



## PARTICULARS OF OIL STRUCTURAL ORGANIZATION

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### ABSTRACT

One of the general problems of all lines of research is the exhibition of various micro- and macroscopic effects. These exhibitions can be characterized by three terms: nonlinearity, nonequilibrium and heterogeneity. The reason for it is the unique in terms of composition and properties test subject - oil and its components. Considering complexity and heterogeneity of its composition, multitude of phases, the presence of colloid-dispersed inclusions, a variety of intermolecular interaction, bonds, interconnections and ordering relationship between the components, oil systems can be put down for as complex systems. Research related to the in-depth studying of the various complexity level oil systems chemical composition are highly topical for establishing causes of complications, arising in various processes, and searching for solution approach.

**Keywords:** oil dispersed systems structure, fractal dimension, asphaltenes aggregation, sedimentation stability.

### INTRODUCTION

Oil is the unique natural object. It's a complex mixture of organic compounds, having various intermolecular interactions: dispersive, Van der Waals, hydrogen bonds, etc., which role significantly increases with the increase of oil system total potential energy, and at reduced temperatures oil passes into structured condition. Such interactions character and result depends on the mutual proportion of oil system individual components. Besides, it matters not only weight percentage of one or another compound class in oil or oil product, but also the distribution of individual components (by the structure and molecular weight) in each class. Modern studying level is determined in the first place by the actuality of more effective and complete oil stock recovery and processing, heavy oil and petroleum residues implication into oil extraction and processing, the request for the increase of valuable commercial oil yield, the actuality of commercial oil quality problems and economic feasibility.

Petroleum crude oils, gas condensates and the corresponding products are characterized by complex chemical composition and aggregate state of separate components, structure and properties. It is known that oil and oil products contain hydrocarbon and non-hydrocarbon components of different nature, molecular weight and structure. Studying chemical composition of petroleum crude oils and oil products one can provisionally draw up four groups: low-molecular and high-molecular hydrocarbons, resinous-asphaltenic materials of nonhydrocarbon nature, and heteroatomic compounds. Physicochemical properties of petroleum crude oils and oil products greatly depend on the quantitative content of components of the above

mentioned composing groups, their qualitative characteristics and reaction degree.

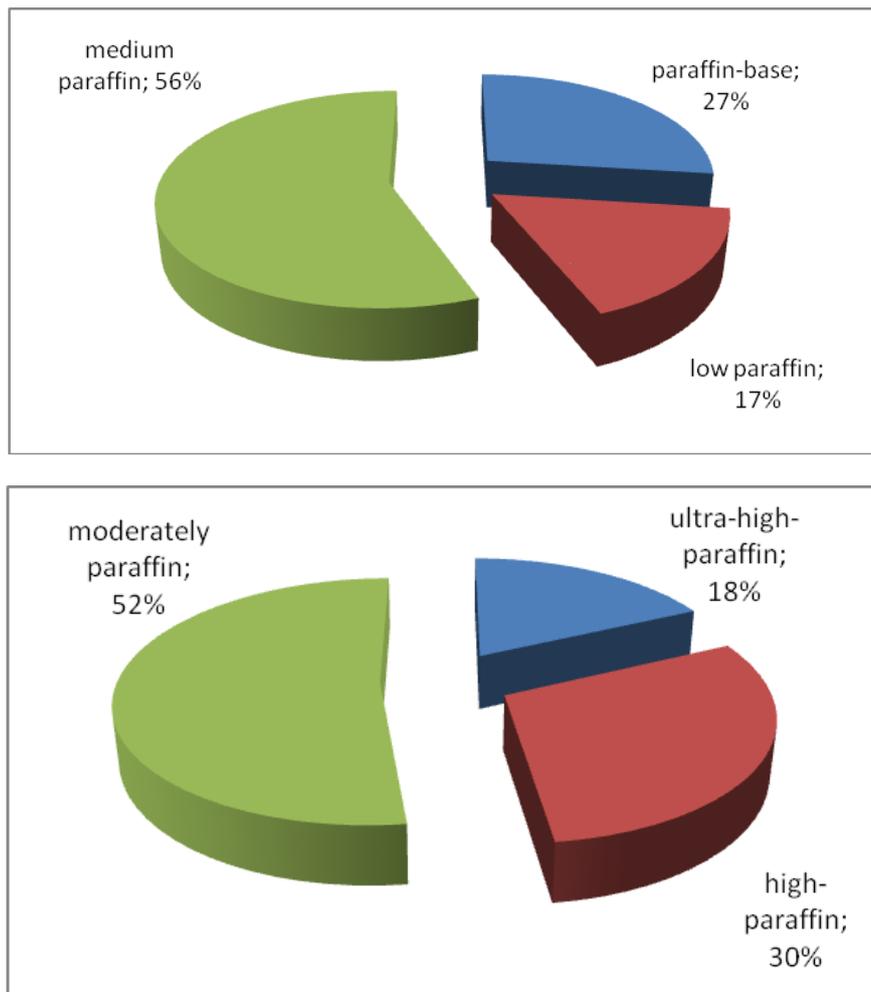
Petroleum crude oils are characterized by high contents of heavy fractions, where the most structurally complex compounds, exerting the most influence on oil system behavior are concentrated.

