oil with 1000ppm of PPD

Table 7. Amount of paraffin deposition without and with PPD.

Sample	Amount of paraffin deposition at, ºC:	
	15	10
1	0,53	0,725
2	0,311	0,498
3	0,208	0,374

Figure 4. Transfer line pressure without and with PPD addition (crude oil at Yamal oil field)



Application of PPD as a ATP washing/cleaning/inhibiting agent

Washing/cleaning effect of DMN PPD, described above, valid not only in the flow of crude oil. At static conditions, for instance, during the transportation of crude oil in tank cars the amount of ATP on the walls of tanks is also decreases and therefore provides more efficient and complete drainage.

We studied high paraffin crude oil with solidification temperature +26°C, ATP content: 10,5% n-paraffin (melting temperature 66°C), up to 2% asphaltenes and up to 10% of tar. When PPD was applied at concentrations of 500-1000ppm the solidification temperature of crude oil dropped from 26°C to 12 и 8°C accordingly. Steel plates were placed into samples of untreated crude oil and crude oil treated with 500-1000ppm of PPD and left for 3 days at 10 and 15°C accordingly. After 3 days the steel plates were removed from solutions and weighted. It was found that in crude oil treated with PPD the amount of paraffin wax crystallized on steel plates was 1.5-2 times less than in untreated crude oil. The results are show in Table 6.

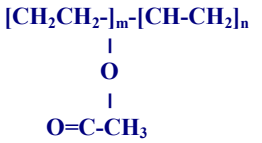
These lab tests were later confirmed by field tests of PPD at tank cars and the results were similar.

POUR POINT DEPRASSANTS: OVERVIEW

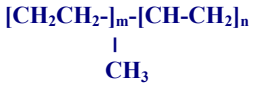
In general PPD are solutions of high-molecular compounds (base component) in aromatic solvent. Additional additives are included to increase PPD effectiveness and provide required properties.

Most common high-molecular compounds are:

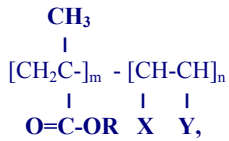
- *copolymer of ethylene and vinyl acetate :*



- *polyethylene and its co-polymers with α-olefins:*



- *polyalkyl-(meth)-acrylates and its co-polymers:*



where n and m are any number, R – hydrocarbon radical, X and Y – functional groups

Molecular weight of polymer is selected based on the crude oil or oil product properties to which PPD is introduced. These polymers are either solid or highly viscose products, thus the additives based on such polymers contain solvent. At certain occasions the concentration of solvent could be as high as 90%. Besides that, additives often contain small quantity of promoting agents enhancing properties of base component.

The solvent used in PPD additives not only dilute additive, but also affects the shape of polymer's macromolecule. This is extremely important for successful application of PPD.

The PPD additives used in crude oil treatment affect spatial pattern of crude oil during the crystallization of containing paraffin.

Paraffin wax containing in crude oil are: n-paraffin and iso-paraffin. The latter have good low temperature properties. The most problematic components of crude oil are n-paraffins. N-paraffins has low solubility in hydrocarbon mixtures and easily crystallizes at low temperatures. As temperature decreases paraffin crystals progressively grow and at some point start aggregating together forming spatial structure. As a result the mobility of crude oil decline sharply. Normally the content of

n-paraffin in crude oil is around 2-10% and their melting temperature is around 60°C, rarely 70°C. Paraffin melting temperature has grater effect than paraffin content on crude oil mobility. The formation of spatial pattern is also affected by tar and asphaltenes content. In general, tar hinders formation and aggregation of paraffin, while asphaltenes facilitate these processes.

The role of PPD is to modify the surface of paraffin crystals in such a way that these crystals will loose their ability to aggregate. In order to optimize PPD effect the size of its macromolecule should correspond the geometry of crystal surface thus for each crude certain adjustments in PPD formula may require.

It is also should be mentioned that the effect of PPD of any time is not permanent and tends to decrease with time due to constant restructure processes in crude oil. Therefore stability studies of crude oil with PPD may require.

DMN Pour Point Depressants

Crude oil currently extracted on many oil fields of Russia and Kazakhstan has a complex physical-chemical and rheological properties. Approximately 10-20% of the crude oil has a high content of asphaltenes and large amount of paraffin waxes with high melting point. Usually, at low temperature paraffin waxes that present in crude oil tend to precipitate which hinder and sometimes prevents transportation of crude oil. The content of crude oil with high amount of paraffin waxes in total amount of extracted crude oil increases every year and hinders the transportation using transfer lines and tank cars.

