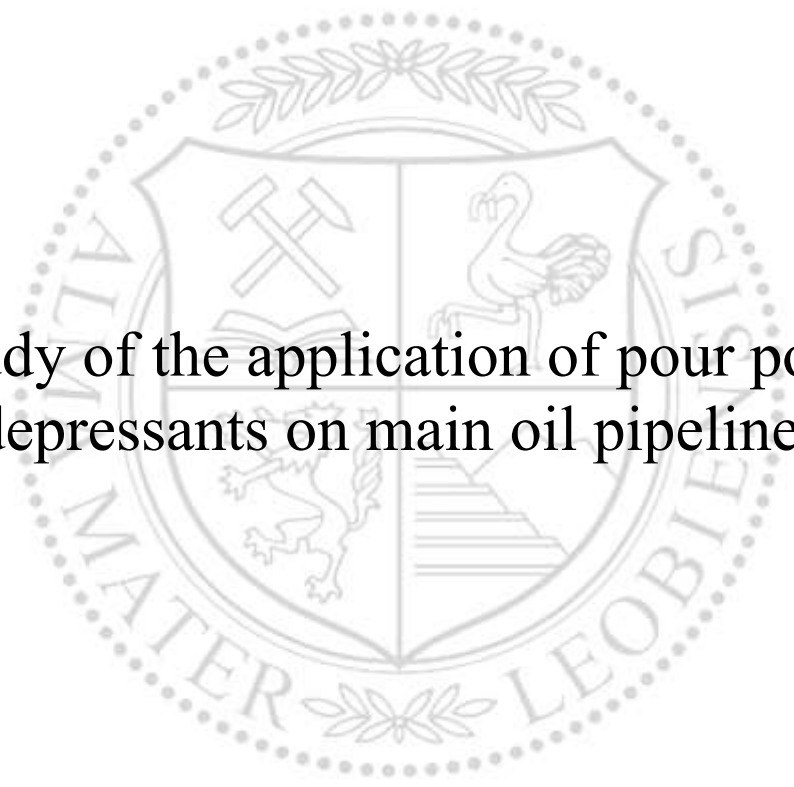




Chair of Petroleum and Geothermal Energy Recovery

Master's Thesis



Study of the application of pour point depressants on main oil pipelines

Nikita Lisovskiy

May 2023



AFFIDAVIT

I declare on oath that I wrote this thesis independently, did not use other than the specified sources and aids, and did not otherwise use any unauthorized aids.

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Furthermore, I declare that the electronic and printed version of the submitted thesis are identical, both, formally and with regard to content.

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Master Thesis 2023

Global Energy Transportation and Storage

Study of the application of pour point depressants on main oil pipelines

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Chair of Petroleum and Geothermal Energy
Recovery



Dedicate this thesis to the all main pipeline workers in my home country

I hope to make their life easier

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Abstract

This work deals with the complexities of transporting and storing highly paraffinic as well as highly solidified oils. The aim was to consider the problems of the use of depressant additives in the use of ultrasound treatment against asphalt tar and paraffin deposits on the surface of the equipment. The second objective was the possibility of activation and stability of additives by ultrasound treatment of oil with them, because in theory the fractured supramolecular structure, accelerated diffusion and the temperature effect contribute to a more effective work of the additives. The results showed that high pour pointing oil becomes more solidified, on both small and large volumes of treatment. In other words, the use of ultrasound to remove asphalt resin paraffin content on high solidification oil carries a risk of solidification of the oil in the tank itself. In the work, experiments were carried out that directly show that when exposed to ultrasound on highly paraffinic oil with a high pour point, an effect occurs according to which the pour point increases. According to our experiments, when the additive and sonication work together, a relatively small synergistic effect is observed at low concentrations of the depressant that is most resistant to sonication. In general, pour point depressants, in addition to the case described above, lose their effectiveness when exposed to ultrasound, both partially and completely, however, there are additives that lose a relatively small part of their effectiveness, thereby being resistant to ultrasound..

Zusammenfassung

Diese Arbeit befasst sich mit der Komplexität des Transports und der Lagerung von hochparaffinischen sowie hochverfestigten Ölen. Ziel war es, die Problematik des Einsatzes von depressiven Additiven beim Einsatz der Ultraschallbehandlung gegen Asphaltteer- und Paraffinablagerungen an der Oberfläche der Anlagen zu betrachten. Das zweite Ziel war die Möglichkeit der Aktivierung und Stabilität von Additiven durch die Ultraschallbehandlung von Öl mit ihnen, weil in der Theorie die gebrochene supramolekulare Struktur, die beschleunigte Diffusion und der Temperatureffekt zu einer effektiveren Arbeit der Additive beitragen. Das dritte Ziel war die Möglichkeit, Ultraschall auf den gefrorenen Abschnitt der Pipeline anzuwenden, um die Arbeiten wieder aufzunehmen, ohne den Rohrabschnitt abzusägen. Die Ergebnisse zeigten, dass Öl mit hohem Pourpointing sowohl bei kleinen als auch bei großen Behandlungsmengen stärker verfestigt wird. Mit anderen Worten, der Einsatz von Ultraschall zur Entfernung des Asphaltharz-Paraffingehalts bei Öl mit hohem Erstarrungsgrad birgt das Risiko einer Verfestigung des Öls im Tank selbst. In der Arbeit wurden Experimente durchgeführt, die direkt zeigen, dass bei der Einwirkung von Ultraschall auf hochparaffinisches Öl mit hohem Stockpunkt ein Effekt eintritt, demzufolge sich der Stockpunkt erhöht. Unseren Experimenten zufolge wird beim Zusammenwirken von Additiv und Beschallung ein relativ geringer Synergieeffekt bei niedrigen Konzentrationen des Depressionsmittels beobachtet, das am widerstandsfähigsten gegen Beschallung ist. Im Allgemeinen verlieren Stockpunktsenker, abgesehen von dem oben beschriebenen Fall, ihre Wirksamkeit, wenn sie Ultraschall ausgesetzt werden, sowohl teilweise als auch vollständig.

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Chapter 1

Introduction

1.1 Background and Context

In general, oil as a source of materials and polymers will disappear only after a very long time. Therefore, in our understanding it is necessary to continue research with high-paraffin oil, which often has properties to solidify at relatively high temperature. We have performed a number of experiments on the effects of ultrasound and depressant additives on the oil individually and together to determine the effectiveness of the ultrasound treatment.

1.2 Scope and Objectives

In this thesis we answer two main questions. Does the effect of additives could be activated after exposure to ultrasound without external heating?

Whether there is a positive synergistic effect on the oil when ultrasound and depressor additives work together?

1.3 Achievements

In this work, it was confirmed that ultrasonic treatment increases the pour point of high-pour oil. As a result, solidification occurs at +15 instead of +8 degrees Celsius. Also, pour point depressants react to varying degrees to the effects of ultrasound, of which one can distinguish those that slightly lose their effectiveness and are stable and have a synergistic effect, as well as those that significantly lose their effectiveness.

1.4 Technical Issues

An important problem during the experiments was that the effect of ultrasound was carried out purely under static conditions. Results under dynamic conditions can vary greatly.

Another important feature is the problem of temperature measurement during ultrasonic treatment, since its growth rate can show us new features of the process.

1.5 Overview of Dissertation

This work discusses the issues of types of transport of highly pourable oil, types and methods of influence of depressant additives on oil. A review of the effect of ultrasound on ARPD and pure oil is presented. In the experimental part we are performing the measuring of the pour point, the preparation of the additive. At the end we compare results of pour point with different additives and oil with and without UST. The data obtained can later be used in the development of schemes for the use of combined ultrasonic treatment and polymer depressant additives on main oil pipelines.

Chapter 2

Literature Review

2.1 An oil perspective for the future

For the time being, it is important to accept the fact that successive steps have been taken towards increasing the share of green energy. However, the issue goes much deeper than one might initially assume. On the one hand, the Paris accords are a crucial indicator of the seriousness of the intentions. The report on coal power generation shows a clear downward trend in Europe and worldwide. Despite this, on the other hand, there is no doubt that coal leads the energy mix in Asia.. The demand for oil as an energy source is still high, but the world has not seen an increase in its share of the energy mix, on the contrary, we can clearly see the constancy of its share, which is then likely to turn into a decline. (BP, 2022; IEA, 2023; Unated nation Climate change, 2023)

Although oil will not cease to be an energy resource for cars around the world, it will be significantly displaced by electricity. Most oil will not be used as a combustible fuel, but as a raw material for the synthesis of new polymers and materials, oils, etc. In other words, oil will not disappear from our lives with green technology, changing its scope of use. Thus, all unresolved problems in oil transportation remain relevant for the foreseeable future. One of them is the pumping of highly viscous and stagnant oil, which will increase significantly in the coming years. (Sudesh et al., 2011)

2.2 Highly viscous and solidifying oil

High viscosity and solidifying oil is oil with a relatively high pour point, a characteristic that directly affects the flow of oil, which is the case when the pour point is equal to or higher than the monthly average minimum temperature. Once the pour point is reached, the oil ceases to exhibit flow properties and cannot be pumped further through the pipeline. The high pour point

is caused by the high content of paraffins and asphalt-resin substances, which create a volumetric structure that prevents the flow of oil.

The presence of such properties does not allow to use usual way of pumping, because during pumping the oil will freeze and form plug preventing further pumping. In general, experts see two main approaches to the problem of transporting high-viscosity oil in the oil transportation system. The first involves the use of various pumping means and methods without changing the rheological properties of the oil itself, without affecting its properties in any way. The second approach is to modify or influence the properties of the oil, thereby allowing it to be pumped. (VASILYEV, G.G., G.Ye. KOROBKOV, A.A. KORSHAK et al, 2002)

The second approach to the methods of work on the recommendations: physical, physico-chemical and chemical:

Physical methods:

- 1) Pressure treatment
- 2) Satellite pipeline with heat agent
- 3) Hot pumping
- 4) Water pumping
- 5) Mechanical treatment
- 6) Magnetic field treatment
- 7) Electric field treatment

Physio-chemical:

- 1) Heat treatment
- 2) Dilute oil with light oil or oil products
- 3) Usage of the depression additives
- 4) Thermo-destructive treatment

Chemical methods considered as deparaffinization and deasphaltanisation by various means. (VASILYEV, G.G., G.Ye. KOROBKOV, A.A. KORSHAK et al, 2002)

Each of the methods could be used in specific situations and have its own pros and cons. Let's describe each method more deeply.

2.2.1 Water pumping of oil

Hydro-pumping is a special method of pumping high viscosity oil together with water by means of special water injection methods. There are three types of pumping.

The first one is pumping oil in a ring of water. Oil and water are pumped in this way, with the high-viscosity oil in a ring of water, and instead of contact between the oil and the pipeline wall, there is contact between the oil and the water. This method of pumping requires special technical devices on the pipeline, some of which are shown in the figure 2.1. (A.A. Korshak, 2008)

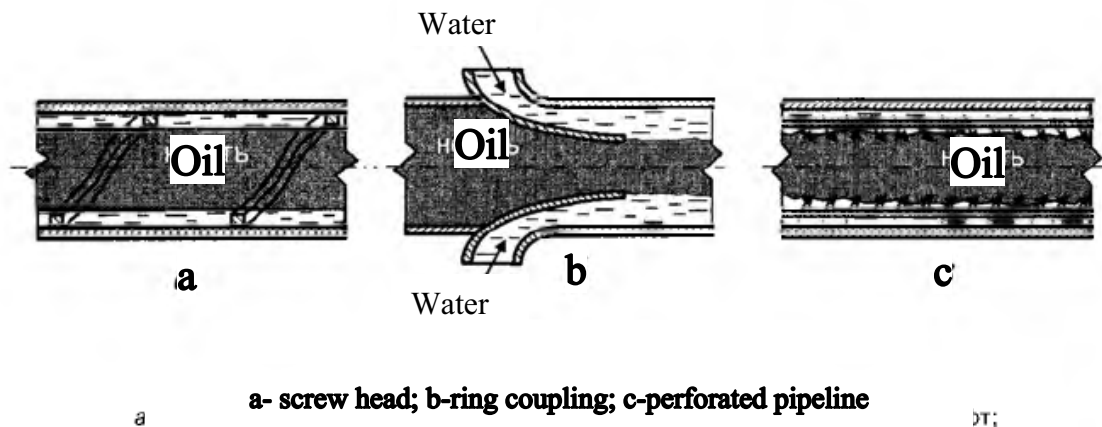
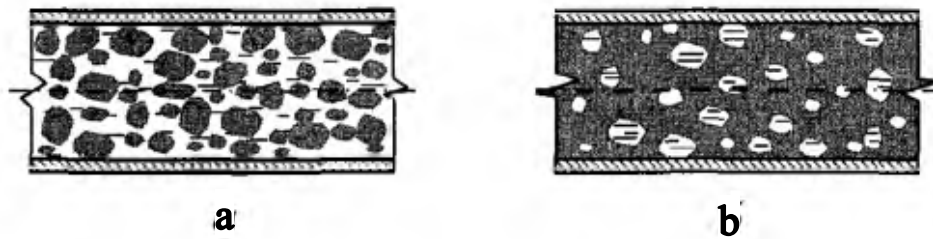


Figure 2.1-Hydro-pumping of oil with different ways of water circle creation(A.A. Korshak, 2008)

Unfortunately, this type of oil hydro pumping has not been used in the industry because the design of the special ring water injection facilities is extremely complicated to build. (A.A. Korshak, 2008)

The second type of hydro pumping is the creation of oil-in-water emulsions. The oil particles are surrounded by water and again there is no contact between the oil and the pipeline wall. This condition is achieved by the addition of surface-active substances. The stability of the resulting emulsion depends on the proportion of water, the type and concentration of the pav and the temperature. (A.A. Korshak, 2008)

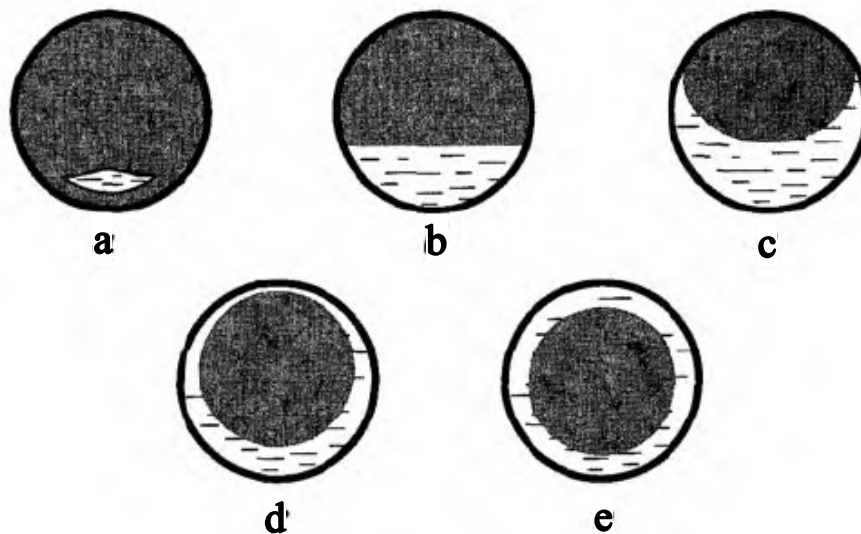
The problem with this method is watercutting of the oil, corrosion, and the possibility of a water-in-oil emulsion becoming a different kind of emulsion. The rheological properties in this type of transport drop significantly and create even more problems during pumping. Both types of emulsions are shown in the figure 2.2 below. (A.A. Korshak, 2008)



Emulsion types a- oil in water; b-water in oil

Figure 2.2-Hydro-pumping of oil in emulsion form(A.A. Korshak, 2008)

The third type of hydro pumping does not involve any addition of surfactants, or special devices for a special way of pumping water. In fact, by adding water to the flow of oil in the pipeline, due to the difference in density and lack of mixing, it is divided into two parts, the lower part of the flow is occupied by water, and the upper part by oil.. Again, the principle is to reduce the contact between the oil and the pipeline wall, which increases the flow capacity. Apart from this kind of distribution, there are also other kinds of distribution. You can see them in the figure 2.3. (A.A. Korshak, 2008)



a - lenticular, b - split flat boundary, c - split curved boundary, d - circular eccentric, e - circular concentric

Figure 2.3 - Different shapes of hydro-pumping of oil (A.A. Korshak, 2008)

2.2.2 Pressure treatment

Pressure treatment refers to the pressure treatment of oil. The process itself consists of increasing the pressure in a sealed vessel with oil to a certain pressure value. Over time, the pressure in the vessel begins to drop to the same final value, and the pressure drop is then repeated as the cycle repeats. It is advisable to carry out such cycles until there is no pressure drop. At the end of such a process a significant improvement of the rheological properties is observed. (A.A. Korshak, 2008)

The explanation for this phenomenon is that the oil is a dispersed colloidal system. The dispersed particles are asphaltenes and the medium is a mixture of hydrocarbons. Here are indicators that may suggest that dissolution of asphaltene micelles has occurred more fully. (A.A. Korshak, 2008)

In spite of a number of advantages of pressure treatment, there are reasons for its rejection at oil pumping stations. Firstly, it is a long process which is not effective for main pipelines with high oil flow; secondly, due to high pressure and metal fatigue, this process will require repair of tanks or pipes where the treatment will take place.

2.2.3 Mechanical treatment

The idea behind this method is quite simple. A three-dimensional structure of paraffin crystals is formed in the oil at low temperature, which, when broken down, improves the rheological properties of the oil. The basis of the method is the application of vibration by various means. The frequency of the vibration ranges from 20 Hz to 250 Hz. The upper boundary is caused by the fact that paraffin at low frequency does not change its crystal structure, and the upper boundary is caused by the fact that the energy is enough already for the oil sputtering and as a consequence the lack of effect (A.A. Korshak, 2008)

Technically it is possible to carry out this operation by means of a vibration sieve, which is shown in the figure below. The big disadvantage is that the treatment must take place in static conditions, for example in a tank, in the flow of oil, these systems unfortunately have no effect. In the case of application in a vessel, again it is of little use in case of high flow.

Unfortunately, the effect is not long lasting as the structure will eventually regenerate and the procedure must be repeated.

2.2.4 Transport with diluents

One way to lower the pour point of oil and improve its rheological properties is to pump with hydrocarbon diluents. From a physical point of view, there are two patterns. The first one is that concentration of paraffins decreases so the saturation temperature of oil also decreases. The

second one is that asphaltenes and resins in diluents also influence paraffin-forming process. (A.A. Korshak, 2008)

A parasitic realization is only possible when it is possible to blend with a lighter oil in the field. Gasoline, paraffin and diesel require firstly a separate infrastructure for transport to the fields which is not feasible, and secondly the need for separation of such a mixture at the end points.

2.2.5 Heat treatment of high pour point oil

Thermal treatment of oil is called heating it to temperatures above the melting of paraffins contained in it (determined by the laboratory) and then cooling with the same laboratory-determined cooling rate. At the same time when heating oil to temperatures below the melting point of paraffins rheological properties significantly deteriorate. (A.A. Korshak, 2008)

As one can see this effect is connected with change of morphology of paraffin crystals and its interaction with asphalt-resin substances. This effect is not observed in large quantities of asphalt-resinous substances. (A.A. Korshak, 2008)

There are many problems with this method in the industry as it is accompanied by high specific costs.

2.2.6 Electric field treatment

For example, when considering the interaction of electric field with hydrocarbons, it was noticed that in interaction with low-conductivity liquids the structure formation and consequently the viscosity decreases. Moreover, according to the data, hydrocarbons are more affected by changes in frequency than by changes in the amplitude of the field strength. (Belyi O. V., 2010; Gerlovin I.L., 1990)

A number of sources indicate the effect of alternating and homogeneous electric fields on the oil. It is noted, that electrokinetic phenomena take place when moving along the pipeline. (Gerlovin I.L., 1990; A. A. Ostapenko, 2000)

On the contrary, in (B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996) it is noted that electrification of oil flow along its way has no significant effect on waxing of oil equipment. The action of the electric field on the oil flow reduces the degree of waxing of the pipeline surface due to the formation of additional charge on the charged particle. The electric field in which a particle is located has a force that deflects it into the region of charges, where it interacts with another particle afterwards

According to the authors of (D.N. Sheikh-Ali, 1965), energy of electric field leads to the destruction of intermolecular bonds of three-dimensional structure of the oil system.