It's very important to know in which state – molecular or disperse - this system is in external conditions survey section. Regularities of behavior and physicochemical properties of the oil system in molecular or disperse state even for identical composition can differ significantly [1].

### Paraffin hydrocarbons influence on oil dispersed systems properties

Real oil systems in view of composition complexity are polyheterophase disperse systems of various types, which complicate identification of their behavior particulars. Thus, wax-bearing crude oil and oil products relate to oil dispersed systems. Paraffins content in petroleum crude oils varies from a share of percent up to 20 %. They mostly consist of n-alkanes, which melting point changes from 22°C for n-heptadecane ( $C_{17}H_{26}$ ) to 115°C for heptane  $C_{100}H_{202}$ . [2]. Term petroleum paraffin usually means a mix of high-chain hydrocarbons - n-alkanes with carbon chain length of  $C_{17}$  and higher [3; 4]. Petroleum crude oils have chilling temperatures from -68 to +60°C.

In paper [5] two-level classification of petroleum crude oils by paraffin content is shown (Figure-1), as well as world petroleum crude oils distribution for paraffin content in accordance with the classification shown in Table-1 from the same literary source.



**Figure-1.** World petroleum crude oils distribution for paraffin content in accordance with the classification shown in Table-1.

**Table-1.** Petroleum crude oils two-level classification by paraffins content [4].

Petroleum crude oils class	Petroleum crude oils subclass	Paraffin content, %
low paraffin		up to 1.5
medium paraffin		from 1.5 to 6
paraffin-base	moderately paraffin	from 6 to 10
	high-paraffin	from 10 to 20
	ultra-high-paraffin	more than 20

N-paraffins consist of flexible molecules and have a tendency to settle parallel to each other on cooling, forming the most stable nuclei crystals. Molecules of *iso*-paraffins are flexible enough, but the presence of side chains result in the emergence of crystalline defects and the formation of less stable nuclei. Cycloparaffins (naphthenes) molecules are large-sized and hard, breaking crystallization process. Therefore nanocrystals formed with the participation of cycloparaffins are the least stable. Thereby paraffin can exist in three forms [6]:

- macrocrystalline - this form can dominate at the expense of alkanes with straight-chains;
- semimicrocrystalline - the intermediate form of macro- and microcrystalline paraffin,
- microcrystalline - this form is characterized by the presence of cycloalkanes (naphthenes) and alkanes with forked chains and often contains asphaltene impurities. It's known that microcrystals show a much smaller capability to cohesion to each other [7].

Cocrystallization of different class hydrocarbons, composing the oil system, result in the formation of irregular needle-shaped crystals, which in the case of chaotic cohesion form a space grid with immobilized liquid phase, resulting in colloid gel formation [8].

In this regard, the system acquires structural and mechanical strength. It has been established [9; 10] that the presence of complex asphaltene compounds promotes paraffin dispersions stabilization.



### Presentation of self-organization and structure formation in oil dispersed systems

Oil is a natural colloid dispersed system, which characteristic property is in the existence of so-called supermolecular structures - the internal adsorption complexes, build of asphaltene and resin molecules that are 10-1000 times larger than molecular. The primary role in supermolecular structures formation is assigned to oil asphaltene molecules.

They are the products of high-temperature catagenetic conversion of hydrocarbons and have a high tendency to association and aggregation at the expense of paramagnetic nature of complexes [11].