There are several ways to overcome this problem. The crystallization of paraffin waxes can be prevented by heating the crude oil to 50-60°C, however this can be economically unfavorable and sometimes is not even possible. It is also possible to mix heavy fraction of crude oil with more mobile “light” fraction of crude oil or other solvents, however most of the time these products are not available in the sufficient amounts. Therefore, it is necessary to use different type of additives. Our series of DMN PPD is one type of such additives aimed to modify structure of paraffin crystals. These additives improve the flow of crude oil and eliminate risk of crude oil solidification at the stage of transportation via transfer lines. Moreover, DMN additives are also contain surfactants and thus also features washing abilities.

DMN PPD prevent normal growth of paraffin crystals and asphaltenes substances and also improve rheological properties of crude oil. In practice it means significant decrease in transportation costs due to decrease in pour point temperature of crude oil after introduction of DMN additive. The effect of additives is usually evaluated by the loss of flow point.

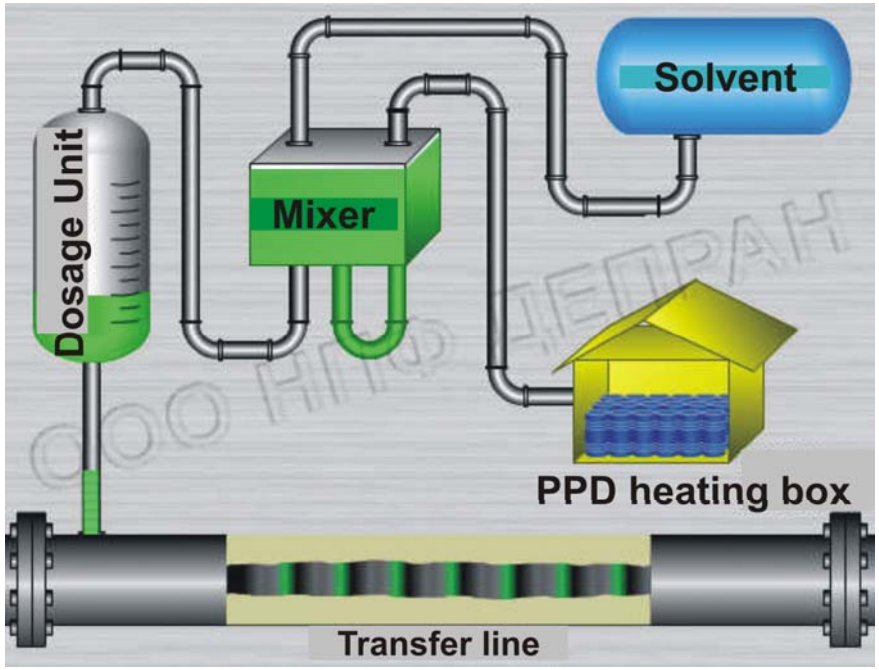
Field use confirms that in many cases DMN additives are the most cost effective modifying agents for heavy fraction of crude oil and their usage provides safe and efficient transportation of crude oil.

Technical Data of DMN Pour Point Depressants

DMN PPD are mixtures of co-polymers of ethylene with vinyl acetate in specially formulated aromatic solvents. DMN additives are well soluble in diesel, benzene, toluene, petrol, kerosene, mineral oils. Not soluble in acetone, ethanol.

Mixing of PPD with crude oil is done using the special additive injection unit.

Figure 3. Schematic representation of PPD injection set up.



Technological parameters of reactant injection unit:

Tanks pressure – atmospheric
Temperature of additive solution – 55 – 60°C
Crude oil temperature at injection point of additive solution within 60 – 80°C
Heating temperature of crude oil depends on crude oil composition
The concentration of injected additive depends on the temperature of soil

Application of PPD at transfer lines

The application of our PPD at transfer lines allows:
- decrease pumping pressure at transfer lines
- eliminate heating of crude oil and following heating of transfer lines
- eliminate risk of transfer lines jam with paraffin during pipeline temporary shut down

Decrease in pressure at transfer lines is related with:
- washing/cleaning effect of PPD; ATP formed during the crude oil transportation are removed from the pipeline walls, thus the throughput diameter increases;
- decrease of dynamic viscosity of crude oil and therefore decrease in resistance head of crude oil during transportation.