Asphaltenes in this case are polar electrically susceptible components included in the structure. Electrical action on the oil disperse system contributes to the appearance of excited molecules of radicals RAC and atomic hydrogen, formed by the destruction of molecules. These processes lead to shortening of carbon skeletons and reduction of branching of chains of oxidized molecules and, as a consequence, reduction of structural and rheological characteristics of oil systems.

2.2.7 Magnet field treatment

The behavior of petroleum systems in magnetic fields is now widely investigated. In (L.A. Artsumovich, 1977) the effect of magnetic treatment of oils on the electrokinetic properties of its main components was studied. It is important to note that structure-forming components of oils have different electric polarizability and magnetic susceptibility, this is the basis of changes in physical and chemical properties. In the electric field in the oil changes the internal structure of oil disperse systems, the adsorption-solvation shell is destroyed, and a large number of primary crystallization centres are formed in the volume of oil flow. The movement of oil flow under changing thermodynamic conditions leads to crystallization of ARPD in the volume, but not on the surface of the pipeline. Under such conditions, a high concentration of resinous asphaltene components is maintained in the volume and a decrease in the temperature of crystallization initiation is observed.

The authors (Y. M. Kagan, 1965) explain the mechanism of action of the magnetic field on the oil disperse systems in the oil flow by the formation of a double electric layer at the solid boundary. It was noted that a constant current formed mainly in the diffusion layer near the inner surface of the pipeline wall, this phenomenon is caused primarily by the oil flow itself. Within the oil stream the electric field strength is extremely low due to the low density of charges generated. When treating oil in permanent magnetic field the orientation of dipoles and change of ARPD deposition conditions on the pipeline surface take place (N.I. Kruglickiy, 1976). The efficiency of magnetic influence depends on the content in the oil of tarry asphaltene components, gas, water and any other inclusions, which form the interface with the oil.

However, in the article (G. M. Mokrousov, N. P. Gorlenko, 1988) it is mentioned, that hydrocarbons by their nature are little susceptible to magnetic field and under conditions of weak magnetic influence (104-105 A/m) it's impossible to influence the internal structure of paraffin crystals or change the conditions of oil-paraffin equilibrium. On the other hand, a significant influence of resinous asphaltene components of oil on the characteristics of paraffin crystals precipitating in constant and alternating electric fields is shown.

In (V.I. Lesin, 1994) it is noted that when an oil system passes between the pipeline wall and the surface of the magnetic device due to metal-containing impurities a large number of

additional centers of ARPD crystallization are formed, which are gas bubbles formed on colloidal micro-impurities.

In (F.G. Unger, L.N. Andreeva, E.R. Geintz, Y.N. Kroneberg), the quantum-chemical approach of the spherically symmetric structure of the oil association was used, according to which paramagnetic particles of the oil system in a liquid dispersion medium have a minor contact zone with paraffinic and naphthenic hydrocarbons, which are oriented relative to the paramagnetic centre in the form of "hedgehog needles". All spins are characterized by a specific direction in the formation's oil disperse system. When an oil system enters a pipe, the rate of associates' sticking together increases because of increase of probability of their collision due to increase of flow velocity in a certain direction. Colloidal particles adhesion rate slows down if sufficiently intense magnetic field orienting spins in the same direction is placed in the pipeline. The energetic properties of the magnetized oil system are maintained until the Brownian motion again reverses the direction of spins of all the molecules, so outside the action of the orienting magnetic field the coalescence of particles begins. The reverse process can be prevented by treating the oil system again in the magnetic field.

The resins and asphaltene components of petroleum systems affect their physical and chemical characteristics according to the nature of the RAC themselves, as evidenced by NMR studies on oils and their fractions. (S. IlyasovE. Z.R. Borsutsky, 2002; S. IlyasovE. Z.R. Borsutsky, 2002). At formation of deposits, they are the main centers, on which the adsorption of crystallizing n-alkanes takes place. resinous asphaltene components of oil are the main components having free surface charges, interacting with a magnetic field. When treated by magnetic field the surface activity of the resinous asphaltene components changes and the hydrocarbon molecules form an orderly and denser packing on them. The magnetic treatment results in a reduction of the interaction energy of the resinous asphaltene components with the n-alkanes and creates more suitable conditions for the exchange of molecules between the dispersed phase and the dispersion medium.

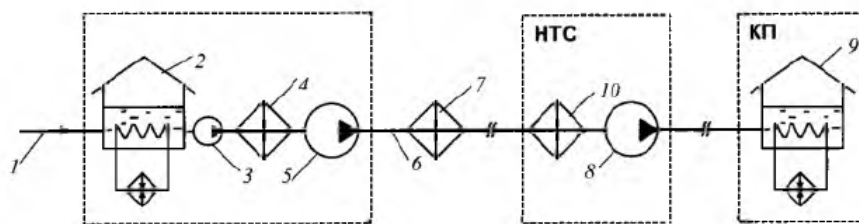
2.2.8 Depression additives main facts

The methodology for applying depressant additives is to mix them with high paraffin oils at a temperature above the melting point of paraffin, usually a temperature of 50-60 degrees Celsius where the majority is in a liquid state. The effect is mainly contained in the change in the setting temperature, while the mechanism is quite complex and directly related to the paraffin crystallization process, so we will devote a separate section to this issue.

2.2.9 Hot pumping

Hot pumping, also known as preheated pumping, is the most common and the easiest way to transport high-viscosity oil. This is due to the relative simplicity of the process and the absence of specific conditions which critically affect the durability of facilities. (A.A. Korshak, 2008)

The principle of hot pumping is to raise the temperature of oil to 50-60 degrees for further transportation. As the oil moves through the pipeline, due to heat transfer through the pipeline wall, it loses internal energy and the temperature decreases. The oil is heated either in the tank or by flow heaters. Therefore, in general, the hot pumping scheme can be illustrated by the diagram in the figure 2.4 below. (A.A. Korshak, 2008)



1 - supply lines; 2,9 – tanks; 3 – charger pump, 4,7,10 – additional heaters; 5,8 - main pumps; 6 – main pipeline; ГТС - head pumping and heating station; HTC - pumping and heating station; КП - pipeline delivery end

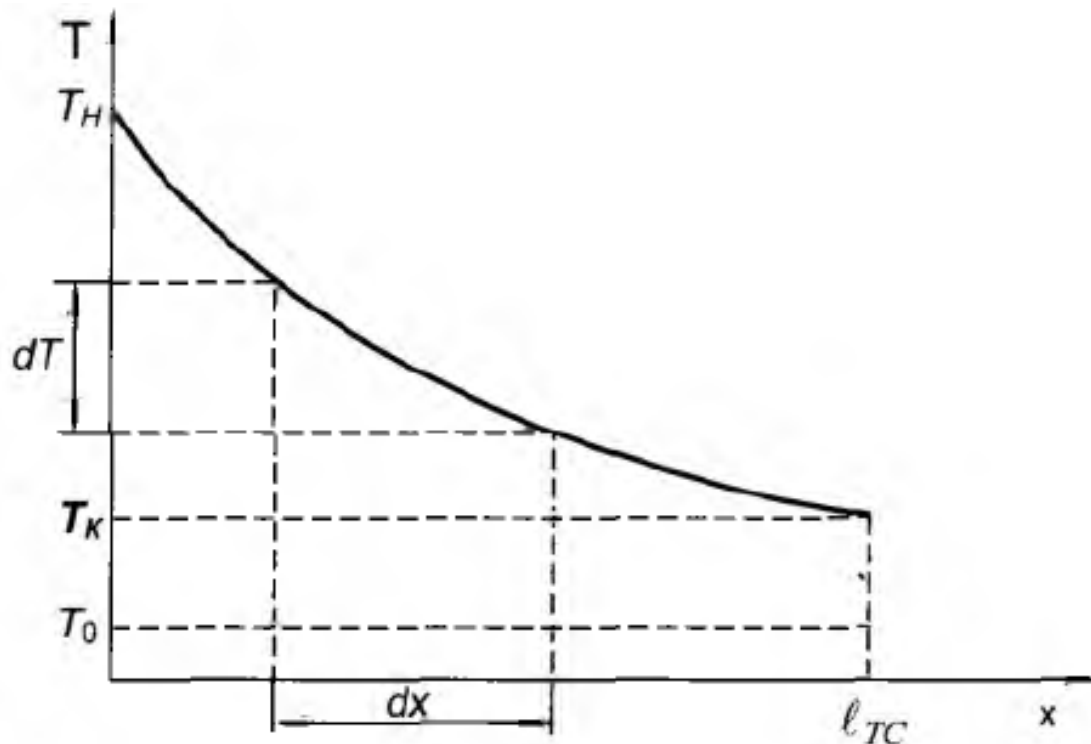
Figure 2.4-Principal scheme of the hot pumping(A.A. Korshak, 2008)

The obvious problems with this method are heat transfer with the environment. When the oil reaches the pour point, as is known, it loses its flow properties and cannot be pumped further. Therefore, first of all the thermal insulation layer is used. Secondly, intermediate oil heating stations are installed on a linear part of oil pipeline. At intermediate stations oil is also heated. The heating point is shown in the figure 2.5. (A.A. Korshak, 2008)



Figure 2.5 - Principal scheme of the hot pumping

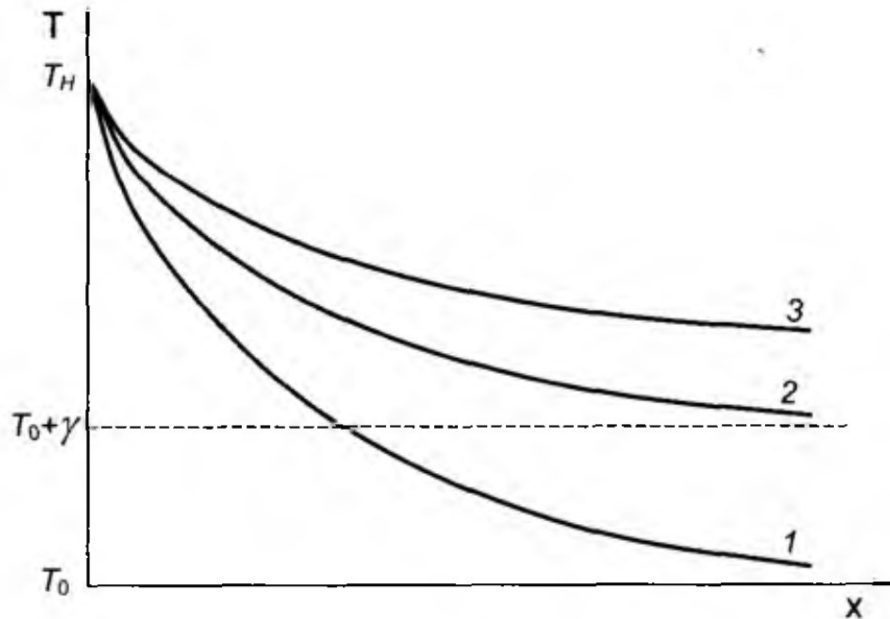
Due to heat transfer, the oil loses temperature. However, this process is not linear. The reason for this is the variation in heat capacity, the heat transfer coefficient in different sections and the different temperature conditions along the length of the pipeline. The influence of different flow modes is of no small importance; in the turbulent section of the pipeline the heat transfer occurs more intensively due to higher Reynolds number than in the laminar section. As a result, the temperature curve for the length of the pipeline is shown in the figure 2.6 below. (A.A. Korshak, 2008)



T_H – temperature of the hot oil at the beginning of pipeline; T_K – temperature of the oil at the end of pipeline; T_0 – ambient temperature; l_{TC} – length of the pipeline

Figure 2.6- Plot of the temperature drop per length during hot pumping(A.A. Korshak, 2008)

However, this graph may vary depending on the actual components. Internal friction in the flow converts a certain amount of motion energy into thermal energy, in parallel, paraffins begin the process of crystallization, which, as it known, is accompanied by heat release, when these two effects are superimposed, the temperature drop graph changes (fig.2.7). The steepness of the oil temperature drop graph is significantly reduced when the influence of internal friction is taken into account. At accounting still heat of crystallization of paraffins even greater decrease in losses of heat in ambient environment is possible. However, it is important to note that all these parameters largely depend on the actual properties and composition of the oil. (A.A. Korshak, 2008)



T_H – temperature of the hot oil at the beginning of pipeline; T_0 – ambient temperature;
 1 – temperature of oil; 2 - temperature of oil if we consider coefficient for internal friction;
 3 - temperature of oil if we consider coefficient for internal friction and heat from wax
 crystallization

Figure 2.7 - Plot of the temperature drop per length during hot pumping with extra conditions (A.A. Korshak, 2008)

The hot oil pumping process can be supplemented and efficiency improved by the addition of depressant additives, as previously discussed, which reduce the pour point of the oil. Thus it is possible to reduce the number of heating stations and the thickness of insulation on the pipes in the design. In operation it is possible to use the current hot pipeline to pump oil with a higher pour point. (Lyapin A. Y., Nekuchaev V. O., Ovchinnikov S. K., Mikheev M. M., 2020; Ляпин et al., 2021)

In fact, this combination of methods has been applied in the Usa-Ukhta pipeline. However, this article describes a problem in the effectiveness of the additive application. Many theories have been put forward as to why the additive performance is poor, but the most important is thought to be the blending of a different grade of oil with the Chikshino ISP. That is, the use of additives requires additional work to assess the effectiveness of additives in particular conditions. (Lyapin A. Y., Nekuchaev V. O., Ovchinnikov S. K., Mikheev M. M., 2020; Ляпин et al., 2021)

In order to assess the effect of additives it is necessary to be familiar with the process of paraffin crystallization, the factors affecting this process and the deposition of ARPD.

2.3 Asphaltenes, resins paraffins and ARPD

Oil is a dispersed mixture of low- and high-molecular hydrocarbon and non-hydrocarbon substances. Its physical and chemical properties are strongly influenced by environmental parameters, temperature, pressure, etc. The oil that is in the reservoir reservoir and produced in the field is crude oil, while the oil that is transported through the pipeline system is marketable oil. The difference is that the marketable oil is desalted, dehydrated and degassed. As mentioned above, oil contains so called asphaltenes, resins and paraffins. Each of these types has a direct impact on the deposition of ARPD as well as paraffin deposition.

2.3.1 ARPD

ARPD is a complex structured system, the base of which are paraffins (40-60 percent of the total mass), resin-asphaltene components (10 - 56 % wt.), oil and inorganic inclusions (sand, clay, salt, water). The composition of ARPD is not fixed and has the possibility to change depending on conditions. (N.G. Ibragimov, A.R. Khafizov, V.V. Shaydakov, F.R. Khaidarov, A.V. Emelyanov, M.V. Golubev, L.E. Kashtanova, K.V. Chernova, D.E. Bugai, A.B. Laptev et al., 2003)

The table below shows the classification of ARPD into groups and subgroups depending on the ratio of mass fraction of paraffin to asphaltene solids.

Table 2.2.1 – Classification of ARPD (N.G. Ibragimov, A.R. Khafizov, V.V. Shaydakov, F.R. Khaidarov, A.V. Emelyanov, M.V. Golubev, L.E. Kashtanova, K.V. Chernova, D.E. Bugai, A.B. Laptev et al., 2003)

Group ARPD	Subgroup ARPD	Ratio of mass paraffin content to the sum of resins and asphaltenes	Content of mechanical impurities
Asphalt (A)	A1	<0,9	<0,2
	A2		0,2-0,5
	A3		>0,5
Mixed (M)	M1	0,9-1,1	<0,2
	M2		0,2-0,5
	M3		>0,5
Paraffin type (P)	P1	>1,1	<0,2
	P2		0,2-0,5
	P3		>0,5

Asphalt-resin substances often constitute a significant proportion of refined oil. In recent years, with declining light oil reserves, their share can be as high as 30 per cent. Physico-chemical properties directly affect the extraction, transportation and processing processes. (Mozgovoy I. V., Davidan G.M., Oleinik L.N., 2005; T. V. Cheshkova et al., 2019)

Asphaltenes are high-molecular oil components, which are powder-like substances of brown or brown colour, they are insoluble substances, and after hardening it is impossible to get rid of

their deposits by melting, this property designates their refractory nature. (Mozgovoy I. V., Davidan G.M., Oleinik L.N., 2005)

Resins are viscous liquids or solid amorphous bodies with a dark or dark brown colour. Their density is comparable to that of asphaltenes. As tar is a high molecular weight substance, its properties depend directly on the fraction from which it was extracted and on the type of oil. (Mozgovoy I. V., Davidan G.M., Oleinik L.N., 2005; Герасимова et al., 2019)

2.3.2 Paraffins

Paraffins are often saturated hydrocarbons from C16 to C64. Under reservoir conditions they are in a liquid state. However, when pressure and temperature drop, the crystallisation process begins. Paraffins also include high molecular weight paraffins, ceresins from C37 to C53, characterized by their high boiling point, molecular weight and solid density. (Bazhaykin et al., 2021; Del García, 2000; Maryin V.I., Akchurin V.A., Demakhin A.G., 2001; S. R. Sergienko, B. A. Taimova, E. I. Talalaev, 1979)

An important addition to paraffins is the distinction between n-paraffins and cyclic paraffins (which include aromatic rings or branched structures). Their ratio varies from oil to oil. The chemical structure of some of the paraffins is shown in the figure 2.8 below.

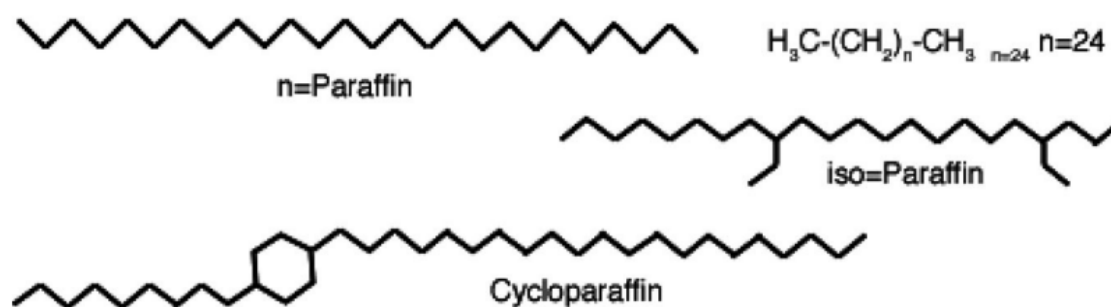


Figure 2.8 - Paraffins types (Adebiyi, 2020)

2.3.3 Paraffin crystallization

The most important aspect that concerns us in the transport of high solidification oil is the process of paraffin crystallization. This process causes the aforementioned loss of fluidity, which makes it impossible to transport this type of oil by pipeline without special pumping methods. In Russia, the above-mentioned hot pumping is the most common method. As mentioned in the work before, it is possible to apply pour point depressants which greatly improve the process, but they will be affected by the crystallization process. In the literature it is described that paraffins can change the morphology of crystals, depending on the presence of certain components. In our case we will describe process of crystallization of mixture of

paraffins. (Adebiyi, 2020; B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996; Fang et al., 2012; Lin et al., 2021)

The important addition is that paraffins can be divided on macro crystalline and micro crystalline in essence the difference consists only that micro crystalline can be in more quantity in oil in comparison with macro. The type of hydrocarbon chain and the number of carbon atoms cause this difference.(Adebiyi, 2020; B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996; Fang et al., 2012; Lin et al., 2021)

In general, the process of crystallization of paraffin should be divided into three successive processes, because this process is not instantaneous and begins only when the oil and paraffin solution becomes saturated. As soon as this has happened, the nucleation process begins. (Adebiyi, 2020; B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996; Fang et al., 2012; Lin et al., 2021)

Nucleation implies the initial stage at which paraffin molecules begin to fall out of the supersaturated solution and settle on the crystallization centres. The crystallization centres can be solid particles or other molecules. (Adebiyi, 2020; B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996; Fang et al., 2012; Lin et al., 2021)

Co-crystallization is the second stage, when the number of deposited molecules increases; the intermediate structure morphologically resembles lamellar or needle-like fragments. At this stage their number is large enough. However, these crystals are not interconnected, which does not hinder fluidity. (Adebiyi, 2020; B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996; Fang et al., 2012; Lin et al., 2021)

The last crystallization step is called agglomeration. Agglomeration involves the fusion of many uncoated paraffin crystals into a complex 3-dimensional structure. In this process a transition from a colloidal system to a gel occurs. The structure of the paraffin crystals substantially interferes with flowability, as oil molecules remain trapped between the paraffin crystals. (Adebiyi, 2020; B.V. Karpov, V.P. Vorobyov, V.T. Kazakov, 1996; Fang et al., 2012; Lin et al., 2021)

In another case, when nucleation makes the centre of crystallization irregularities on the surface of the pipeline or when co-crystallization hits the wall, further growth is possible on the pipeline wall as well. The figure 2.9 shows the above described case.