Asphaltene molecules in solutions have a tendency to aggregation even at rather low concentrations. According to Akhmetova [12] and Rogacheva [13] asphaltene is present in oil medium in the form of individual molecules at concentrations below 1-2 mg/l, according to Evdokimov [14] - at concentrations below 5-10 mg/l. When exceeding this concentration the oligomer (dimer and dimer pairs) are formed [15]. Formation of stable nanoaggregates from 6-10 asphaltene molecules [16; 17] happens at critical nanoaggregate concentration (this term was proposed by Prof. J. Shobl) [18], which value varies for different asphaltenes from 50 to 200 mg/l [15; 17 - 22]. In this case, the aggregates of 2-10 nm are formed. Upon further asphaltene concentration increase there increases the number of nanoaggregates, but not their sizes. For asphaltene concentrations in the solution of approx. 2-5 g/l the clusters are formed from the aggregates [16;17; 23].

Asphaltenes form the central part (core) of supermolecular structures, which according to the classification by Z.I. Syunyaev bear a name of complex structural units [9]. In publications, the complex structural units asphaltene core in oil is often described as quasispherical layer stacking-structures 1.5-2.4 nm in thickness from flat polycondensed aromatic molecules of uniform density. However, the studying of crude oil by using method [24] shows that the most (70-90 %) part of asphaltene core actual radius R is presented by amorphous irregular structures with rather low degree of order. This points out the fact that structurally the core has irregular density, which decreases from the center to the periphery. Such peculiarities are appropriate for the so called fractal objects, first described by Benoit Mandelbrot [25] and a little bit later by Jens Feder [26], and also in papers by B.M. Smirnov [27; 28] and V.I. Roldugin [29].

Fractal structures consist of approx. 8-10 nanoaggregates [17; 30 - 35].

Sizes of the cluster for different asphaltenes can vary from 6 [17] to 30 nm [30], and according to some reports - up to 100 nm [16]. With further increase of asphaltene concentration (more than 5 g/l) the floccules [16;17] or various nanophases of flocculated nanocolloids [36] are formed in the system, which sizes can exceed 100 nm [16;17; 37] and which aggregation can result in the loss of sedimentation stability [16].

The growth of asphaltene aggregates, their flocculation and loss of sedimentation stability is also

observed when adding low-molecular n-alkanes (precipitators) into asphaltene toluene (benzene) solution. In this case, the asphaltene solution will be characterized not by critical nanoaggregate concentration, but by the onset point, i.e. the concentration of precipitators at which the flocculation of asphaltenes takes place and their settling out from the solution starts. Information about the stability of asphaltene aggregates, forming upon precipitator addition, is very contradictory. According to studies [38 -40], asphaltene aggregates achieve stable state within several days. During this period they repeatedly transform, changing their composition, structure and sizes.

Fractal aggregates with their unique structure in large measure predetermine physicochemical macrocharacteristics of oil colloid systems in general. Therefore there's a large amount of paper dedicated to fractal studying [29; 33].

The basic property of oil dispersed systems is continuous multilevel self-assembly and rearrangement of complex nanoaggregates when changing thermodynamic conditions under the influence of natural and technogenic factors [33].

Drawing the clear line between resins and asphaltenes is rather complicated. According to papers [2; 41] in genetically related series of hydrocarbons - resins - asphaltenes, the tendency to gradual depletion in hydrogen and enrichment in carbon is observed. The fraction of aromatic structural elements and the degree of their condensity is increased. The fraction of carbon in the peripheral part is decreased. The specific gravity of atoms in the molecules central core is also increased.

Resins and asphaltenes also differ by oxygen and nitrogen contents. Oxygen mostly concentrates in resins, while nitrogen - in asphaltenes. As a rule asphaltenes content in petroleum crude oils is lower than resins content. The ratio of resin to asphaltenes fluctuates in various petroleum crude oils from 9:1 to 7:3. Asphaltenes composition heterogeneity creates difficulties upon detection of their true structure.