Application technology of PPD

The most important controllable parameters for successful PPD application are:
- water cut of crude oil,
- crude oil temperature at point where PPD is introduced,
- dissolution of PPD (DMN-2005 only) in specially formulated auxiliary solvent,
- temperature of PPD before introduction to crude oil,
- mixing process of PPD with crude oil.

Water cut at crude oil have negative effect on PPD abilities. Based on our data the significant negative effect starts at 1-2% of water cut and at 5% of water cut render application of PPD to be practically useless. Therefore we recommend to introduce PPD after dewatering of crude oil.

Crude oil temperature at PPD introduction point should be 10-15 higher that melting temperature of containing paraffin. This requirement is due to necessity to break down paraffin spatial structure. If this requirement is not fulfilled than the introduction of PPD could be useless.

The temperature at the introduction point of PPD also affects the stability of solidification temperature of crude oil during storage.

Table 6. Temperature effect of PPD introduction on crude oil solidification temperature.

Temperature, °C:	
Introduction of PPD	Crude oil solidification
50	- 14
60	- 18
70	- 20

Sometimes auxiliary solvent is necessary for facilitating mixing PPD with crude oil. In general customer will receive PPD in a form of gel with the solidification temperature around 40°C. We normally supply PPD as a concentrate to cut transportation costs while allowing customer to choose solvent based on the existing conditions. Normally one will use diesel fuel, gas condensate, aromatic solvents, etc. However, if PPD effect in crude is very small the selection of proper solvent will greatly enhance PPD performance. Another advantage of using auxiliary solvent is the possibility to prepare concentrated solution of PPD at fairly low viscosity and solidification temperature.

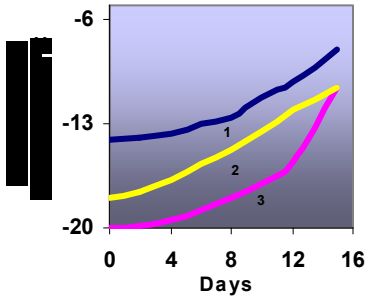


Figure 2. Dependence of solidification temperature of crude oil during storage from PPD introduction temperature:

1-50°C,
2-60°C,
3-70°C

Table 1. Physicochemical properties of DMN series PPD

Appearance	Gel/liquid substance
Density at 20°C, g/cm^3	0,880-0,900
Kinematics viscosity, cSт, at 50°C, no more than	50-750
Self-ignition temperature, °C	300
Pour point, °C, no less than	15-40
Solubility: - In water - In crude oil and petroleum products	None soluble Fully soluble
Pour point depression of heavy crude oil fraction, °C	No less than 10
Pour point depression, °C	10-20

HAZARD CLASS: 3, sub-class 3.3. UN CODE: Code 1993

Effect of DMN PPD on low temperature and rheological properties of crude oil

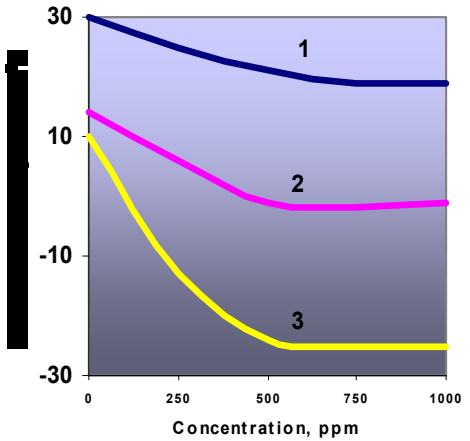


Figure 1. Effect of DMN PPD on different crude oil

№	*Paraffin, %*	*Tar, %*	*Asphaltenes, %*
1	21	3	1
2	7	17	5
3	7	6,5	0,2

Based on the relationships exhibited on Fig 1. it is clear that optimal concentration of PPD is around 100-500ppm.

Table 2 exhibit temperature effect of DMN PPD on several crude oil acquired all over Russia and CIS.

In general, PPD concentration over 500ppm, with few exception, has no noticeable effect on solidification temperature (Ts) of crude oil. Moreover, sometimes concentration of PPD over 500ppm can have retroactive effect.