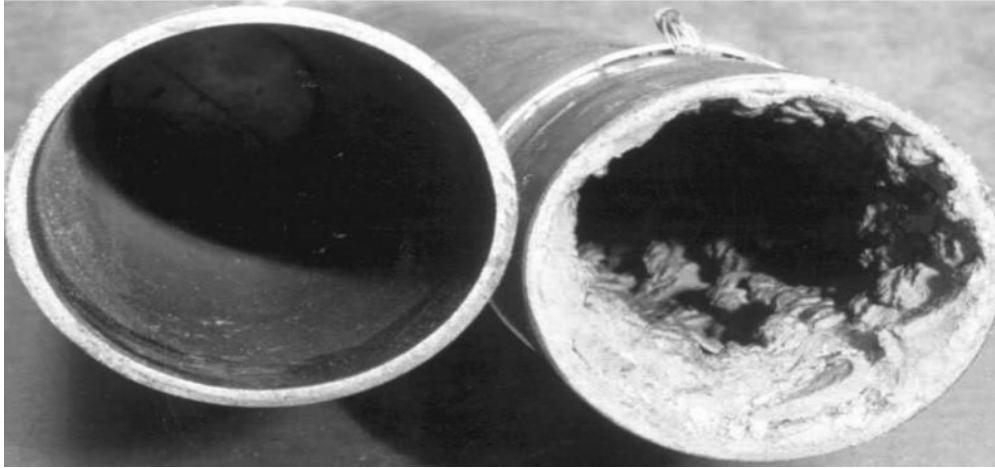


Figure 2.9 - Process of the wax precipitation(Adebiyi, 2020)

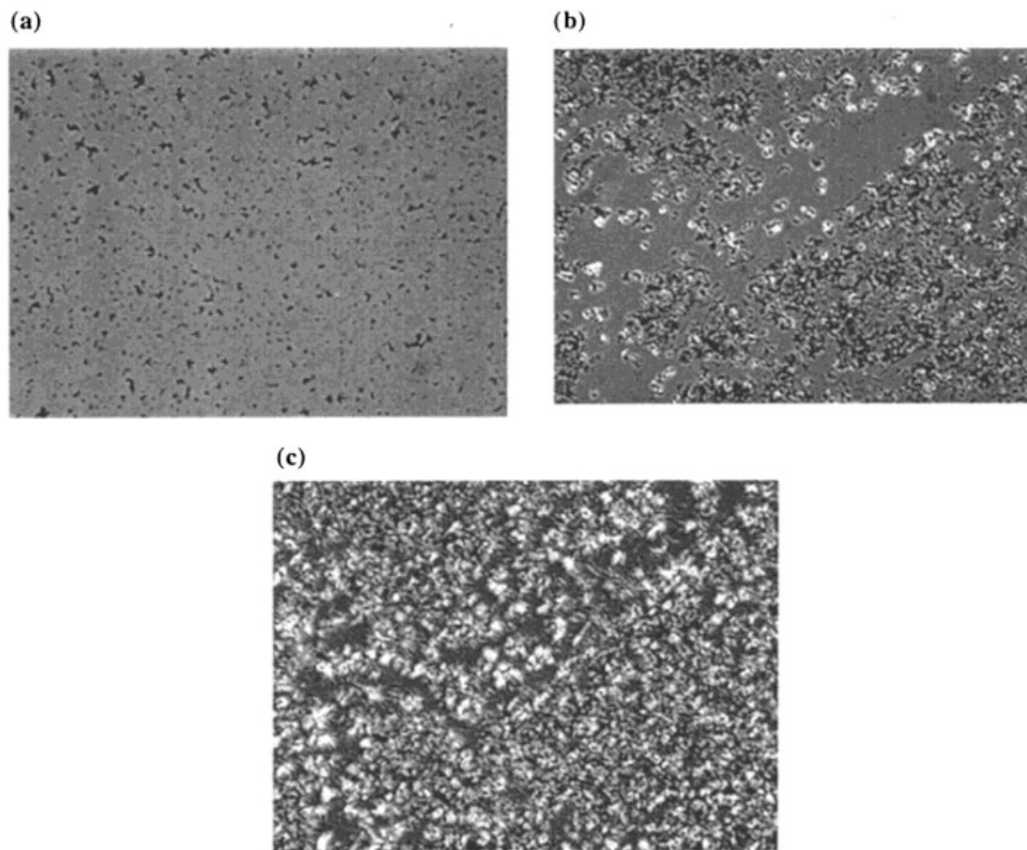
As a result, the crystallisation process can be described as follows: first of all, molecules at the crystallisation centres drop out of the supersaturated solution and gradually grow into a complex 3-dimensional structure, which in turn prevents the oil from flowing.

2.3.4 Influence of asphaltenes and resins on the crystallisation process of paraffins

The influence of resins and asphaltenes on the crystallisation process of paraffin has long been a mystery with no clear answer. On the one hand, the complete absence of any influence from the RAC in general has long been noted, but on the other hand, there is evidence of the opposite, both positive and negative.

Experimentally, some studies have confirmed that in oils with asphaltene content above four percent, a significant decrease in pour point and decrease in shear stress were observed, which in turn indicated an influence not only on the amount of precipitated paraffin, but also on gel structure. (Герасимова et al., 2019)

Further investigations showed that during crystallization paraffins interact with asphaltene molecules by means of alkyl chains, which in turn generates changes in this process. At the nucleation stage when paraffin molecules precipitate on crystallization centres, asphaltene molecule becomes as peculiar centre, it becomes possible due to the above mentioned interaction of alkyl chains. The effect of asphaltenes can actually be seen in the figure 2.10. From which the influence of asphaltenes in the different stages of the interaction can be seen. (T. V. Cheshkova et al., 2019)



*Figure 2.10 – Main effects of asphaltenes on WAT: (a) higher WAT, (b) at WAT, and (c) lower WAT
(Del García, 2000)*

The oil's crystallization process has not been perceived as a factor for a long time, similarly to asphaltenes. The pour point of oil also decreases as the ratio of asphaltenes to resinous components increases. Experiments show that the resins do not affect the paraffin molecules so much as the asphaltene molecules, by coating them and making them more stable. Thus, the resins counterbalance the depressor effect of asphaltenes. (Del García, 2000)

Another point of view should be mentioned. Tars enveloping asphaltenes create agglomerates, which become crystallization centres, and it is necessary to note, that paraffin saturation temperature of oil decreases at this interaction.

As it is visible from above influence of resins and asphaltenes on temperature of saturation of oil by paraffins and process of crystallization of paraffins has a complex character caused both by their ratio and qualitative composition.

2.4 Principle of depressant additives

First of all, it is necessary to correctly classify depressant additives according to their operating principle, as this principle determines the scope, efficiency and method of action on the oil.

In general, three types of additives can currently be distinguished according to their principle of action: EVA additives, combined type copolymers and nano-hybrid additives. The types can be seen in the figure 2.11 below. (Cao et al., 2022; Chen et al., 2010; N. Li et al., 2018; W. Li et al., 2021)

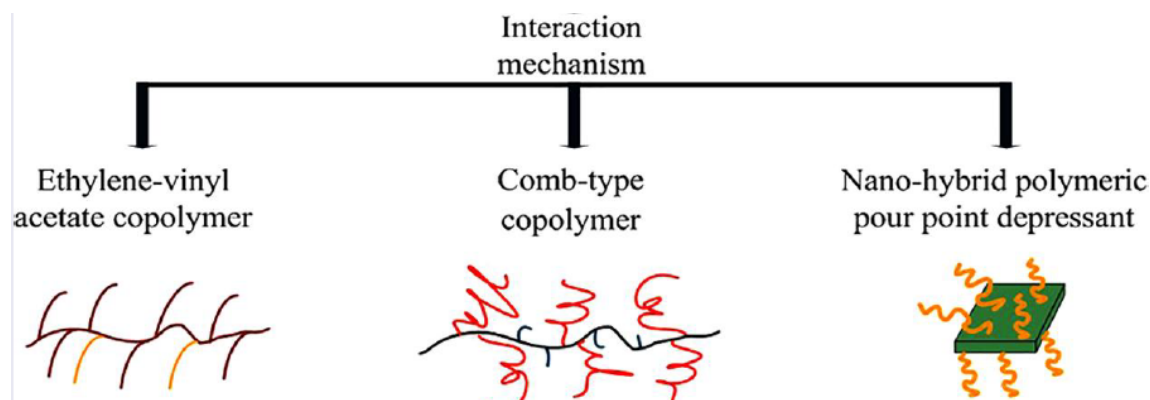


Figure 2.11– Types of the interactions (N. Li et al., 2018)

If we consider the effects of depressant additives, they affect the crystallisation process itself and act in three stages of the crystallisation process. The three stages of paraffin crystal formation have been outlined above. The work of the additives lies in the interaction between the paraffin molecules and the additive molecules. (Cao et al., 2022; N. Li et al., 2018; W. Li et al., 2021)

In the nucleation stage, as mentioned above, the paraffin molecules precipitate and act as new crystallization centres. The presence of depressant additives helps to screen these centres of crystallization and prevents its further growth. Thus we obtain a larger number of crystallization centres but at the same time smaller ones. (Cao et al., 2022; N. Li et al., 2018)

The interaction of paraffin molecules with molecules of polymeric depressant additives also occurs in the adsorption and crystallization phase, which starts at temperatures around paraffin precipitation temperatures. (Cao et al., 2022; N. Li et al., 2018)

In the adsorption phase, paraffin molecules are adsorbed onto additive molecules. This results in their co-crystallization. Under the influence of a depressant, paraffin crystals change their morphology during growth from a lamellar and needle shape to a denser spherical shape. (Cao et al., 2022; N. Li et al., 2018)

An example of how polymer additives of different types work can be seen in the figure 2.12. From this you can clearly see the change in crystal morphology in all four cases. These differences are caused by the fact that the additive molecules also have different shapes and properties. (Sharma et al., 2019)

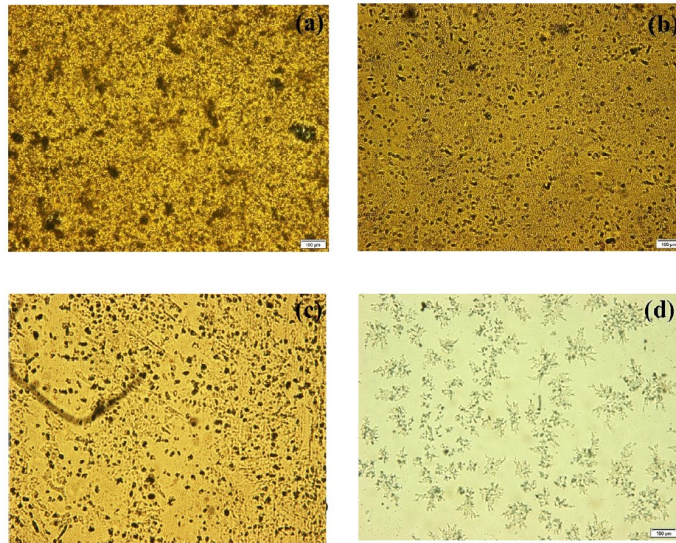


Figure 2.12 – Real type additives affect on crystal morphology a). oil and oil samples with the PPDs (b). Phoenix, (c) PMMA-0.5% GO, (d) PMMA-1% GO (Sharma et al., 2019)

The figure 2.13 below. shows schematically how crystallisation occurs without and with depressant additives, it is important to note that the number of crystallisation centres is significantly higher than without them. (Lin et al., 2021)

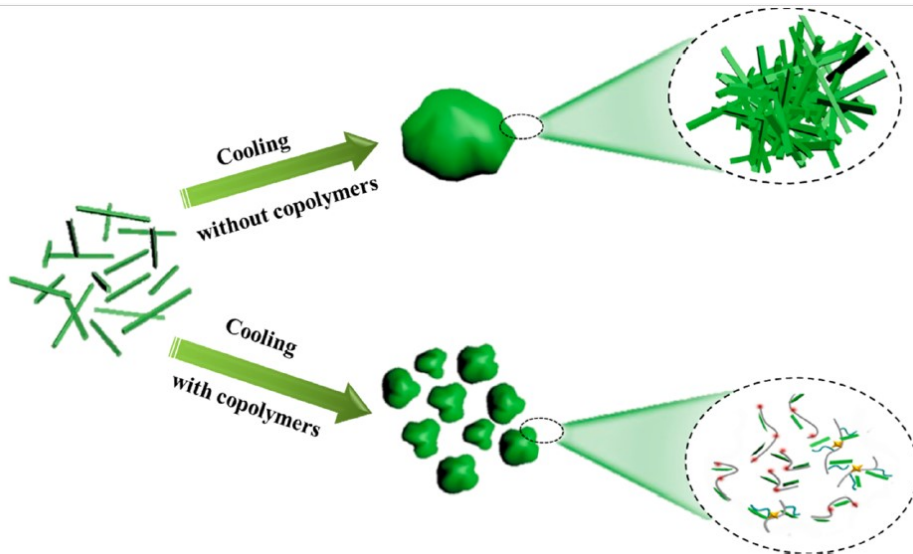


Figure 2.13 – Comparison of the crystallization processes (Lin et al., 2021)

In general, the additive interaction process is depicted in the figure 2.14 below. It shows that the interaction is due to the opposite polarities of the paraffin molecules and the additive molecules. (N. Li et al., 2018)

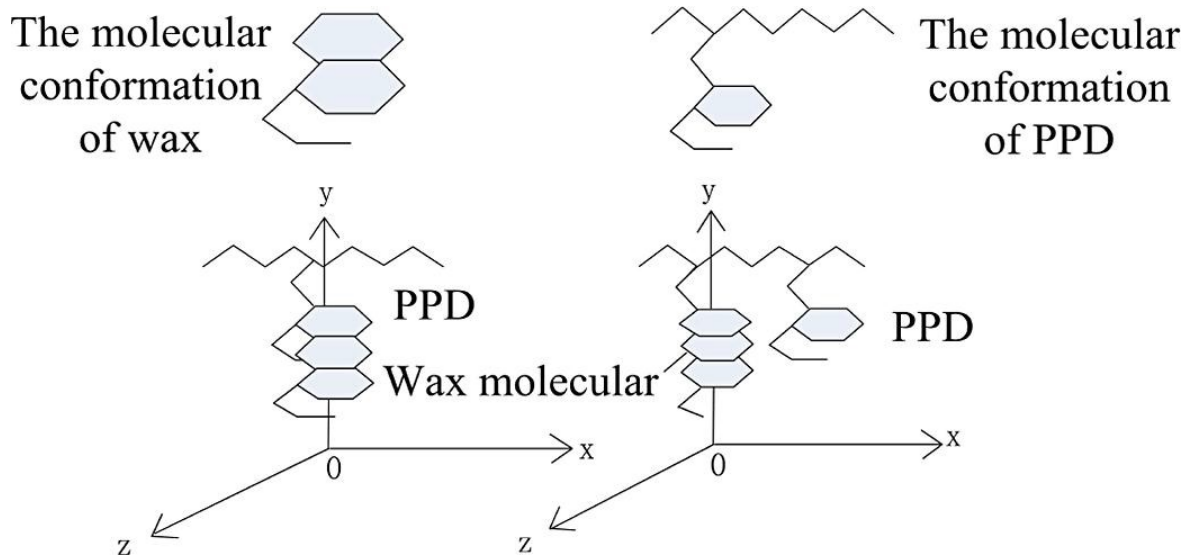


Figure 2.14 – Structure of the interaction between paraffins and PPD (N. Li et al., 2018)

Because of this arrangement and growth, there is another feature in crystal growth. The feature can be seen in the figure 2.15. below. The peculiarity consists in further crystal growth. It is no longer growing along the Y axis because of the interaction shown in the figure above, it appears that the X and Z axes are growing faster.

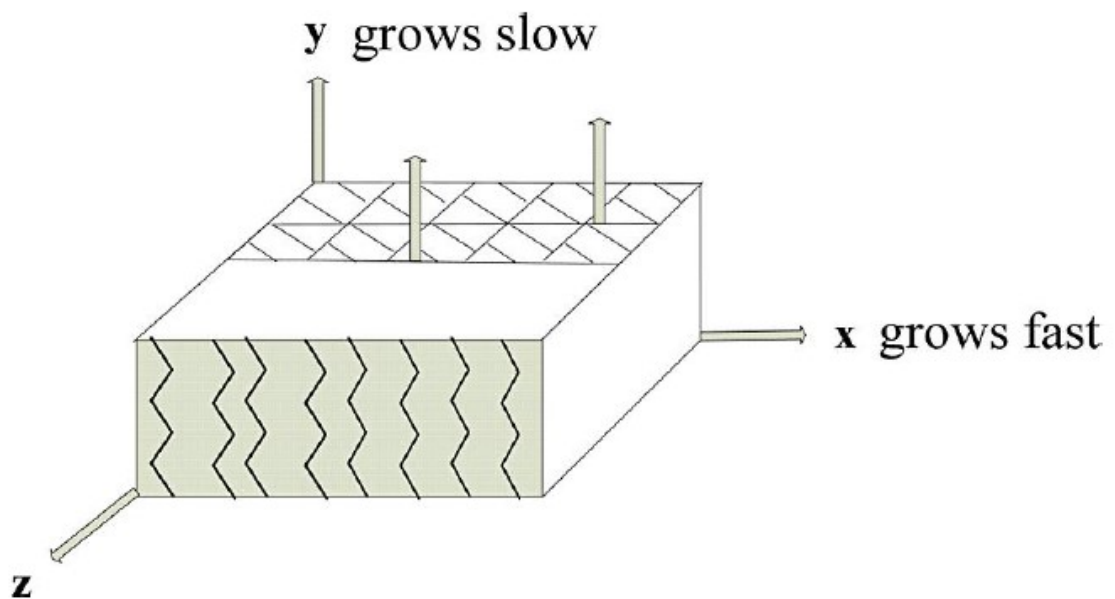


Figure 2.15 – Growth of the paraffin's crystal with PPD (N. Li et al., 2018)

As it becomes clear, a large number of spheres appear in the volume of oil, which already form a dispersed oil-paraffin system. Due to large contact surface between liquid oil and paraffin crystals a large amount of free energy is formed in this system. This energy can be released by increasing the size of the crystals, but it will still result in a three-dimensional gel structure, since there are no barriers to the crystals forming a net-like structure. Depressor additives

promote formation of a solvent layer on the interface, changing the nature of the interaction and preventing further interconnection of the crystals, thereby reducing the amount of free energy in the system. (Cao et al., 2022)

2.4.1 EVA type additives

EVA additives or otherwise ethyl vinyl acetate due to the fact that they appeared earlier than everyone else as a means of reducing the pour point and application in other industries and, as a result, received the lowest cost to date.. The chemical structure is shown in the figure 2.16 below. and a 3-D representation of the monomer in the figure 2.17. EVA is a copolymer of polyethylene, which is a crystalline phase in solution in the figure shown on the left and also a copolymerised vinyl acetate co-monomer which in turn is a non-crystalline phase and is shown in the figure on the left. In general, this design allows both the nucleation centre and the morphology of the paraffin crystals to be changed. (Cao et al., 2022; N. Li et al., 2018)

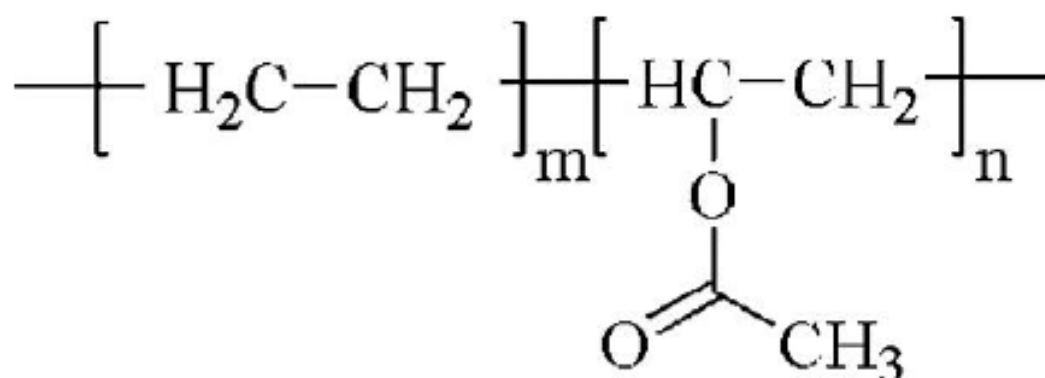


Figure 2.16 – Chemical formula of PPD EVA (N. Li et al., 2018)

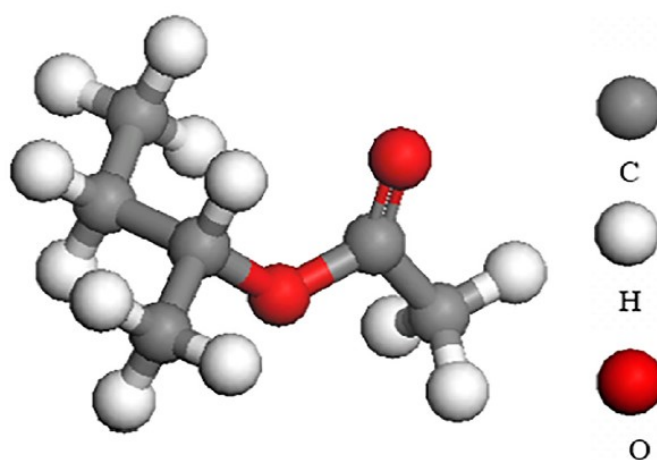


Figure 2.17 – Chemical structure of PPD EVA (Cao et al., 2022)

It is worth mentioning that since the additive acts on paraffin molecules, its maximum effect will be observed only when paraffins are in molten state. Another important factor is the mass content of vinyl acetate groups. Of all the contents, EVA with 30 percent of these groups shows the best qualities and results in practice. However, in tests with higher amounts of asphaltenes, it shows the best efficiency at 80 percent. The mechanism of this additive is shown in the figure 2.18 below.