There are several hypotheses of asphaltene origin in oil. The most common is based on strong composition and structure resemblance of oil asphaltenes with bitumoid and kerogen asphaltenes. According to this hypothesis, oil asphaltenes are large soluble kerogen fragments, underwent catagenetic transformation in the process of oil formation [42]. Alternatively, there's an opinion that oil asphaltenes are of secondary origin, i.e. they are the product of oil components transformation in the process of their catagenetic transformation [43]. According to Kontorovich [43] in nature the realization of both of the above-mentioned asphaltenes origin mechanisms is possible.

Quantitatively asphaltenes do not dominate in oil composition: their contents can make up from trace quantities in light crude and up to 16-20 % in high-viscosity crude oil. The interest in asphaltenes studying is provoked by their detrimental effect on oil systems properties. Thus, petroleum crude oils with high asphaltene contents are characterized by high viscosity, which requires the use of expensive technologies to

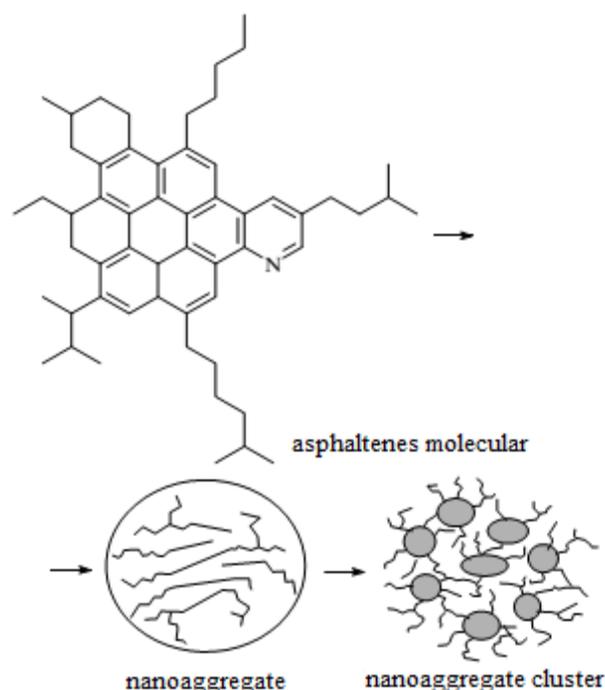


increase oil production and easing its transportation [44 - 47]. High asphaltene contents causes problems when oil refining, because they decrease end product yield and poison catalysts [1]. Lower viscosity petroleum crude oils with low asphaltene content are in most cases unstable in relation to asphaltenes settling out [48; 49], which results in the borehole, surface equipment and pipeline bridging, and also requires extra investments for conducting cleaning and repair works. Besides, asphaltenes exert a great impact on the wettability of formation [50] and stability of oil-water emulsions [51; 52].

Characteristic properties of resinous-asphaltenic materials are considerable molecular weights, the presence of various heteroelements in the composition, the polarity, paramagnetism, high inclination to intermolecular interactions, polydispersity and exhibition of strongly pronounced colloid and disperse properties. Alongside with carbon (88%), hydrogen (up to 10%), oxygen, nitrogen and sulfur resinous-asphaltenic materials also contain micro quantities of metals (V, Ni, Fe, Ca, Mg, Cu, Ti, Mo, Co, Cr, etc.) The total heteroatom (up to 14%) and metal content, as well as their ratio in resin and asphaltene molecules varies over a wide range and depending on oil chemical nature [1; 2; 53].

The authors [54] showed that asphaltenes are the mixture of compounds with wide solubility interval. In aromatic solvents, they form colloidal phase, consisting of high molecular cut of asphaltenes, dispersed by the low molecular cut. In paper [55] the supposition was made that there's a hierarchy of asphaltenes, expressed in dependency to individual structural types of high molecular asphaltenes of certain types of low molecular asphaltenes, which explains polydispersity of asphaltenes colloidal particle. Asphaltenes complexity of structure and self-organization is discussed in paper [56], where extraction, adsorption chromatography and chemical destruction methods are used to demonstrate that there are relatively low molecular fragments as part of asphaltene macromolecules, represented by linear and forked alkane, mono- and polycyclic naphthenic, mono-, bi-, tri- tetra- and pentacyclic aromatic structures, their phenyl- and naphthene derivatives, benzo-, dibenzo- and naphthobenzothiophenes, carbazoles and benzocarbazoles, higher fatty acids ethyl ether, dibenzofurans and fluorenones, as well as acids, amides and sulfoxides. Asphaltenes molecular and colloid properties are subjects of a lot of studies, conducted for the last decades [17; 57 - 60].