Table 2. Temperature effect of PPD on crude oils

Crude oil	Density, kg/m^3	Content of, %		PPD concetra-tion, ppm	Ts, C		Depression, °C
		asphalte-nes+tar	paraffin		without PPD	with PPD	
Siberia							
West - Siberian	836.7	8.6	2.2	250	-22	-45	23
East - Siberian	834	4.82	1.83	250	-30	-55	25
NMP, Usinsk	853.2	21.74	6.84	500	14	-2	16
North oil	880.3	12.5	8.4	500	16	-20	36
Yakutia	870.8	12.7	2.63	250	-28	-48	20
Ukrain	804.5	6.04	2.3	500	-11	-40	29
Kazakhstan							
Akshabulak	818	11.21	14.8	100	10	-6	16
Ashisai	854.4	16	22.3	500	22	10	12
Mangyshlak	843.8	10.522	14.1	100	27	14	13
Kumkol	811	8.5	12	100	8	0	8
East - Kalmykia							
Kaspian	795.4	2.36	19	500	26	12	14
North Komsomol'sk	807	4.19	20.5	750	30	20	10
Sostinsk	809.3	6.3	22.8	500	19	10	9
North - Komi							
West-Synatyskoe	820.5	6.81	7	500	10	-22	32
South-Listvenichnoe		6.46	10.66	1000	26	2	24
South-Lyzskoe	841.2	7.1	21.3	100	34	30	4
Others							
1	834	3.93	4.41	500	10	-20	30
2	829.7	4.94	5.12	500	-20	-45	25
3	835.5	5.6	14.7	1000	20	-8	28
4	840	8.6	2	500	-17	-40	23

* T_s– solidification temperature

Table 3. Change it solidification temperature of crude oils in time with addition of 500ppm of DMN-2005 PPD.

Crude oil	Days			
	0	1	4	16
West-Synatyskaya (initial T_s =+14°C)	**- 18**	**- 18**	**- 17**	**- 12**
Stavropol (initial T_s =+26°C)	**+ 12**	**+ 14**	**+ 14**	**+ 14**
Kaspian (initial T_s =+28°C)	**+ 8**	**+ 8**	**+ 12**	**+ 14**

The effect of PPD introduced into crude oil is diminishing with time (Table 3). It can be explained by time sensitive structuring processes occurring in crude oil. The stability of depression properties of PPD depends not only on PPD itself, but also correlates with crude oil properties. The worse rheological and low temperature properties of crude oil the less effective would be PPD. However, this rule not always applicable.

The solidification temperature of crude oil determines its ability to flow within the transfer line at lower temperatures. However one should also consider shearing force of crude oil. Shearing force is determined by rheological parameters of crude oil such as: dynamic and plastic viscosity, initial and stress limit shift. There is a correlation between solidification temperature and rheological parameters: the lower solidification temperature, the lower viscosity and shear shift. The correlation is purely qualitative and has no quantitative relationship.

Introduction of PPD in crude oil changes dynamical characteristics of crude in order of magnitude or more.

Table 4. The effect of PPD on rheological characteristics of crude oil (numerator without PPD, denominator with 500ppm of DMN-2005).

Crude oil sample	Initial shear stress, Pa	Maximal shear stress, Pa	Plastic viscosity, Pa*s
NMT (at T=+10°C)	**22,8 / 2,3**	**1,3 / 0**	**0,224 / 0,077**
Kaspian (at T=+25°C)	**26,6 / 2,2**	**9,6 / 0,2**	**0,096 / 0,033**
West-Synatyskaya (at T= +10°C)	**11,5 / 0**	**2,4 / 0**	**0,067 / 0,021**

Application of DMN PPD for heavy oil products

Decrease in solidification temperature of reduced crude usually pursues the following goals:

- release of middle distilled fractions for more qualified application;
- conversion of low grade reduced crude into higher grade, i.e. IFO 360 grade fuel can be converted into IFO 180 or IFO 30;
- improvement of flow-ability of reduced crude.

Table 5. The results of PPD application for various reduced crude

Initial product	Kinematic viscosity mm^2/s	Content, %			Paraffin melting tempera-ture,°C	Initial Ts, °C	PPD concen-tration, ppm	Ts, °C with PPD after 7 days
		asphaltenes	tar	paraffin				
Reduced crude	38.4	0.33	8	17.3	57.5	30	1500	8
Reduced crude	95.5	3	17.3	4.4	56	3	1000	-20
Reduced crude	32.5	3	17.3	4.4	56	-7	500	-20
Reduced crude	24.2	0.33	8	17.3	57.5	24	1500	-6