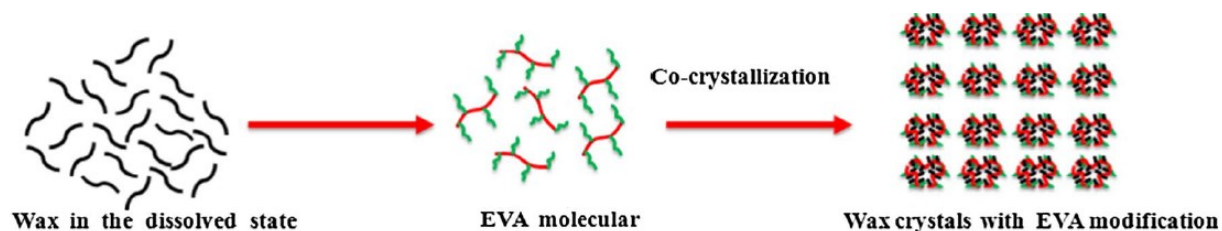


Figure 2.18 – Process of the work of the EVA PPD (Huang et al., 2018)

In general, EVA is a clear-coloured pellet and can be used in a variety of applications. It is dissolved in paraffin, diesel fuel, etc., which allows for different concentrations of additives for different applications.

The DPN-1 additive used in the Usa-Ukhta pipeline is a solution of EVA in diesel fuel. When oil was added to Chiksha PCS, the effect of this additive was significantly reduced due to the fact that the oil already contained paraffin crystals. However, when the oil was heated to 70 degrees Celsius the additive started working again. This case confirms that the additive is most effective at dissolving most paraffin waxes. (Lyapin A. Y., Nekuchaev V. O., Ovchinnikov S. K., Mikheev M. M., 2020; Ляпин et al., 2021)

2.4.2 Comb-type copolymers

One of the varieties of polymer additives is the comb type, in contrast to EVA, alkyl chains are located on the polymer chain like a comb. The polar groups are amine, ester and also aromatic bonds. The alkyl side chains are non-polar. The presence of non-polar groups increases their interaction with paraffin crystals and accelerates crystal growth in all directions. (Deshmukh & Bharambe, 2008; N. Li et al., 2018)

Polar groups have the ability to interact with asphaltenes in the oil solution. As indicated earlier, asphaltenes themselves are already crystallization centres for paraffin. However, these groups on the one hand can influence interaction of asphaltene molecules with each other and thus improve fluidity of oil, on the other hand, polar groups also contribute to interaction of paraffin and asphaltene molecules, turning them in turn into new crystallization centres in other words now they become even more. However, it should be noted that the efficiency in this case has an upper limit. (N. Li et al., 2018)

The efficiency of additive application is greatly influenced by the size of side chains. Research has shown that the highest efficiency is demonstrated by additives with side chain length approximately equal to the value of average carbon atom number of paraffins in respective oil.

The principle of additive operation and its interaction with paraffins and asphaltenes is shown in the figure 2.19 below, as can be seen from the figure paraffin molecules are fixed by co-crystallization between non-polar branches. The polar groups surrounding the asphaltenes can effectively disperse the asphaltenes into a decentralised state and prevent the formation of a network structure. (N. Li et al., 2018)

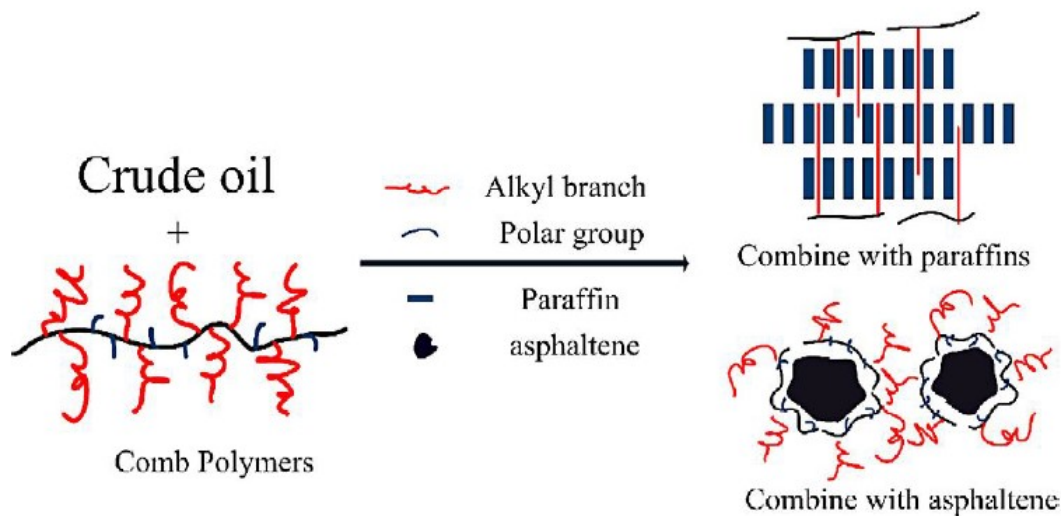


Figure 2.19 – Comb types PPD work process (N. Li et al., 2018)

These two factors directly affect the rheological properties of oil and improve its flowability, i.e. these additives are also rheological.

2.4.3 Nano-hybrid polymeric pour point depressants

In general, the previous types of additives are now overwhelmingly popular in use, but the limitations of their use and durability have long been known. Nano materials and nano composites are capable of outperforming these additives through various effects.

Nanoparticles can effectively disperse paraffin and asphaltenes, inhibiting nucleation and crystallization of paraffin. Compared to conventional polymeric depressors, nanohybrid polymeric depressors combine the advantages of nanomaterials and conventional polymeric depressors, thereby effectively improving the performance of conventional polymeric depressors. A possible mechanism of depression of high pour point oil with nanohybrid depressors is shown in the figure below (fig.2.20). (Huang et al., 2018; Mao et al., 2020)

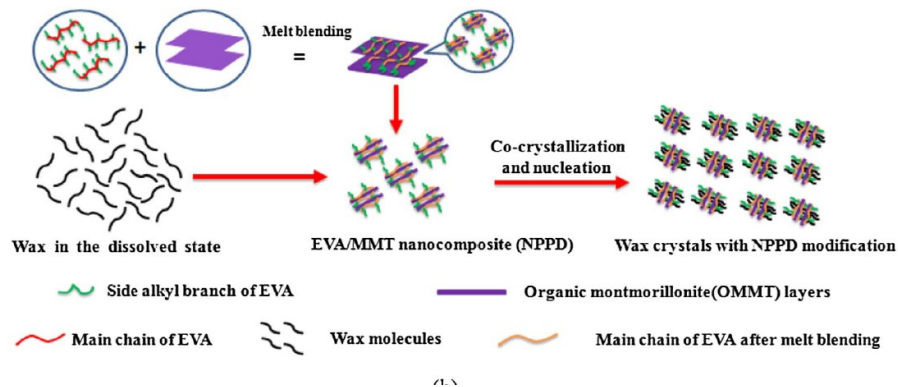


Figure 2.20 – NPPD work process (Huang et al., 2018)

The application of nanocomposites has been tested on oil and their effectiveness has thus been confirmed.

The results of oil treatment with nano additives as well as with EVA additives at 200 ppm can be clearly seen in the figure 2.21. The difference can be seen with the naked eye in the shape of the paraffin crystals. (Huang et al., 2018)

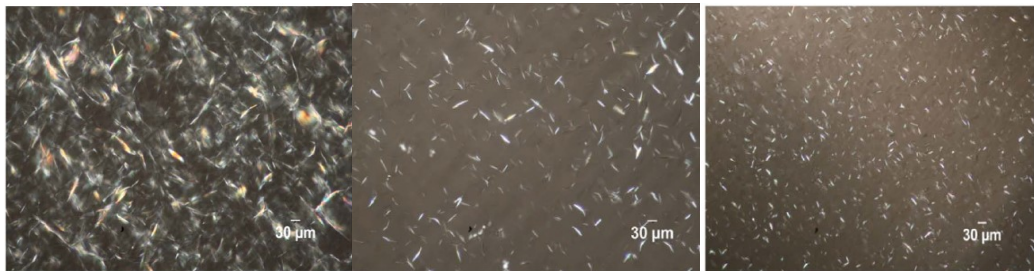


Figure 2.21 – NPPD and EVA crystal modification (Huang et al., 2018)

When it comes to optimum dosage of such additives, it is worth looking at the picture below... With increasing dosage of nanocomposite additives an improvement in rheological properties was noted, in general it is noticeable that the gelatinous structure is reduced. At the same dosage they are more effective than conventional polymeric additives. (fig.2.22) (Yao et al., 2016)

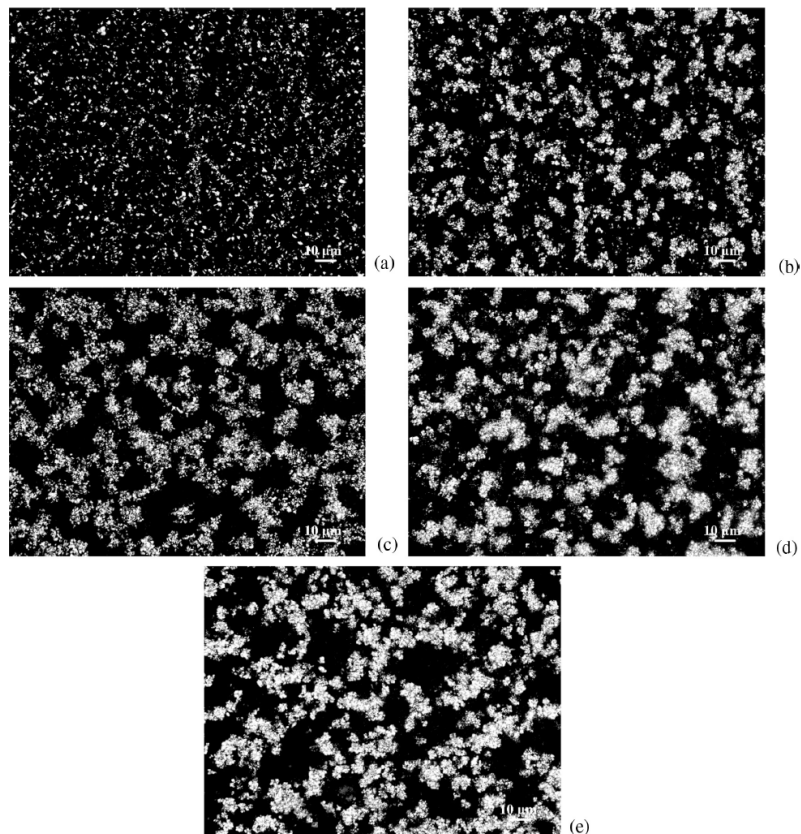


Figure 2.22 – Crystal modifications depending on of NPPD concentration (Yao et al., 2016)

2.5 Factors affecting the use and effectiveness of depressant additives

In general, the performance of depressant additives can be affected by various factors. The paraffin composition is generally considered to be the main one.

2.5.1 Paraffins

As stated earlier, paraffins include a number of different hydrocarbons in terms of structure and size. This composition is unique to each oil and, as previously stated, the crystallization process is dependent on the composition. Studies have shown that the composition of paraffins also affects the performance of additives. Additives are most effective with paraffins with a carbon number of at least 24. (N. Li et al., 2018)

2.5.2 Asphaltenes and resins

As previously discussed, polymeric depressant additives are surface active substances. Asphaltenes and resins are also asphaltene and resin. Because of these facts a mutual interaction between additives and asphaltene and resin cannot be excluded. (N. Li et al., 2018)

In this paper, surface tension coefficients of Difron 4201 additive, resins and asphaltenes of different mass contents were examined. The results are shown in the table below (Gurbanov et al., 2021)

Table 2.2 - Coefficient of surface tension of asphaltene components of the depressant additive "Difron-4201" and model oil, (MH / m) (Gurbanov et al., 2021)

Sample	Concentration, % mass				
	0.1	0.3	0.5	0.7	1
Difron – 4201	34,8	39,2	40,1	40,12	40,12
Asphaltene	51,6	53,2	54,4	54,41	54,41
Resin	35,2	38	41,6	41,6	41,6

Коэффициент поверхностного натяжения увеличивается согласно величине массовой концентрации компонента во всех случаях, при этом его прирост с повышением снижается так у депрессора, смол и асфальтенов заметный рост прекращается при концентрациях свыше 0,5. (Gurbanov et al., 2021)

Given the specific nature of the interaction of crystal and wax molecules with the additive, depressant additives must have a surface tension coefficient at least lower than that of asphaltenes and resins for best performance. In general, asphaltenes are the most polar constituents in oil so it is not surprising that their coefficient is the highest. (Gurbanov et al., 2021)

It is worth noting that since the surface tension coefficient of resins is close to the surface tension coefficient of the depressor, this fact would indicate the effect on the performance of the depressor itself.

2.6 The effect of the use of ultrasonic treatment on oil and ARPD

Sound waves with a frequency above 20 kilohertz are usually referred to as the ultrasonic range. The treatment of oil with ultrasound is not fully understood, but in general it is worth dividing it into two fundamentally different areas. The first one is ultrasound treatment of sludge and ARPD deposits, in which case mechanical treatment and surface cleaning is the key. The second direction is the effect of treatment directly on the oil. Let's consider each of these directions separately.

2.6.1 Comparative characteristics of the ultrasonic ASPO cleaning method

At the moment, there is a sufficient basis for the study of this issue. In the basis of this phenomenon to the forefront is that firstly this treatment was supposed to be used for cleaning of ARPD, abroad this application was suggested for stimulation of bottomhole formation zone and intensification of production. Such authors as H. Hofstatter, I. Beresnev, F. Van der Bas and others were dealing with these issues. However, it should be noted that there is a need for periodic cleaning of equipment from ARPD, as this problem has consequences of varying degrees of importance, as well as short and long term consequences. (М. В. Павлов et al., 2017; Хасанова К.И. et al., 2013; Хурамшина Регина Азатовна, Валеев Анвар Рашитович, et al., 2021)

2.6.1.1 The ARPD problem and current solutions

First of all, it is worth recalling that ARPD are mainly deposits on the surface of equipment in the oil pipeline industry. These deposits are found throughout the length of main pipelines, process pipelines, tank bottoms at both pumping stations and tank farms, etc. An example of these deposits can be seen in the figure 2.23 below. (Хасанова К.И. et al., 2013)



Figure 2.23 – ARPD deposits on the surface of the pipeline

The first consequence of ARPD deposition on main and process pipelines is the reduction of the cross-sectional area of the pipeline, which leads to the problem of reduced productivity and increased specific pumping costs. In addition, the relative roughness of the pipeline wall increases to a large extent, which also increases these effects. (Хасанова К.И. et al., 2013)

Secondly, deposits also contribute to the acceleration of corrosion of the pipeline wall, while due to the uneven process, the roughness grows many times, this leads to an increase in specific energy consumption during pumping due to friction losses, as well as a decrease in reliability and the cost of maintenance and repairs. (Хасанова К.И. et al., 2013)

The internal cavity of the oil pipeline is periodically cleaned to reduce the negative consequences. This usually involves mechanical cleaning by means of various pig designs and sizes, the commonly used CKP-4 pig is shown below, as well as the “CKP-4” pig immediately after the pipeline cleaning procedure. On the figures 2.24 and 2.25 below you can see Pig CKP-4” itself and after cleaning procedure of the pipeline. (Хасанова К.И. et al., 2013)



Figure 2.24– Pig SKR-4 before usage



Figure 2.25 – Pig SKR-4 after cleaning procedure

In tanks it is also possible for ARPD to accumulate at the bottom of the tank. Cleaning is nowadays possible by means of devices for flushing out these deposits. One of these Diogenes is shown in the figure 2.26 below. The principle of these devices is to create a flow at the bottom of the tank that lifts the bottom sediments away from the bottom (fig. 2.27). However, not all sediments can be removed by this type of cleaning and then mechanical cleaning with brushes, possibly using reagents for better removal, is carried out. (Хасанова К.И. et al., 2013)



Figure 2.26 – Diogen 700

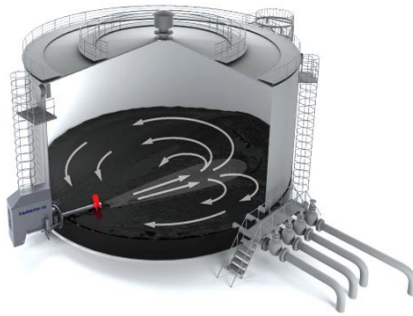


Figure 2.27 – Principles of work of the Diogen

2.6.2 Effect of ultrasound on ARPD

The above mentioned problems in oil transport and storage can be overcome by using the effect of ultrasound on ARPD. As described above, cavitation bubbles occurring at the wall-film interface can cause the ARPD to collapse. The mechanism is shown in figure 2.28. (M. B. Павлов et al., 2017)



Formation of a bubble at the surface under a layer



Separation piece of film from the surface at pulsation bul

Figure 2.28 – ARPD under ultrasonic treatment (M. B. Павлов et al., 2017)

The cavitation bubble generates a high temperature inside, and when it collapses, an enormous pressure is generated. The process itself proceeds at high speed. This phenomenon has been experimentally verified by experiments. In them, a contaminated plate was placed in a transparent cube of water (fig. 2.29). In the course of the experiment, cavitation on the surface of the plate was observed as well as turbidity in the water, directly indicating that the plate in question was purified in the process (fig. 2.30). The result of the experiment was a significant purification of the contamination film. The figure 2.31 below shows the result of the experiments. (М. В. Павлов et al., 2017; Т. И. Безымянников et al., 2018; Хурамшина Регина Азатовна, Соколова Виктория Владимировна, et al., 2021; Щурова Елена Владимировна et al., 2020)

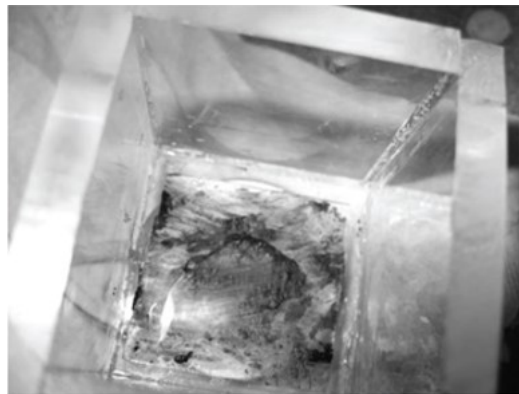


Figure 2.29 – Glass cube with ARPD on it (М. В. Павлов et al., 2017)

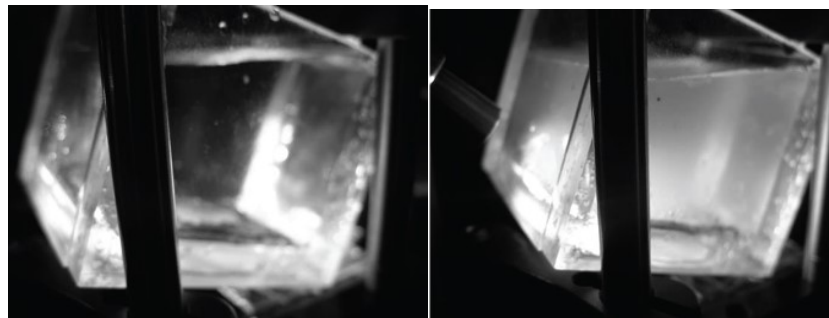


Figure 2.30 – Condition of the water before and after treatment (М. В. Павлов et al., 2017)

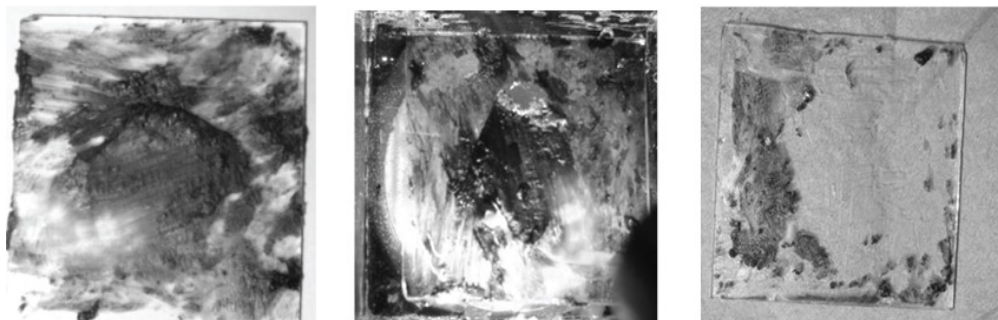


Figure 2.31 – ARPD under ultrasonic before(a), during(b) and after(c) treatment (М. В. Павлов et al., 2017)

As can be seen from the results of the experiments, the plate is indeed cleaned of ARPD and water turbidity in the process. However, there is an additional effect of dispersion and emulsification of liquid under the influence of ultrasonic treatment.