A complete overview of papers, dedicated to studying of asphaltenes, is cited in the paper [61], where Yen-Mullins model [62; 63] of asphaltenes molecular and colloid state description was used as a basis (Figure-2).



**Figure-2.** Hierarchy organization stages of asphaltenes supermolecular structures [17].

This model reflects several levels of asphaltenes structural organization both in solvents and petroleum crude oils.

There're several levels of asphaltenes structural organization: molecular and dispersive state, where the asphaltenes are in the form of separate layers; colloid state, which is the result of particles formation with specific dimensions; dispersed kinetically stable state, arising from particles aggregation, and dispersed kinetically unstable state, accompanied with precipitation [9].

In paper [64] structure hierarchy depending on asphaltene molecules concentration is described by the scheme: molecules - nanoaggregates - nanoaggregate clusters.

It's known [61] that asphaltenes have a molecular mass distribution over the range from 500 to 1000 g/mol with the peak at approx. 750 g/mol, besides among possible hypothetical asphaltene molecular structures the "continent" ("island") type model predominates, having a pronounced center, presented in the form of aromatic ring condensed system. Reliability of cited data is confirmed by good correlation of the results, obtained by various instrumental methods: mass spectrometry [63; 65; 66] and diffusion methods [19; 67].

Average asphaltenes molecular mass conforms to the molecule with seven condensed aromatic rings, and precisely this structure is capable of forming "continent" type molecule. This model was dubbed "continental" [18]. Another type of asphaltene molecule was proposed in paper [68; 69]. Asphaltene molecule consists of small aromatic clusters, interconnected by methylene, sulfide, ester and oxygen bridges. Peripheral substituents include linear and forked aliphatic groups, etc. Similar asphaltene



molecules structures were dubbed "archipelago". In crude oil, both types of asphaltenes in various proportions are found.

### Oil systems structure and composition research methods

For a long time the opposing views has existed about the inner structure of asphaltene molecules: does the molecule contains the single PAS ("island" structure) or several bonded together with similar compounds ("continental" structure) [68]. This problem was solved by asphaltenes time-resolved fluorescence depolarization (TRFD) experiments [70].

In TRFD experiments single asphaltene molecules PAS in the toluene diluted solution are excited and polarized by laser radiation. Fluorescence duration is only several nanoseconds and can be measured by the corresponding methods [71]. With time the rotary motion results in depolarization of molecule ensemble and fluorescence signal decay, though characteristic correlation time of rotary motion is related to molecule sizes by Stokes–Einstein equation [70]

$$\tau_c = \frac{\eta V}{kT}$$

where

- $\eta$  - is solution dynamic viscosity;
- $V$  - molecule volume;
- $k$  - Boltzmann constant;
- $T$  - sample temperature.

By comparing with model test substances solutions in toluene by correlation time it was discovered that asphaltene average molecular weight is 750 amu. "Sun paint" with a molecular weight of 755 amu and octaethylporphyrin with a molecular weight of 535 amu were used as model test substances [70].

It should be noted that in the specified papers [70; 71] the asphaltene solutions fluorescence depolarization was observed in the spectral range from 370 to 650 nm, which corresponds with rotational correlation times from 0.1 to 1 ns. These times correspond to highly diluted asphaltene solutions in toluene at temperatures not more than 100 °C, prepared for conducting the above-mentioned experiments.

Nevertheless, the question about the limits, in which the  $\tau_c$  for crude oil asphaltenes can vary at higher temperature and pressure, typical for hydrocarbon material modern production and refining conditions, is still open.

According to TRFD experimental data, almost linear dependence of correlation time from asphaltene molecules PAS fluorescence emission wavelength was discovered, besides the emission wavelength is connected with molecule size as a result of quantum confinement effects in nanoparticles [72; 73]: fluorescence spectrum of smaller molecules is shifted towards short-wave region (blue shift). Fluorescence emission wavelength correlation time change indicates that polyaromatic cores of various sizes are not bonded together, but asphaltene molecules are monomeric themselves, i.e. they have "island"

structure with one PAS per molecule. If they were bound together, then depolarization of one molecule as a result of its size increase would last much longer, increasing the  $\tau_R$ , and the same size molecules would have broad fluorescence spectrum up to red as a result of various size PAS interaction inside the molecule [70]. Later the "island" structure of asphaltene molecules was confirmed in other papers [74; 75].