As we can see this effect can be applied in the pipeline transport of oil. In theory, it is possible to install evenly spaced ultrasound sources on the bottom of the tank, while their work will not cause mechanical damage to the bottom, this is important because if present, the corrosion process is accelerated. Thus we avoid corrosion and increased roughness. However, if the implementation of this system in a tank is relatively simple, on the whole length of the pipeline, it will significantly increase both operating and capital costs. On already constructed pipelines this system generally does not appear to be feasible. (М. В. Павлов et al., 2017; Т. И. Безьянников et al., 2018; Хасанова К.И. et al., 2013; Хурамшина Регина Азатовна, Валеев Анвар Рашитович, et al., 2021; Хурамшина Регина Азатовна, Соколова Виктория Владимировна, et al., 2021; Щурова Елена Владимировна et al., 2020)

2.6.3 The effect of ultrasonic treatment directly on the oil

It is now well known that when ultrasonic waves pass through liquids, there are successive zones of compression and rarefaction in the liquid, which ultimately leads to cavitation phenomena. Cavitation generally shows tensile strength of liquid bodies and manifests itself in the formation of bubbles in liquid bodies. However, the formation of cavitation bubbles is similar to the crystallisation process, it occurs similarly on discontinuities and inclusions in liquids. A single micro nucleation is sufficient for cavitation to occur. If gas bubbles are present in the liquid, their increase will be observed first. It is especially relevant for oil, as oil is a dispersed system with various inclusions and, strange as it may seem, there is no cavitation as such an entity. At the same time cavitation is divided into two types depending on its cause hydrodynamic arising from the flow around the obstacles and ultrasonic arising from treatment with ultrasound. (Feldman, 1989; K. Semionescu, 1970; V.A. Kargin, 1967)

If we talk about the effect of ultrasound treatment on polymer systems as natural (starch, rubber, etc.) will be found that their viscosity decreases. Such natural polymers are characterized by thixotropic liquefaction during passage of acoustic waves. The viscosity partially relaxed after removal of the ultrasonic load. Apart from the breaking of weak Van der Waals bonds, leading to a change in viscosity, the effect of ultrasonic vibrations is accompanied by destruction of macromolecules. Decrease of structural viscosity was also observed for solutions of synthetic polymers (polyacrylates, polystyrene, polyvinyl acetate, nitrocellulose). By the example of polystyrene it was shown that at different initial values of macromolecules the value of the latter after a long treatment in the ultrasound field is close to the minimum value of 30000 a. m. It is considered that the main factor of cavitation that influences the efficiency of

macromolecule degradation of polymers is the intensity of the ultrasound field. The higher it is, the higher number of cavitation bubbles and higher destruction rate is. (A. A. Berlin, 1958; V.A. Kargin, B.M. Kovarska, L.I. Golubenkova, 1957)

The macromolecular chain length also affects the rate of degradation of polymers (V.A. Kargin, 1967). As a result of these studies it was shown that the rate of degradation of macromolecules is linearly related to molecular mass and the attainable destruction limit decreases with increasing intensity of ultrasonic field. Cavitation bubbles contribute to breaking the bonds of molecules located near them, which is caused primarily by the large amount of deformation exerted on the molecules.. It is characteristic of rigid-chain polymers that bonds located in the centre of the macromolecule are loosened. According to the authors, the observed degradation is caused by the action of high intensity shear forces, rather than by the thermal and electrical effect of the cavitation process.

In (Kemalov A.F., Ganieva T.F., Fakhrutdinov R.Z., Khazimuratov R.H., Kemalov R.A., 2006) the effect of ultrasonic treatment on depressor properties of polymer solutions was studied. It has been experimentally proven that ultrasonic treatment of polymer solutions in an olefin solvent leads to the degradation of associates in solution, which leads to the effect of improving depressor properties. Scientists believe that this is due to a more uniform distribution in the solution after processing. It was noted that with increasing the duration of the ultrasonic treatment the relaxation time of the polymer in the solution increased, the values of viscosity and density of the solution decreased.

Thus, the development of chemical reactions in the ultrasonic field is closely connected to the phenomenon of cavitation, which is a process of bubble formation and disappearance of bubbles in a liquid medium under the action of ultrasonic waves accompanied by intense hydraulic impact. Exposure of the polymer solutions under study to acoustic field energy results in a decrease of viscosity and molecular mass as a result of fragmentation of chains into active particles. (M. A. Margulis., 1986)

Petroleum, its fractions and residues are not molecular solutions but colloidal disperse systems under ordinary conditions. Oil with high RAC content is characterized by anomalies in viscosity, electrophysical and other properties in the same temperature ranges.

In this (M. A. Margulis., 1986) work, oil with different chemical natures was treated. Under the influence of ultrasonic treatment, high-molecular molecules of various structures degrade, and the released radicals tend to combine with each other to form new high-molecular hydrocarbons of various structures, all this has experimental confirmation. The maximum effect was observed in paraffinaceous resinous oils.

In (B.P. Tumanyan, 1997; Ye et al., 2008) the possibility of using acoustic treatment to prevent scale formation on the oil equipment in the production, storage and transport of hydrocarbons was shown. Inorganic salts, which are in a dissolved state in formation water, crystallize during acoustic treatment due to an increase in the diffusion rate and other factors. The formed crystals are less deposited on metal parts and are much more carried away with water streams.

Changes in the rheological properties of oil from the Luzanovsky field occurred under the influence of both chemical reagents and after ultrasonic treatment. (M. A. Ershov, M. S. Mullakaev, D. A. Baranov, 2013; M.S. Mullakaev, 2011). It was shown that ultrasound leads to the destruction of the supramolecular structure of the oil dispersion system due to nonlinear acoustic effects. When used together, chemical reagents are uniformly delivered throughout the volume and prevent the recovery of destroyed supramolecular formations.

Pliss et al. (A. A. Pliss, V. P. Zolotov, A. V. Yakimov, 2007) conducted research to study the effect of ultrasonic treatment on the physical and chemical properties of oil from the Golubevsky field. It was shown that the viscosity of oil after 5 minutes of acoustic treatment decreased by 3 times. The authors explain this by the fact that under the influence of ultrasound there is a destruction of the structural lattice formed by molecules of paraffins, resins and asphaltenes. It is noted that after cessation of exposure the system is restored due to random Brownian motion. Changing the viscosity of oil Golubevsky field when exposed to an acoustic field, is due to the destruction of weak intermolecular van der Waals bonds. The authors believe that irreversible decrease in oil viscosity occurs when the intensity of ultrasonic vibrations 10 W/cm² or more.

The behavior of asphaltenes in petroleum systems when exposed to ultrasound has been studied in (Najafi & Amani; Shedid, 2004). Solvent concentration, temperature and ultrasonic treatment time were varied. The results showed that the size of asphaltene clusters in oil systems decreased under the influence of ultrasound. It was observed that after 10 min of acoustic exposure there was a tendency for asphaltene precipitation to decrease. It was also shown that increasing the ultrasonic treatment time and field frequency could significantly improve the permeability of carbonate formations. The mechanism of ultrasonic treatment action on asphaltenes has been proposed. According to the authors, under the ultrasound action asphaltene aggregates decompose and the subsequent recombination of the formed radicals, which leads to the formation of a new asphaltene particle.

The study of changing rheological properties of high-paraffin oil of Kharyaga field was carried out in (B.A. Ostashchenko, 2007). It was shown that resin paraffin content with the addition of water can significantly improve rheological properties of oil and significantly prolong the relaxation period of these properties. The author assumes that the long period of recovery of

structural and mechanical properties of oil is caused by blocking hydrogen and hydroxonation of water active parts of paraffin molecules, destroyed in the ultrasonic field.

In the work of Promtov M. A. (Promtov, 2017) shows that to influence the kinetics of distillation and cracking processes, which are the main technologies of oil and petroleum products refining, is possible by various chemical and physical methods, resulting in the restructuring of complex structural unit, changing the core radius and the thickness of the adsorption-solvate shell complex structural unit.

In the technology of intensive separation of hydrocarbon raw materials (TIRUS) the ultrasonic cavitation conditions is used, in the action of which there is a thermomechanical impact on the oil, initiating a low-temperature destruction of its components without the use of catalysts (V.A. Zolotukhin, 2004).

Work (A. K. Kurochkin [et al.], 2005) describes the "Visbreaking-Thermocat" technology, which is based on mild thermal cracking, intensified by acoustic treatment of the fluid under study. The ultrasonic field energy is injected into the liquid resulting in changes of hydrodynamics and dispersion stability of liquid media. The cavitation method results in significant reduction of coke formation processes and intensification of destruction processes, as well as considerable reduction of cracking temperature up to 410 °C, pressure from 2,5 to 0,2 MPa, and several times reduction of equipment metal consumption.

SulphCo'sopocask technology uses powerful ultrasound to treat a mixture of crude oil and water to change the molecular structure of water and hydrocarbons (A.F. Nemchin [et al.], 2002). The technology uses catalysts developed by SulphCo. As a result, as in other studies, the authors of this study showed an increase in light fractions, which could arise from high-molecular components, whose content was reduced. An important result was also the reduction of the sulfur content in the oil.

The transformation of oil residues under the action of ROC has been studied by the authors (I. R. Telyashev, A. R. Davletshin, R. R. Vezirov, 1996). It was noted that as a result of acoustic treatment there is a change in the chemical composition of the oil residue, namely, the content of asphaltenes increases and the content of paraffin-naphthenic hydrocarbons decreases. It is also shown that with increasing frequency of ultrasound decreases the degree of conversion, and with increasing intensity of treatment there is a rapid overheating of the sample under study.

Besov A.S. et al. on the example of n-decane and n-octane showed the principle possibility of the processes of chemical destruction of hydrocarbons in the cavitation region with additional influence of an electric field (A. S. Besov [et al.], 2003). The electric discharge arising inside the cavitation bubble leads to the formation of free radicals. It was shown that the above method of exposure to n-decane and n-octane produces about 2% of unsaturated hydrocarbons (ethylene

and 1-alkenes) and aromatic compounds, mainly benzene. Also on the example of n-decane in (Suslick et al., 1983) it was shown that ultrasound exposure leads to breaking of intermolecular bonds followed by recombination of various radicals and formation of new substances.

Cavitation was believed to have a negative effect on pipeline walls, namely it increases wear and tear on the working parts, which can significantly shorten their service life. In this connection, the effect of ultrasonic cavitation on oil pipeline condition was investigated. The authors (Крапивский Евгений Исаакович et al., 2011) showed with the help of remote electromagnetic diagnostics complex that cavitation process is not so destructive as it was supposed by many researchers. The process of pipeline structure change takes place, but serious destruction of the pipeline inner surface is not observed. These changes are only characterised by a slight increase in the stress state of the pipeline.

In (V. N. Khmelev, S. N. Tsyganok, Yu., 2012) the effect and effectiveness of ultrasonic impact on the process of separation of stable emulsions into their components has been studied. During processing at a frequency of 44 kHz and a power of 4 W/cm², water drops became larger, began to fall out and settle on the bottom of the vessel. The process of separation of the emulsion showed an efficiency in direct proportion to the increase in exposure time. The authors found a direct dependence of separation intensity on the radiation area of ultrasonic oscillations. In the absence of ultrasonic vibrations, separation ceased.

The optimum ultrasonic treatment conditions for high viscous and non-Newtonian liquid media were determined in (V.N. Khmelev, A.V. Shalunov, R. N. Golykh, S. S. Khmelev, 2014). Based on the results of these studies, a model of cavitation area formation was proposed, which made it possible to identify the distribution of cavitation zones in different sizes and shapes of technological volumes.

In the monograph (V. N. Khmelev, G. V. Leonov, R. V. Barsukov, S. N., 2007) describes the results of research and development aimed at solving problems of improving the efficiency of processes of chemical and related technologies through the optimization of ultrasonic influence on various media. Considered the creation of specialized vibrating systems capable of establishing and maintaining the mode of ultrasonic influence with maximum efficiency, recommendations for the use of ultrasonic equipment in industry, agriculture and households are given.

Thus, many currently produced oils are characterized by high paraffin content, which deteriorates their low-temperature properties and creates certain difficulties during transportation and storage. To improve the viscosity-temperature properties of oils various physical methods of treatment are applied. One of the most promising methods of oil treatment is ultrasonic exposure. As a result of ultrasonic treatment of oils by intensive acoustic field

there can be a breakage of intermolecular bonds, which is explained by the occurrence of cavitation processes in the oil disperse system. Processing of paraffinic oils with high content of resino-asphaltene components leads to improvement of structural-mechanical parameters at optimal time, temperature and pressure. On the other hand, since PPDs are polymeric additives, they may be destroyed during ultrasonic treatment.

The paper considers the effect of ultrasonic treatment on oil disperse systems. The author applies it in static conditions at a frequency of 22 kHz. The treatment time varies from 30 seconds to 15 minutes for each oil. At the same time for paraffinic and high-paraffinic oil it is clearly seen that with increasing treatment the result becomes more significant in the case of changing the pouring temperature. However in the first case the pour point decreases and in the second case it increases on the contrary with the difference being most noticeable at 15 minutes treatment. This pattern is observed for any high-paraffin oil, regardless of the content and ratio of resinous asphaltene components. As the treatment time increased, the solidification temperature increased. Thus, as a result of ultrasound treatment of Verkhne-Salatovskoe oil field the oil increased its pour point from +8 to +17 degrees Celsius. The results of processing at different times can be seen in the table 2.3 below. (R.V. Anufriev, 2017)

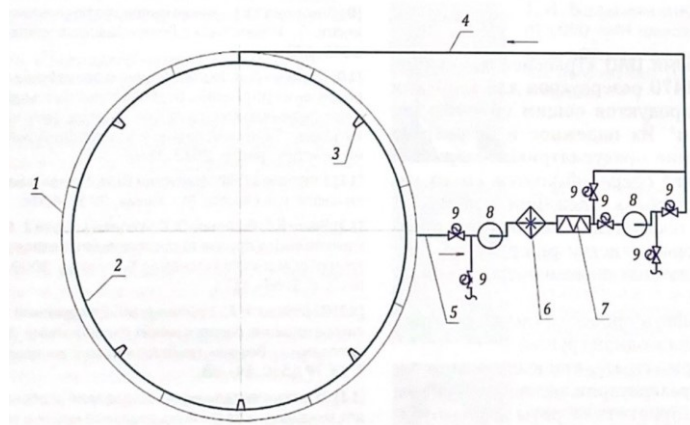
Table 2.3 - Verkhne-Salatovskoe oil field pour point measurement (R.V. Anufriev, 2017)

Time of UST, min	T _{por point} , °C
0	+8
5	+ 11
10	+ 16
15	+ 17

The author of the work also considered the reasons for this phenomenon and believed that the reason is the changes in the oil dispersed system under the influence of ultrasound treatment, which contributed to the increase in pour point. (R.V. Anufriev, 2017)

2.6.4 The effect of ultrasonic treatment directly on the oil with ARPD

This paper considers the use of ultrasound to remove bottom sediments, but in contrast to the simple treatment wax sediment inhibitors were used. The scheme was to circulate oil according to the scheme shown in the figure. the oil was pumped out of the tank, heated, treated with ultrasound and then back into the tank, eroding the sediments. (Fazlyev et al., 2021)



: 1 – tank to be cleaned; 2 – ring pipe (Dy 100);
 3 – hydraulic monitor; 4 – receiving pipe (Dy 150); 5 – discharge pipe (Dy 150); 6 – heat exchanger; 7 – ultrasonic device;
 8 – axial diagonal pump (UODN-360-250-250); 9 – electric gate valve

Figure 2.32 – Scheme it self (Fazlyev et al., 2021)

In this work, the authors subjected the oil to ultrasonic treatment together with wax inhibitors. The treatment occurred at a frequency of 20 kHz at three different power levels. The efficiency of the treatment was calculated based on the amount of dissolved ARPD mass in the oil. As the intensity increased, the result improved and at maximum power the effect reached a 40 percent increase in mass compared to the untreated oil. In general, the results can be seen in the figure 2.33 below.

Состав смеси Composition of mixture	Мощность ультразвукового генератора, % Power of ultrasonic generator, %	Амплитуда колебаний, мкм Amplitude of vibration, microns	№ пробы Sample No.	Масса нефти с АСПО, г Mass of oil with asphalt-resin- paraffin deposits, g	Эффект, г Effect, g
Нефть + 10 % АСПО Oil + 10 % asphaltene-resin- paraffin deposits	-	-	1	1,5631	-
	50	15	2	1,6116	0,0485
	75	22	3	1,7982	0,2351
	100	30	4	2,5059	0,9428

Figure 2.33 – Effect on oil with ARPD (Fazlyev et al., 2021)

It is important to note that ultrasound contributed to the synergistic effect of the combined effect of ultrasound on the oil, this was observed both visually and in the reduction of viscosity. At the same time, the authors believe that such treatment can reduce the pour point.

The result of this treatment is that by changing the dispersion medium of oil paraffins become dissolved in the oil. The result of the internal survey is shown in the figure 2.34. In other words, the positive effect of the combined effect of inhibitor additive and ultrasound on highly paraffinic oil has been achieved. (Fazlyev et al., 2021)

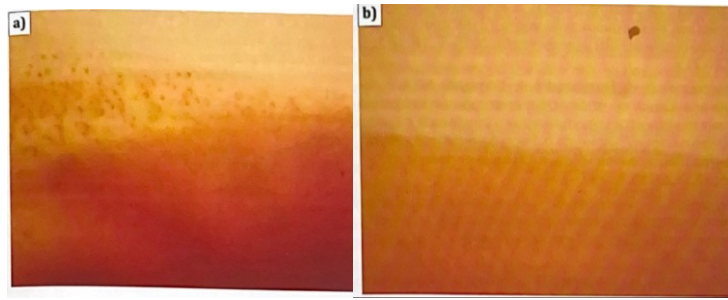


Figure 2.34 – Effect on paraffins, a – before, b – after (Fazlyev et al., 2021)

Chapter 3

Technical Chapter

In this chapter we discuss the research methods, equipment and standards involved in studying the effects of ultrasound on oil and oil depressant additives. In general, our task is primarily to measure the pour point of oil under different injection conditions. Furthermore we will treat oil with ultrasonic waves in order to check the possibility of activation of the pour points, not by the temperature but by the ultrasonic treatment.

3.1 The main stages and components of an experiment

In general, the experimental part will consist of four phases. The first phase is to measure the properties of the oil itself without additives. For us the density is the target, because it will be used for measuring the dosage of the depressant additive. And also the pour point as a key parameter in relation to which we can measure the efficiency of the treatment. In total, we will conduct at least 5 experiments. The layout of this phase is shown in Table 3.1 below.

Table 3.1– Plan of the first phase of experiment

Measured parameter	Repeated	Standard of measurement
Density, kg/m ³	2	GOST 3900-85
Temperature of crystallization, °C	3	GOST 20287-91

The second phase is to measure the pour point of oil with three different additives at the dosages shown in Table 3.2. The pour point measurement procedure will be carried out according to GOST 20287-91. Each experiment will be repeated at least twice. The result of this phase shows the effect of depressant additives only. (GOST 20287-91; GOST 3900-85)

Table 3.2– PPD dosages in

Concentration of depressant, ppm	50	100	250	500
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The third phase will already consist of measuring the pour point at different concentrations of additives and ultrasonic treatment. In this case, the additive concentrations are the same as in the second phase to be able to assess the impact of ultrasonic treatment.

The fourth phase is to measure the pour point of the oil, only treated with ultrasound. The reason for checking the interaction of pure oil with ultrasound is that the pour point may, based on our assumptions, have to increase. This temperature will allow us to evaluate the effect of ultrasound itself on the oil.

3.2 First phase of the experimental part

As mentioned earlier, this is the initial phase and only considers the physical properties of the oil itself. It is important to understand that the oil provided to us is marketable. It is already prepared for transport and use according to standards. For us this means a low content of water, dissolved gases (both hydrocarbon and carbon dioxide, nitrogen and oxygen), mineral impurities, salts as well as metals and their ions in the oil itself.

3.2.1 Measurement of density

The density is measured according to GOST 3900-85. This standard requires a areometer, a measuring cylinder and a thermometer. The cylinder and areometer must comply with GOST 18481-81. According to it, we can use general-purpose areometers of series "AON-X", where X is a number of areometers in accordance with definite density range of GOST 18481-81 annex. Such areometer is shown in figure 3.1 below. A cylinder with a capacity of at least 100 ml is also shown in figure 3.2 below. (GOST 18481-81)



Figure 3.1 – Densimeter

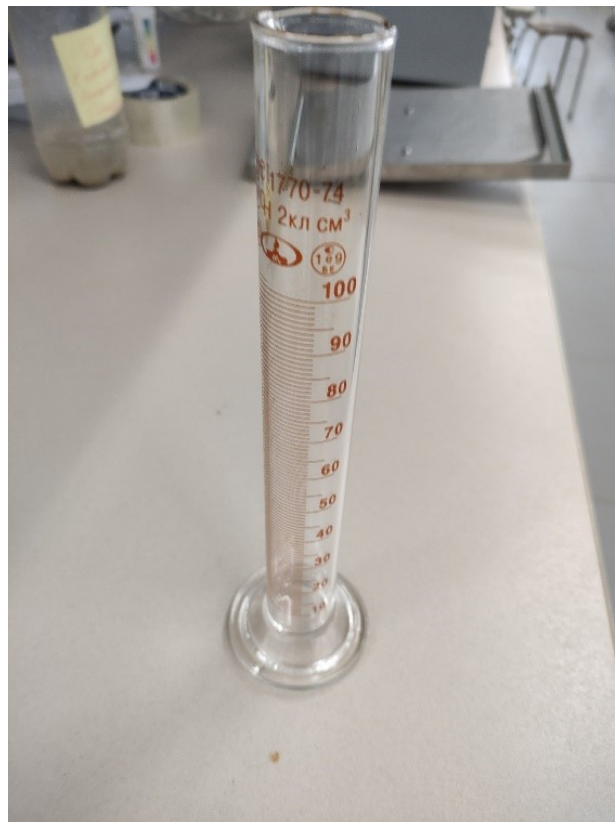


Figure 3.2 – Measuring cylinder

Place the areometer cylinder on a flat surface. Pour a 100 ml sample of the product to be tested into a cylinder of the same temperature as the sample, avoiding the formation of bubbles and losses from evaporation by keeping it at room temperature for a long period of time when there is sufficient fluidity of the oil. The temperature of the poured oil sample is measured before and

after the density measurement to avoid thermal expansion. Air bubbles that form during mixing or pouring are removed with filter paper for a clear view of the interface.

The clean and dry areometer is slowly and carefully lowered into the cylinder with the tested product, holding the areometer by its upper end to avoid wetting the part of the rod above the immersion level of the areometer.

When the areometer settles down and stops oscillating, read out from the top end of the areometer with the eye at the level of the areometer. The indication of the scale located at the level of the liquid mirror is an indication of the density of oil according to the hydrometer, while it is necessary to take into account the surface tension of the liquid and the wetting of the surface of the hydrometer, while repeating the experiment 2 times to eliminate errors.

The density should be recalculated to the temperature 20°C, taking into account thermal expansion of areometer glass. This is done according to the formulas:

$$\rho_t = \rho_{at} \cdot K \quad (3.1)$$

where ρ_t - real density of oil with temperature t ,

ρ_{at} - density of oil with temperature t , shown by the areometer,

K – coefficient for temperature of glass expansion of areometer.

When measuring density in liquid media with a hydrometer, due to the effect of temperature, thermal expansion of the hydrometer glass is possible. Since our series of hydrometers was verified at 20 degrees Celsius, we will take this into account using the formula below for the thermal expansion coefficient.:

$$K = 1 - 0,000025 \cdot (20 - t) \quad (3.2)$$

where t – temperature of oil.

After conversion, we round up first to integers. Then we round up to tenths, but remember the part we have removed. In other words, if we had 756 we round up to 760, but remember to subtract 4. Then, according to the measurement temperature and rounded density from the conversion tables in GOST 8.610-2004 we define the density at 20°C. (GOST 8.610-2004)

3.2.2 Pour point measurment

The pour point of oil requires a special approach, in our case we carry out these measurements and the procedure in accordance with the GOST 20287-91 standard. In general, in the process it is necessary to observe heating to a certain level and cooling no faster than the required speed, until the oil loses its fluidity. This temperature is taken as the pouring temperature.

The sample is filled into a transparent flask beforehand up to the mark (fig. 3.3), then the flask is placed into a LOIP LT-116a circulation thermostat (fig. 3.4), heated to 55.1 °C. A thermometer graduated in 1 °C is attached to the flask (fig. 3.5).



Figure 3.3 – Glass flask

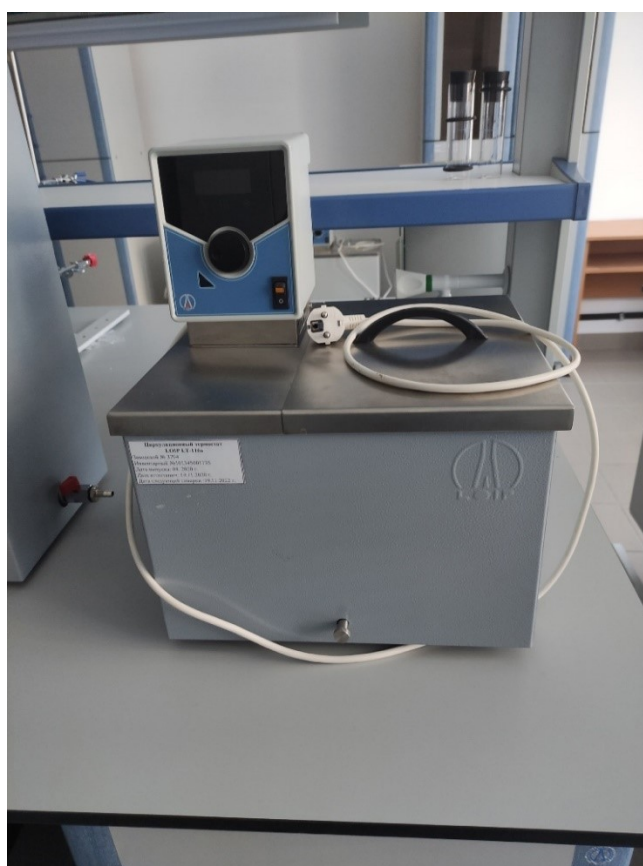


Figure 3.4 – Circulation thermostat LOIP LT-116a



Figure 3.5– Measuring thermometer

As soon as the oil sample reaches a temperature of 50 ± 1 °C, remove the tube, remove the remaining liquid on the outer surface of the wall, and leave to cool at room temperature. Once the sample tube cools down to a temperature of 30 ± 5 °C we move on to the next step.

After cooling in air the flask with sample is placed in the tray from LAB-CTT equipment set (fig. 3.6) and then placed in LOIP FT-311-80 cryothermostat (fig. 3.7). When the temperature drops, the flask is removed and placed on a 45 degree inclined tripod. As soon as the oil sample at an inclination of 45 degrees and within 1 minute will not have any manifestation of the movement of the liquid mirror, then the temperature at which the observation was made is the stagnation temperature of this oil. .



Figure 3.6 – LAB-CTT kit for Cryo-thermostat LOIP FT-311-80



Figure 3.7– Cryo-thermostat LOIP FT-311-80

3.3 Second phase of the experiment

In this phase we determine the pour point by heating the oil in parallel with the depressant additive at a mixing temperature of 50 °C,

Initially an oil sample (50-100 cm³) is taken and measured with the measuring cylinder used earlier. The total tank of oil is pre-stirred and the temperature is measured; the data are entered in a table to convert the density of oil at a given temperature according to a formula:

$$\rho_{t1} = \rho_{20} + \xi \cdot (20 - t) \quad (3.3)$$

where ξ - is the coefficient of thermal volume expansion, 1/deg;

t - is the temperature at which the density is required, °C;

ρ_{20} - is the density of the liquid under standard conditions ($t = 20$ °C, $P_a = 0.1013$ MPa).

The coefficient of thermal volume expansion is depending on the oil density at 20 °C and will be calculated by the formula:

$$\xi = 1,825 - 0,001315 \cdot \rho_{20} \quad (3.4)$$

The oil in a closed vessel is placed into a LOIP LT-116a circulation thermostat where it is heated to a temperature of 50 °C and allowed to stand for 30 minutes. The depressant is also loaded into the thermostat for heating and maintaining the input temperature of 50 °C.

Depressor additive is introduced into the oil sample with the help of micropipette "KOLOR" (fig.3.8) and stirred on the stirrer of LAB-PU-02 type (fig.3.9) for 5 minutes.



Figure 3.8 - Micropipette "KOLOR"



Figure 3.9 - Stirrer of LAB-PU-02

The amount of depressant additive in cm^3 is calculated according to the formula:

$$V_{ppd} = \frac{C \cdot (1 - N) \cdot \rho_o \cdot V}{10^6 \cdot \rho_{ppa}} \quad (3.5)$$

where V_{ppd} – required volume PPD, microl;

C – concentration of the additive, g/t (ppm);

N – water cut;

ρ_o – density of oil at several temperature, g/cm^3 ;

ρ_{ppa} – density of the pour point depressant at $50\text{ }^\circ\text{C}$, g/cm^3 ;

V – volume of the sample of the oil, cm^3 .

A sample of oil with an additive is poured into the test tube, filling it up to the mark. Further, the cooling process is similar to the previous phase: cooling at room temperature to $30 \pm 5\text{ }^\circ\text{C}$ and subsequent placement in a cryothermostat. After cooling in air the flask with the sample was placed into the tray from the LAB-CTT equipment set and then placed into a LOIP FT-311-80 cryothermostat. When the temperature drops, the flask is removed and placed on a tripod inclined at a 45 degree angle. The first temperature value at which there is no movement of the free surface of the liquid within 60 seconds is taken as the required temperature of solidification of oil.

3.4 Third phase of the experiment

When determining the pour point at $20\text{ }^\circ\text{C}$, a 50-100 cm^3 oil sample in a sealed vessel is first incubated for 30 minutes at $20\text{ }^\circ\text{C}$ in a LOIP LT-116a thermostat and then the calculated quantity of additive is injected using a "KOLOR" micropipette. The additive is heated at 50 degrees and incubated at this temperature in an analogous thermostat. The sample with the additive is stirred for 5 minutes on a stirrer of the LAB-PU-02 type. The sample is then poured into a beaker placed inside the ultrasonic treating unit, where it will be affected for 15 minutes. At the end of the treatment, the beaker is removed, the oil is stirred with a glass rod and poured into a test tube marked, closed and the temperature after treatment is measured. The data is recorded. During ultrasonic treatment, heating is often observed, therefore, when heated above 35 degrees, we will not be able to immediately place the sample in the cryothermostat, therefore, as in other phases, we cool it at room temperature to 30 ± 5 degrees and only then continue cooling in the cryothermostat. The pour point is determined according to the same criteria as in the previous phases.

3.4.1 Ultrasonic unit and treatment process

The ultrasonic unit is a complex consisting of a cabinet, the generator itself and a cooling thermostat, shown in figure 3.10 and principal scheme in figure 3.11. Inside the cabinet on the stand the test tube is installed into which the tip - the source of ultrasonic vibrations in figure 3.12.



Figure 3.10 – Ultrasonic treatment unit, 1 – cabinet, 2 – control device, 3 – thermostat

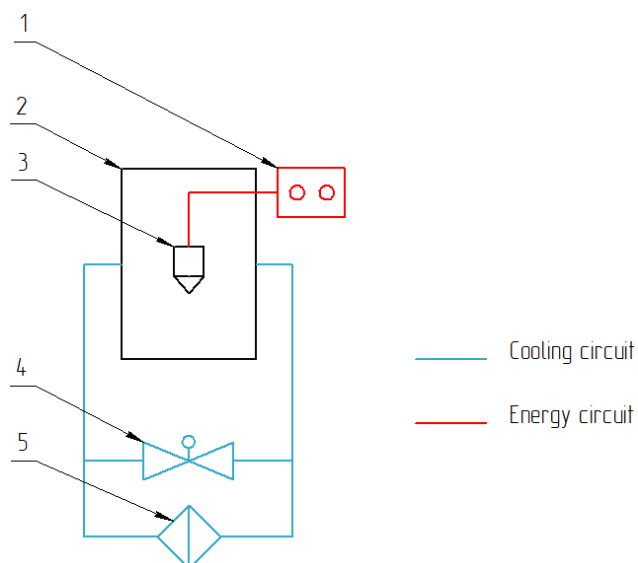


Figure 3.11 – Ultrasonic treatment unit, 1 – control device, 2 – cabinet, 3 – probe and generator, 4 – cabinet, 5 – thermostat

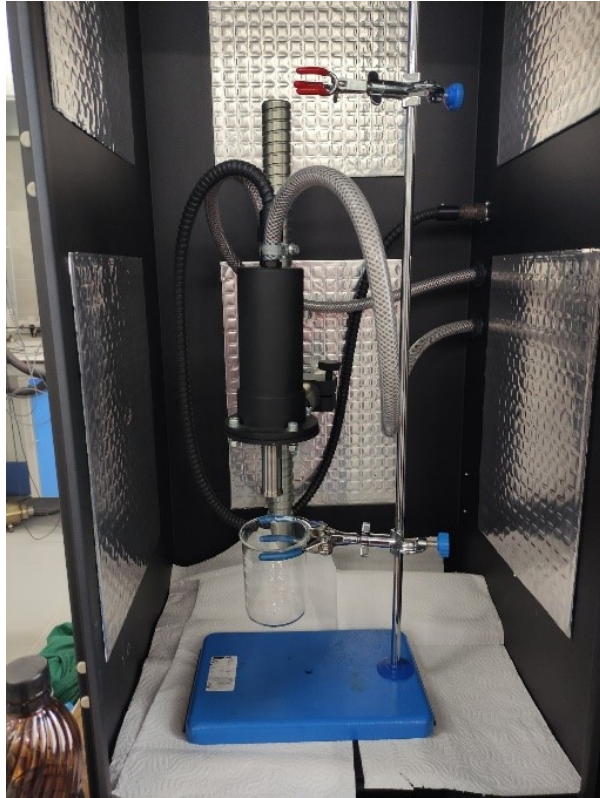


Figure 3.12 - Source of ultrasonic vibrations

The probe itself can be of three types: constricting, straight and expanding (fig. 3.13). When setting up the device, first select the type of nozzle, then set the frequency, power, pulse time, pause and timer. In our case, the following parameters are selected: frequency 22 kHz, power 60 per cent, pause 0 seconds, pulse 1 second, timer set for 15 minutes.

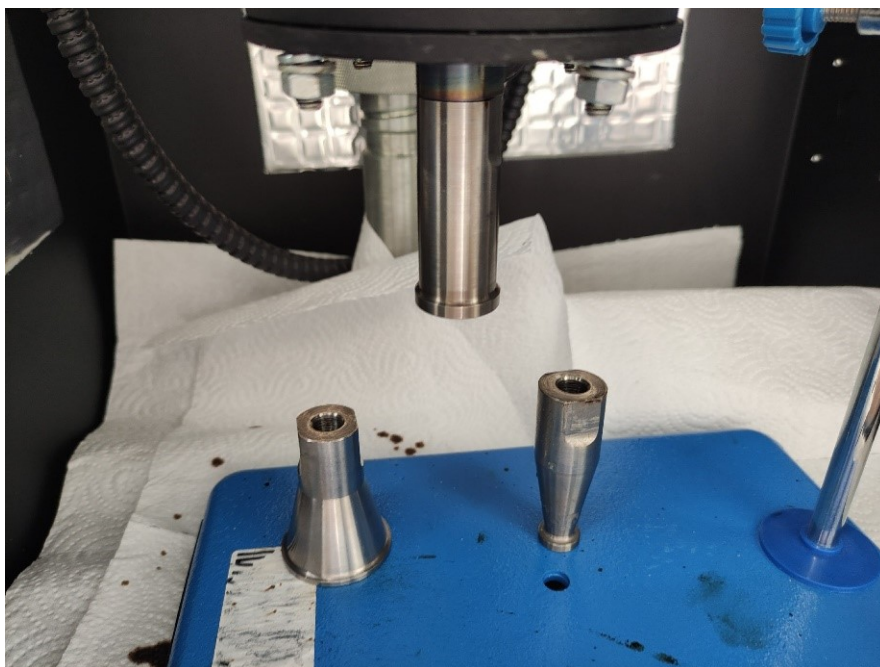


Figure 3.13 – Probe types

3.5 Fourth phase of the experiment

At the last stage of the experiment, we will consider the effect of ultrasonic treatment only on highly pourable oil, in this experiment there will be no depressant additives, while the pure effect of the treatment itself will be revealed. The procedures themselves carried out with highly congealing oil almost completely coincide with the previous one

3.6 Pour point additives characteristics and properties

We needed three samples of depressant additives to investigate the possibility of depressant activation by ultrasound. Manufacturer of additives scientific-production association "Chimtech" provided samples of additives Chimtech 4980 and Chimtech 5978. Ecoplastics Ltd. also presented ethylene vinyl acetate of EA33400 brand from producer LG Chem containing 33% of vinyl acetate groups in mass number. From this polymer we will make additive DPN-1.

3.6.1 Pour point additives Chimtech series

The additives provided by "Chimtech" Chimtech 4980 (fig. 3.14) and Chimtech 5978 (fig. 3.15) are EVA polymer rasters, but the solvent, mass number of vinyl acetate groups is unknown as it is a trade secret. These additives are in commercial form, i.e. ready for direct use and mixing with oil.



Figure 3.14 – Chimtech 4980



Figure 3.15 – Chimtech 5978

Figure 3.14 shows that Chimtech 4980 at room temperature is a white turbid monolithic gel-like mass. When heated to 50 degrees, it becomes a viscous, sticky, transparent liquid with a yellowish colour. Density of the given additive at temperature value 50 0C varies within the limits from 0,800 to 0,920 g/cm³.