The number of condensed rings in the asphaltenes was confirmed by using direct molecular visualization [76], optical and emission methods, with the application of calculation using the molecular orbital method [74; 77].

Colloidal properties of oil dispersed systems are known for a long time, as well as the high disposition of oil components to associate formation. The debate was prompted by the oil system associate structure, i.e. complex structural units nature and formation mechanism of oil dispersed systems, as well as its behavior in the presence of light oil components (solvents) [9;11]. Experiments proved that when diluting oil by saturated hydrocarbons the rejection of asphaltenes from hydrocarbon medium occurs with sediment formation, and when adding aromatic hydrocarbons the ultimate solubility of all oil components is observed. These aspects are highly important for oil compounding. In paper [78] the contribution of hydrogen bonds to self-organization processes of associated structures in oil solutions and their strength are studied.

For isolate asphaltene from oil for the purpose of studying their property to precipitate from the oil system when adding low-molecular n-alkanes is used. With some minor exceptions [79] with the increase of carbon atoms in n-alkane the volume of asphaltene sediment is decreased, and the level of high molecular mass components with a higher degree of aromaticity and lower H:C ratio is increased [80-82].

Asphaltene aggregation process selectivity is established. When studying asphaltene aggregation dynamics it was established [38; 84] that in unstable petroleum crude oils (with low aromatic HC: saturated HC ratio, where HC – hydrocarbons) the asphaltenes are characterized by low aggregation speed. By contrast stable petroleum crude oils with high aromatic HC : saturated HC ratio are characterized by higher asphaltene aggregation speed.

It is pointed out on the existence of weak energy bonds (e.g., bonds in resin and asphaltene molecules, hydrogen bridges). Resin and asphaltene molecules are the aromatic and acyclic structures, containing condensed and uncondensed fragments, connected by bridge links - CH<sub>2</sub>-O - R, - CH<sub>2</sub>- S - R, etc.

Resinous materials are present almost in any oil products, starting from gasoline fraction, and finishing with residuals, with the exception of highly hydrotreated light fractions [85]. The energy of these bonds is very low and is approximately 0.5–25 kJ/mol [86]. This suggests that weak energy external actions can have weak impacts on oil dispersed systems condition. They can result in homolytic dissociation of heterocompounds and hydrocarbons with low energy bonds, particularly



diamagnetic resin molecules (with new radicals occurring in the process), hydrogen bonds deformation or breakup, as well as at the expense of multipole-multipolar interactions changes.

Intermolecular interactions are characterized by comparatively low energies (electrostatic 5-100 kJ/mol,  $\pi$ - $\pi$ -stacking 1-50 kJ/mol, hydrogen bonds 8-40 kJ/mol, Van der Waals forces 0.4-4 kJ/mol; for comparison C-C covalent bond energy in benzene molecule exceeds 500 kJ/mol). However, calculations by molecular mechanics and molecular dynamics method for asphaltenes from vacuum residue for oils from Khafji oilfield (Saudi Arabia) under vacuum showed that hydrogen bonds between asphaltene molecules are broken at 523 K, and interactions between polyaromatic cores ( $\pi$ - $\pi$ -interactions) remain stable up to 673 K, which is the temperature, at which the covalent bonds are broken [87]. This indicates that aggregates, built at the expense of multiple noncovalent interactions, are strong enough. High thermal stability of asphaltene aggregates in the solutions was confirmed in papers [88; 89].

"Continental" type molecules form strong and stable stacking aggregates at temperatures up to 400 °C [89; 91 - 96].

## CONCLUSIONS

Thus, the problems of the colloid systems aggregate and kinetic stability are studied over a number of years. For the last decades, stability studies are developing intensively. The emphasis is upon methods permitting defining oil dispersed systems stability at common and elevated temperatures. Intermolecular interactions, which are responsible for oil dispersed systems structure, play an important role in these systems.

Studying of a basic group structure of the molecules, composing oil dispersed systems and intermolecular interaction types, represents particular scientific interest and determines continuous problem solving of various process tasks, related to forecasting, development and landmark opportunities for intensifying of processes in production, transportation and refining of oil and oil products.

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