As shown in figure 3.15, Chimtech 5978 at room temperature is a white, cloudy, monolithic, gelatinous mass. When heated to 50 degrees it becomes a viscous, sticky, transparent liquid and yellowish in colour. The density of this additive at 50 0C ranges from 0,820 to 0,940 g/cm³.

3.6.2 Ethylene vinyl acetate EA33400 and additive DPN-1

EVA at room temperature are transparent pellets 3 to 4 mm in diameter (fig. 3.16). They cannot be used by themselves as depressant additives. It has to be developed on its own.



Figure 3.16 - Ethylene vinyl acetate EA33400

DPN-1 is a 16 wt% solution of EVA polymer in winter diesel fuel. The main difference between summer and winter diesel is in its composition. The winter grade contains depressant additives that improve fuel properties at negative temperatures. This allows it to be used in cold and extreme conditions without encountering blockages in the fuel system. It also cleans more deeply from dissolved paraffins compared to summer grades. This solvent is widespread in the Russian Federation and easy to use.

Preparation of the additive begins with measuring out 32 g of EVA granulate and 168 g of diesel fuel. The mass is measured on a laboratory balance (fig. 3.17). A clean chemical beaker (fig. 3.18) is placed on the scale and its weight is recorded. Then the beaker is filled to the required mass and the data are recorded again. After the beaker has been emptied, the weight of the beaker is also measured so that the amount remaining on the beaker walls can be taken into account.



Figure 3.17 – Laboratory scales



Figure 3.18 – Laboratory beaker

At room temperature EVA does not dissolve in diesel fuel, therefore we put them into a container and gradually heat them up in a circulating thermostat to 80 degrees Celsius. While heating, periodically remove the container and stirring for 1 - 2 minutes on a stirrer, type LAB-PU-02. When the temperature of 80 degrees Celsius is reached, keep the container for at least 30 minutes and stir again. Repeat the procedure several times until a homogeneous solution is obtained. The final concentration is calculated by the formula 3.6

$$C_{DPN-1} = \frac{m_{EVA}}{m_{EVA} + m_{df}} \cdot 100\% \quad (3.6)$$

where m_{EVA} – total mass of EVA, g;

m_{df} – total mass of winter diesel fuel, g;

C_{DPN-1} – achieved concentration, %.

The density of this fit will be measured by pouring 100 cm³ of additive preheated to 50 degrees Celsius into a measuring cylinder on a scale to measure the mass. With the known mass and volume the density is calculated.

Chapter 4

Results and Discussion

4.1 Results Section

We will divide the results of our experiments into two subsections, one of which will be the results of measurements of oil quality together with the additive and the additive together with the ultrasonic treatment. The other will deal with all the other measurements and processes we will do with crude oil without additives, which we will look at first

4.1.1 Measured oil qualities

Here we are only looking at the properties of oil

4.1.1.1 Density measurement

The density measurement was carried out according to GOST 3900-85 according to the plan described above. The oil temperature before and after was 21.5 degrees Celsius in both tests (fig. 4.1). The areometer showed a density of 881 kg/m³ in both cases as well. The density measurement itself is shown in figure 4.2.



Figure 4.1 – Temperature measurement after density measurement



Figure 4.2 – Density measurement

In doing so, we remember to recalculate to a density at 20 °C. To do this, we will first use the effect of the thermal expansion of the glass according to formula 3.1 and 3.2.

$$K = 1 - 0,000025 \cdot (20 - 21,5) = 1,000038 \frac{1}{^{\circ}\text{C}}$$

$$\rho_t = 881 \cdot 1,000038 = 881,033 \approx 881 \frac{\text{kg}}{\text{m}^3}$$

As the effect of glass expansion is quite small, we round up to a whole. Then we use the conversion tables from GOST 3900 to determine the density of oil at 20 °C, which is 882 kg/m³.

Our task for the future is also to recalculate the density of oil using formulas 3.3 and 3.4 at temperatures between 18 and 25 degrees Celsius (the results of the calculations are presented in Table 4.1 and a plot on fig.4.3).

$$\xi = 1,825 - 0,001315 \cdot 882 = 0,6652 \frac{1}{^{\circ}\text{C}}$$

$$\rho_{21} = 882 + 0,6652 \cdot (20 - 21) = 881,3 \frac{\text{kg}}{\text{m}^3}$$

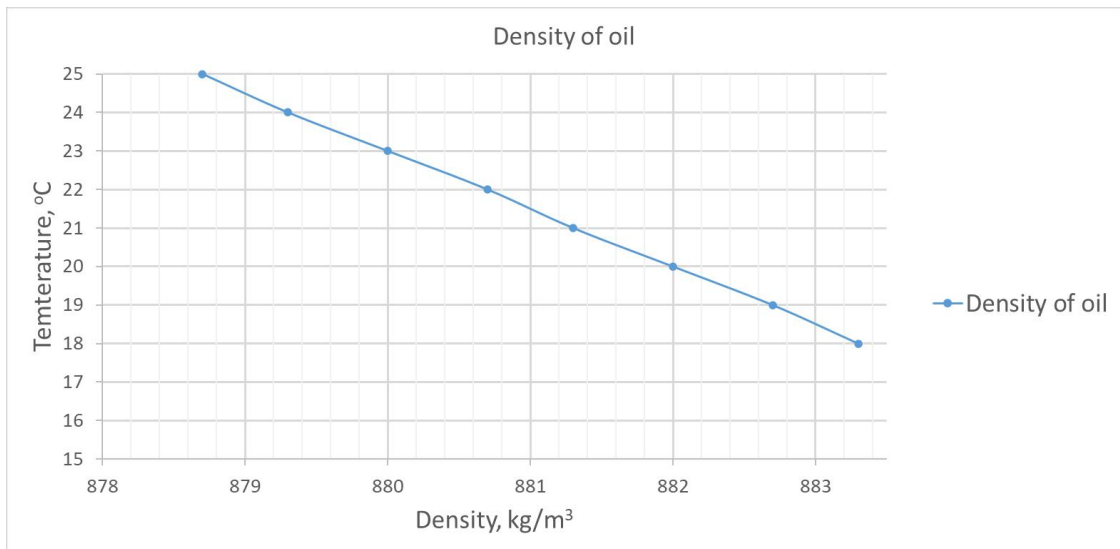


Figure 4.3 – Density of oil

4.1.1.2 Pour point measurement

As previously discussed, the volume of the sample is placed up to the mark, the test tube is closed, a thermometer is placed in it, the test tube (fig. 4.4) is placed in the thermostat and incubated for 30 minutes after reaching a temperature of 50 degrees Celsius (fig. 4.5).



Figure 4.4 – Oil in the flask with thermometer

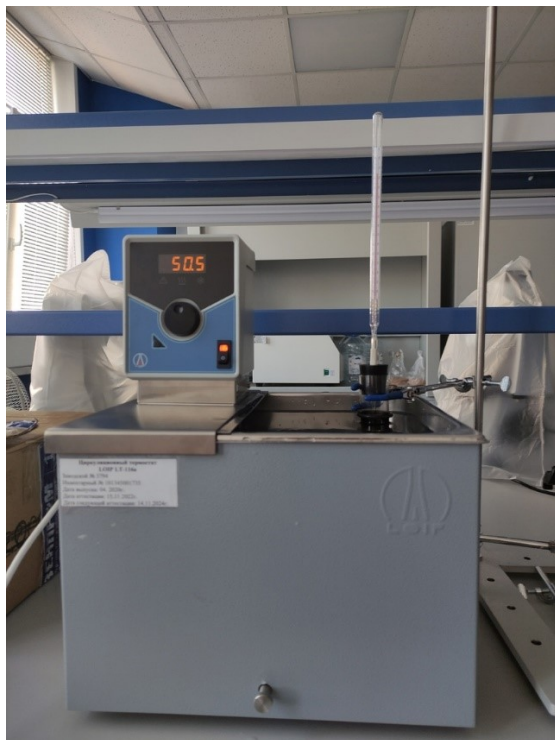


Figure 4.5 – Flask in thermostat

The test tube was then placed in a cryothermostat and checked periodically for movement of the liquid interface mirror. When it was present (fig. 4.6) the tube was kept in the cryothermostat . Then when the mirror movement became less noticeable the tube was placed on a tripod set at an angle of 45 degrees to the horizon (fig.4.7).

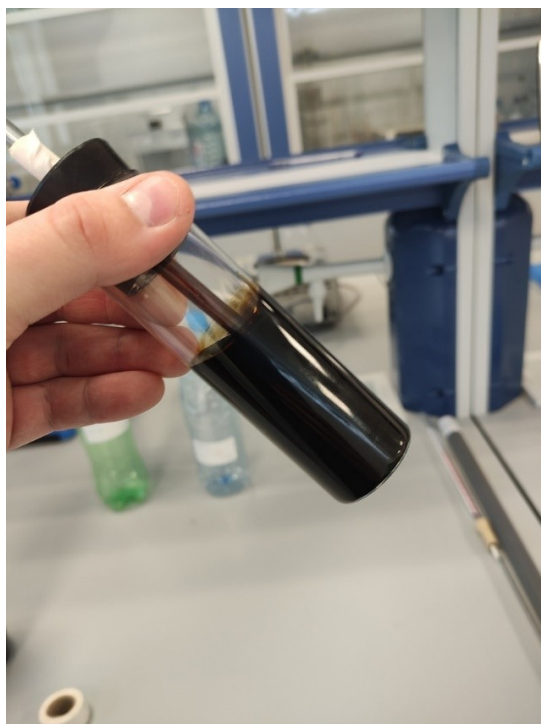


Figure 4.6 – Checking of movement

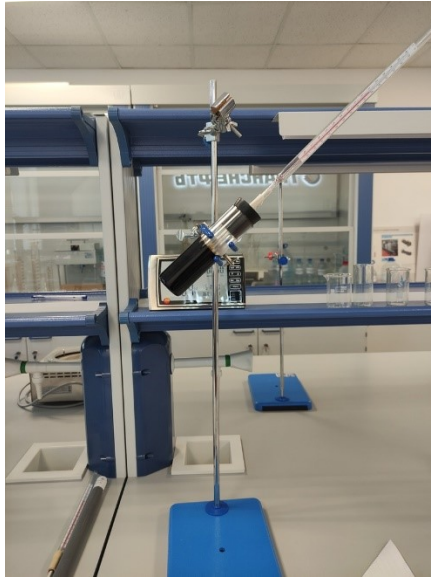


Figure 4.7 – Checking of liquid surface movement

As a result of three experiments, we noted that the pour point of oil is +8 degrees, which directly confirms its high pour point, while the result in all experiments was the same.

4.1.1.3 Effect of ultrasound treatment on oil properties

In this subchapter we will look at the facts that arise when treating oil with ultrasound.

An oil volume of 100 cm³ at 20 degrees Celsius is placed in a beaker. The tip is then immersed (figure 4.8) and the treatment begins.

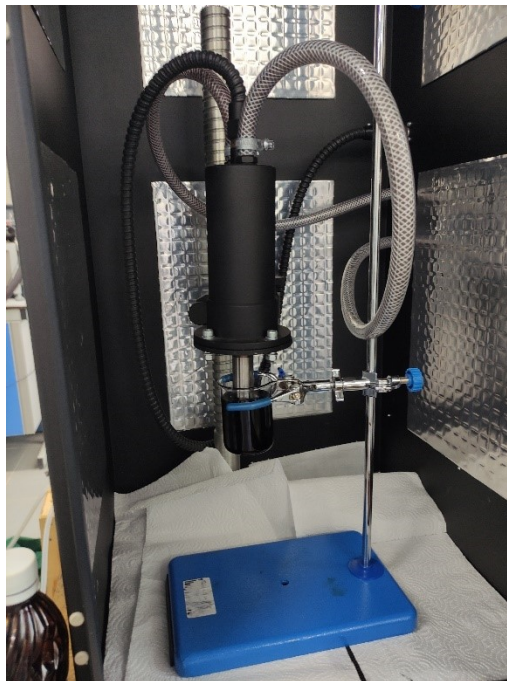


Figure 4.8 – Immersed tip

After switching on the ultrasound, wave-like disturbances on the surface of the liquid appear, after about 30 seconds the formation and growth of bubbles on the surface occurring at the walls of the beaker and the tip itself (fig.4.9), but they do not coalesce and grow over time. Since the glass is transparent, white dots on the inner surface are visible through the chamber, we perceive this fact as a movement of gas bubbles due to acoustic cavitation (fig.4.10).

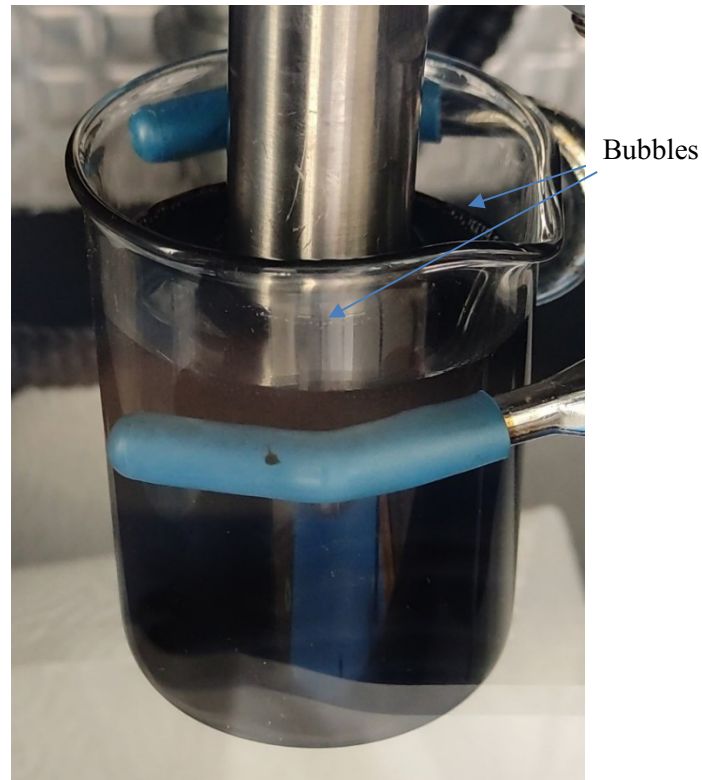


Figure 4.9 – Waves and bubbles on the surface at the beginning

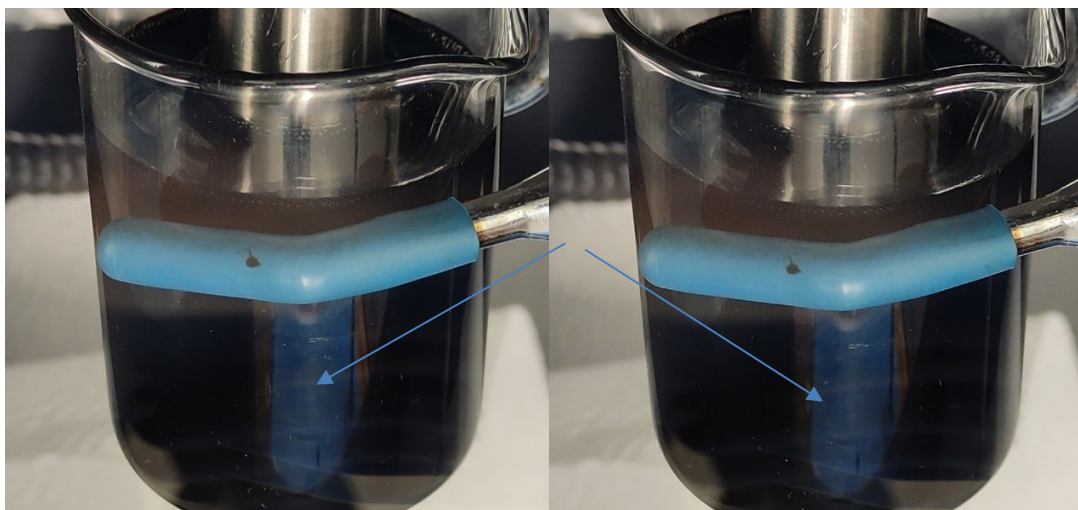


Figure 4.10 – Movement of the cavitation bubbles

With further processing the formation of bubbles gradually increases and they start to collapse on the surface near the walls and the nozzle (fig. 4.11). The process intensifies further and the

collapse and growth of the bubbles resembles boiling (fig. 4.12). In this case, it is important to note the instantaneous cessation of the process of bubbling on the surface of the oil immediately after the cessation of treatment.



Figure 4.11 – Intensification of the bubbles growth



Figure 4.12 – Boiling like characteristic of surface

According to our measurements after UST, the temperature of the oil increased to 47 degrees Celsius. The pour point was also measured at +15 degrees Celsius.

4.1.2 Experiments with oil and additives together

In this subsection we will look at experiments with additives and oil. This will also include the process of preparing and measuring the properties of additive DPN-1. As this is not a raw material and we have to make it ourselves.

4.1.2.1 Preparation of additive DPN-1

DPN-1, as presented earlier, is a 16 per cent mass-based solution of EVA in winter diesel fuel. In this way, we need 168 grams of winter diesel and 32 grams of EVA pellets for 200 g additive mass. Data about measurements of containers before filling, in full condition and after emptying are presented in table 4.1.

Table 4.1 – Masses of components

	EVA	Winter diesel fuel		
Mass of empty flask before, g	34,6285	34,6285	34,7675	34,8191
Mass of full flask, g	66,6416	86,8275	94,3441	91,39
Mass of emptied flask, g	34,6285	34,7675	34,8191	34,8191
Mass of the reagent, g	32,013	52,338	59,525	56,5709
Total mass, g	32,013	168,1559		

Determine the final concentration using formula 3.6.

$$C_{DPN-1} = \frac{32,013}{168,1559 + 32,013} \cdot 100\% = 15,993\%$$

We are quite happy with the result. As for the appearance, at room temperature it is a turbid extremely viscous solution of pale yellow colour, at temperature of +50 degrees Celsius it is a transparent solution of yellow colour, however quite viscous, the appearance is presented in figures 4.13 and 4.14



Figure 4.13 – DPN-1 in room temperature



Figure 4.14 – DPN-1 in injection temperature

To inject the additive, we will need to know its density at the insertion temperature, namely 50 degrees, pour it into the cylinder at 50 degrees. The mass of the cylinder is 140,667 g, the mass together with the additive is 221,993 g, so the mass of the additive itself at 100 cm³ is 81,326 g, those density is 813,26 kg/m³.

4.1.2.2 Effectiveness of additives

When evaluating the efficiency of measuring the additive in different proportions in an oil volume of 100 cm³, we measure the temperature during filling and use the calculation formula for the density of the additive in microliters. Since the filling temperature is important in each subsequent batch, we identify tables 4.2, 4.3 and 4.4 , which presents the results of calculations according to formula 3.4, where the filling temperature is indicated, we take the totality of fats from chart on figure 4.3, the totality of Chimtech additives after consultation with acceptance

was taken as an average between two boundary values i.e. approximately 0.86 g/m³ Chimtech 4980 and 0.88 g/m³ Chimtech 5978, respectively.

Table 4.2 – Results for Chimtech 4980

C, g/t (ppm)	50	100	250	500
Temperature of oil during pouring, °C	21	21	22	22
Volume of the additives, microliters	5,1	10,2	25,6	51,2
Pour point, °C	5	-8	-26	-29

Table 4.3 – Results for Chimtech 5978

C, g/t (ppm)	50	100	250	500
Temperature of oil during pouring, °C	21	21	21	21
Volume of the additives, microliters	5	10	25	50,1
Pour point, °C	7	-10	-12	-16

Table 4.4 – Results for DPN-1

C, g/t (ppm)	50	100	250	500
Temperature of oil during pouring, °C	23	22	22	22
Volume of the additives, microliters	5,4	10,8	27,1	54,2
Pour point, °C	6	0	-20	-21

In the graph below (fig. 4.15), you can clearly see the effectiveness of additives relative to oil without them.

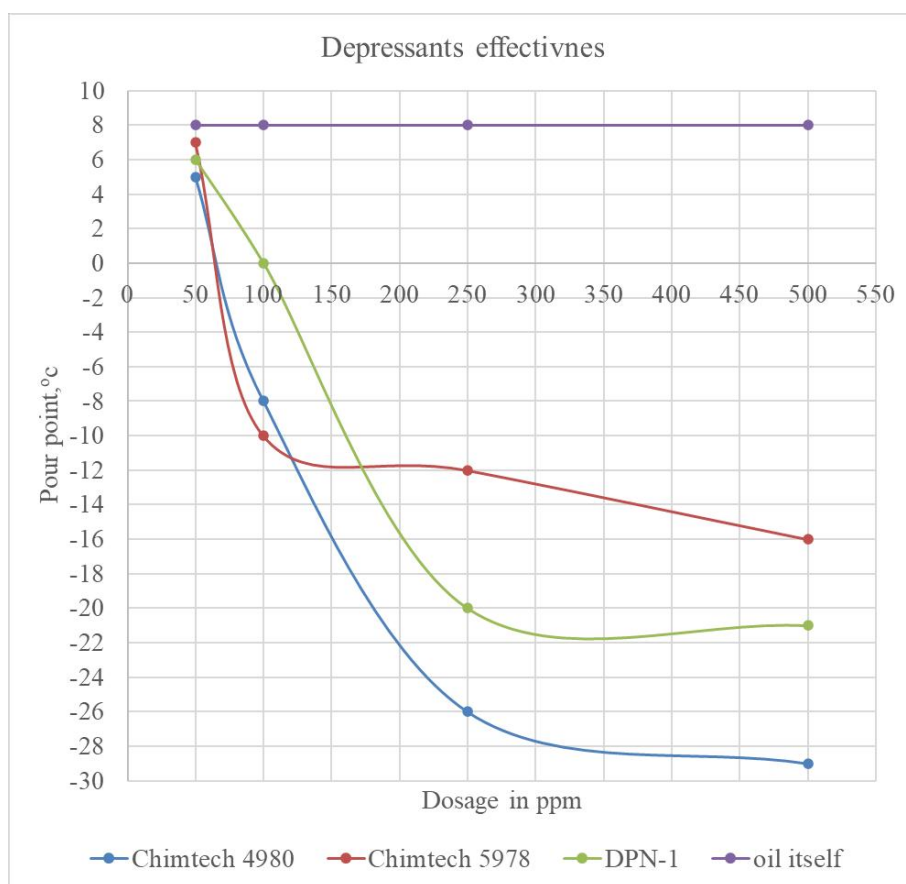


Figure 4.15 – Depression additives effectiveness

In general, the process took place according to the plan described in the second phase, the oil and additives were heated together in one thermostat, the oil was kept at a temperature of 50 degrees, as can be seen in figure 4.16. Next, the additive was instilled using a “KOLOR” micropipette, as can be seen in figure 4.17. There was mixing, reheating in a sealed test tube together with thermometers and placing them in a cryothermostat according to figure 4.18.



Figure 4.16 – Oil and additives in thermostat

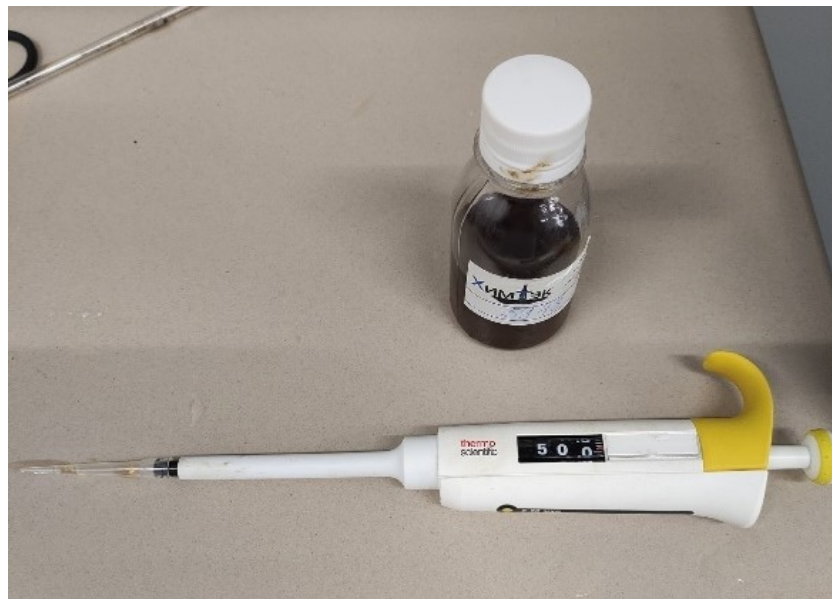


Figure 4.17 - Instilling using a "KOLOR"



Figure 4.18 – Oil in cryostat

4.1.2.3 Effectiveness of additives with ultrasonic treatment

In the case of oil sonication, we get the following results for each of the additives presented in tables 4.5, 4.6 and 4.7. In them we record the additive dose at an oil temperature of 20 degrees, also the temperature of the oil after sonication and the pour point results.

Table 4.5 - Results for Chimtech 4980 after ultrasonic treatment

C, g/t (ppm)	50	100	250	500
Temperature of oil during pouring, °C	20	20	20	20
Volume of the additives, microliters	5,1	10,2	25,6	51,2
Temperature of oil after ultrasonic treatment, °C	54	55	54	56
Pour point, °C	3	10	-22	-26

Table 4.6 - Results for Chimtech 5978 after ultrasonic treatment

C, g/t (ppm)	50	100	250	500
Temperature of oil during pouring, °C	20	20	20	20
Volume of the additives, microliters	5	10	25	50
Temperature of oil after ultrasonic treatment, °C	51	54	52	55
Pour point, °C	15	15	17	-1

Table 4.7 - Results for Chimtech DPN-1 after ultrasonic treatment

C, g/t (ppm)	50	100	250	500
Temperature of oil during pouring, °C	20	20	20	20
Volume of the additives, microliters	5,4	10,8	27,1	54,1
Temperature of oil after ultrasonic treatment, °C	54	61	53	51
Pour point, °C	12	11	10	3

In the graph below (fig.4.19), you can clearly see the effectiveness of additives relative to oil without them after sonication.

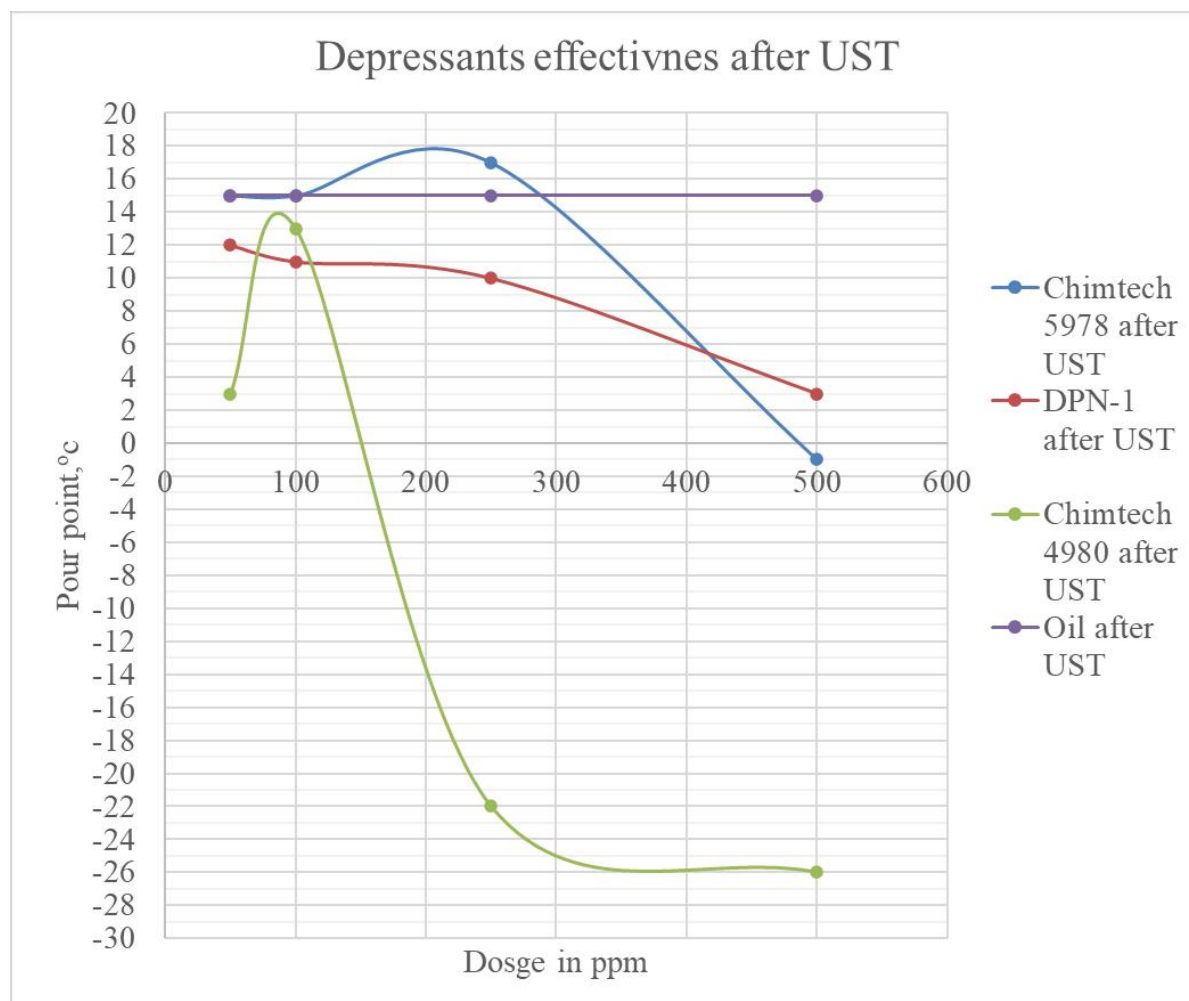


Figure 4.19 – PPD effectiveness after UST

All processes occurring with oil with an additive are completely similar without it, since the volume of the additive does not radically affect the physical properties of oil at room temperature, but it does not have a noticeable effect on oil during ultrasonic treatment.

4.2 Discussion Section

In general, it is important to note that, according to the experiments, the oil is indeed highly curable. The influence of ultrasound brought the opposite effect to the expected effect, i.e. instead of lowering the pour point, it will increase. The authors see the reason in the fact that ultrasound treatment causes a violation of the supramolecular structure and, because of this, the formation of a three-dimensional lattice in the process of paraffin crystallization.

As we can see from the experiments carried out with additives, it is worth paying attention to the fact that, in general, it is obvious that with an increase in concentration, the effect increases, while when moving from concentrations of 250 to 500 ppm, no cardinal change is observed. Thus, we find the very raft in which the addition of an additive will not reduce the setting temperature any more as significantly as the previous dose. on the pipeline, such additives are used with doses of 150 ppm. according to our studies, such a dose is really justified. with proper mixing, these additives provide a pour point below zero degrees, which is simply impossible in a hot pipeline under normal operating conditions. All the representation of the results can be seen on the graph below(fig.4.22).

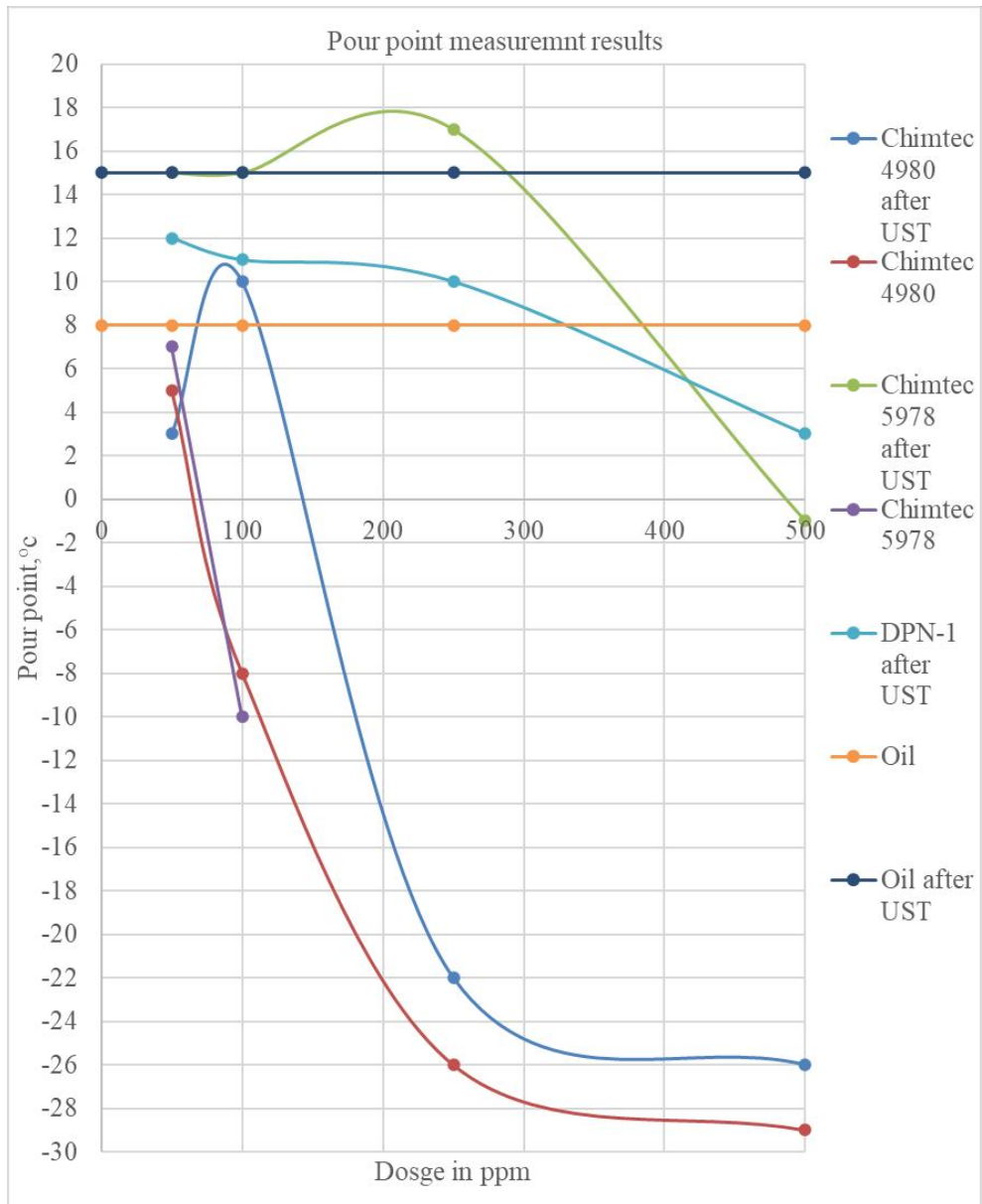


Figure 4.20 – Depressant effectiveness in different conditions

As for the ultrasonic treatment of oil, it turned out that 15 minutes of exposure to ultrasound at 22 kHz can affect the action of additives. From our point of view, cavitation bubbles that could be seen on the surface of the glass when the temperature of the oil increases, enhance diffusion and, as a result, intensify the process of formation and collapse of bubbles, since with increasing temperature, the elasticity value of the oil increases. At the same time, the power of these bubbles is so high that, most likely, the polymer additives could be possibly destroyed under its influence. This is indirectly confirmed by experiments, in all cases except for one, the results are worse than they were before ultrasonic treatment. At the same time, the oil in all cases heated up to approximately 54-55 degrees, which means that most of the paraffins, coupled with diffusion, should have melted and evenly distributed throughout the volume along with the additive. That is why, in the case of the Chimtek 4980 additive at a dose of 50 ppm, the result was better than without ultrasound treatment. An important addition is that different additives showed different degrees of resistance to ultrasound, the chimtek 4980 additive showed itself best, with the exception of the second experiment, where the role was most likely played by mixing of the oil for some reason and the additive did not work properly (fig.4.22). Additive Chimtek 5978 is completely destroyed by ultrasonication in concentrations up to 250 ppm inclusive, which indicates its complete incompatibility with ultrasonic treatment (fig.4.22). DPN-1 showed an average result in reducing the pour point by 3-5 degrees compared to conventional ultrasound -treated oil (4.22). From the above, we can say that additives can be divided according to the degree of influence of ultrasonic exposure on them: stable and unstable, the former slightly reduce their properties, while the latter almost completely lose them after ultrasonic treatment.

In general, we successfully answered all the questions posed. If you look at the results of the work (R.V. Anufriev, 2017), it turns out that we have achieved similar results really oil when treated with ultrasound increases its pour point, in other words, the results of our experiments partially coincide, even the pour point of oil from the Upper Salad field is extremely similar to ours. As we have stated before ultrasonication is a very promising means for reducing ARPD in pipelines and tanks, thus we conclude that it is not suitable for tanks containing highly pourable oils, both with and without an additive. However, experience with Chimtek 4980 shows that the diffusion and heating effect, coupled with good ultrasonic resistance at the operating temperature of the pipeline, allows to achieve better results compared to traditional applications without ultrasound treatment. Also it is important to understand that paraffin deposition inhibitors are not the same as depressants and vice versa. The mechanism of their work is different and acts at different stages of crystallization or works at the molecular state of paraffin.

Chapter 5

Conclusion

5.1 Summary

The results obtained by us are empirical data for this particular oil when it is treated with ultrasonics, as well as when it is treated with ultrasonics along with additives. The effectiveness of additives at various concentrations, as well as their safety over time, is considered. These experiments and observations will help us in the future to answer our goals.

5.2 Evaluation

Our objectives were to consider the use of depressant additives on the main pipeline in conjunction with ultrasonic treatment, as well as the effect of ultrasonic treatment on the oil itself, so based on the results of experiments we can clearly answer the questions we posed at the beginning.

The first task was to check the possibility of ultrasonic cleaning of the equipment surface from ARPD in the presence of solidified oil inside. The result was that such activities are extremely risky due to the fact that the freezing temperature of oil increases, which means that the oil can freeze in the equipment or tank and then its removal can cause much more problems than just cleaning of ARPD. Also, if the oil was with an additive, there will be a decrease in its efficiency, and different additives are differently resistant to it.

The second goal was to show the possibility of activating the additive by ultrasonic treatment without resorting to heating, but based on experiments ultrasonic treatment promotes heating due to acoustic cavitation, while reducing the effect of the additive. Only one experience with the most stable Chimtech 4980 additive showed a better result compared to the treatment without it.

The first two objectives and experiments showed the opposite result from the expected, but it will help to improve the use of ultrasonic oil treatment and avoid critical errors in the future.

5.3 Future Work

In general, in this work it is possible to further consider the effect of ultrasonic treatment on oil at different intensities, frequencies and treatment times, as well as to vary the volume of oil for each case. In this case, it is indeed possible to reduce the pour point due to the action of ultrasonic alone. Also, we would like to get a few different samples of oil from different fields in order to be sure that this phenomenon is a rule, and not a special case. It is possible that this technology will possibly find its application as a tool to reduce the consumption of additives by 2-3 times.

The second problem is the way the oil is processed. Open processing is not exactly the same as in-line oil processing, so further work will be to consider the possibility of building a bench that simulates oil in-line processing.

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Nomenclature

ρ_{t1}	Density at $t1$	[kg/m ³]
ρ_{20}	Density at 20 °C	[kg/m ³]
ξ	Linear coefficient	[1/°C]
t	Temperature	[°C]
V_{ppd}	Required volume of PPD	[microl]
C	Concentration of the additive	[g/t],[ppm]
N	Water cut	[Part]
ρ_o	Density of oil at several temperature	[g/cm ³]
ρ_{ppa}	Density of the pour point depressant at 50 °C	[g/cm ³]
V	Volume of the sample of the oil	[cm ³]
ρ_t	Density corrected after areometer metering at t	[kg/m ³]
$\rho_{\alpha t}$	Density showed by areometer at t	[kg/m ³]
K	Coefficient for temperature of glass expansion of areometer	[1/°C]
m_{EVA}	Total mass of EVA	[g]
m_{df}	Total mass of winter diesel fuel	[g]
C_{DPN-1}	Achieved concentration of DPN-1 PPD	[%]

Abbreviations

ARPD	Asphalt, resin, and paraffin deposits
NMR	Nuclear magnetic resonance
EVA	Ethylene vinyl acetate
PPD	Pour point depressants
PCS	Pipeline commissioning station
RAC	Resin asphaltene content
UST	Ultrasound treatment
WAT	Wax appearance temperature