

Nadejda Bondar¹
Anatoliy Denysyuk²
Yuriy Simonov³
Olena Tertyshna⁴
Lyubov Snizhko⁵

ASPHALT-RESIN-WAX DEPOSITS ANALYSIS WITH PETROLEUM REFINERY EQUIPMENT USAGE

^{1,2}PAT “Ukratnafta”

Svishtovska street 3, 39610, Kremenchuk, Ukraine

^{3,4,5}Ukrainian State University of Chemical Technology

Haharina avenue 8, 49005, Dnipropetrovsk, Ukraine

E-mails: ¹bondar-nv@ukratnafta.com; ²denisiuk@ukratnafta.com; ³simonov13@yandex.ru;

⁴t_elen2000@bigmir.net; ⁵lsnizhko@mail.ru

Abstract. *The methodology and analysis of wax deposits formed in-water-cooling tower, cistern and tank from wax petroleum were developed. It was shown, that deposits consist of organic (>90%) and inorganic components – the first one was enriched by high molecular wax hydrocarbons, the second one – by mechanical impurities. The methods of deposits utilization were proposed.*

Keywords: analyses; asphaltene – wax – paraffin deposits; composition.

1. Introduction

In the terms of petroleum-processing Asphalt-Resin-Wax Deposits (ARWD) are being formed in tanks for storage of raw materials a sharp change in temperature occurs in rail tank cars, the cooling towers and other equipment. Thus, in the tank of the cubic capacity 50 000 m³ “dead” balance exceeds 10% by weight.

Depending on the content of solid hydrocarbons in the petroleum and place of sampling, composition of deposits varies, but in general they represent a structured system with the core of asphalts and adsorb solvates layer of petroleum resins. Normally ARWD(s) consist of 40–60% solid wax (a mixture of solid n-alkanes with 18-35 carbon atoms in the molecule and melting temperature 45–65°C, iso-alkanes and aromatic hydrocarbons or naphthenic nucleus in the molecule), 10–56% resins and asphalts, water, sand and inorganic salts [Ahmetov et al. 2008]. Resins, in turn, contain up to 98% aromatic and naphthenic structures, and heterocyclic compounds including nitrogen, sulfur, oxygen and metals (Fe, Mg, V, Ni, Ca, Ti, Mo, Cu, Cr). The main directions of deposits investigation are as follows: selection of appropriate solvents and developing ways to remove deposits [Ivanova et al. 2011]. In industrial practice solvents are being selected rather empirically without using quantitative criteria and calculations. Experimental methods are based on the preparation of certain extracts by dissolving of small amount of deposit in various organic solvents, bi-distilled water, mineral acids and subsequent analysis of the extracts.

The aim of the study is to analyze the chemical composition of deposits derived from different equipment of industrial processing, selection of solvents and quantification of capabilities of either utilizing or recycling deposits.

2. Experimental part

The deposits were collected from cooling towers, cistern and petroleum storage tank.

We began the analysis of deposits from separating the latter into organic and inorganic fractions applying of organic solvents such as hexane, toluene, four-chloride, carbon, sulfur ether, acetone, light petroleum fractions.

The portion of organic substances was calculated after their dissolution and evaporated till the constant weight reached. The maximal temperature of organic matter concentrate depending on the solvent boiling point taken for extraction is to be determined in every single case. Mass fraction of organic matter X_{or} is calculated such as:

$$X_{or} = \frac{m_2^{or} - m_0^{or}}{m_1^{or}} 100,$$

where m_0^{or} , m_1^{or} , m_2^{or} – mass of empty porcelain cup, mass of the sample taken for extraction, and mass of the cup with residue after extraction (g), respectively.

Potential composition of organic substances was measured by gas chromatograph (Agilent HP 6890) and UV - spectroscopy on a spectrophotometer (Cary-50).

To determine the mass fraction of inorganic substances and their composition filter with deposits residue has been washed from organic substances and placed in the oven with the temperature 105°C for reaching constant weight. Mass fraction of inorganic X_{in} substances was calculated such as:

$$X_{in} = \frac{m_2^{in} - m_0^{in}}{m_1^{in}} 100,$$

where m_0^{in} , m_1^{in} , m_2^{in} – filter masses, deposits batch taken for extraction and filter with residue after extraction (g), respectively.

Afterwards, the residue was being burned during 5 hr in a muffle furnace at the temperature of 550°C, then ash was treated by mixture of nitric and hydrochloric acids (1 : 3 volume proportion - “aqua regia”); then acid has been evaporated and the residue was dissolved in bi-distilled water in a volumetric flask 100 cm³. The amount of metals was measured by atomic - absorption spectroscopy method using spectrometers AAS-1N and C-115.

The volatile substances mass fraction at temperatures 105°C (X_{105}) was determined and calculated after the samples were being dried for 40 min until constant weight obtained. The portion of X_{105} was calculated such as:

$$X_{105} = \frac{m_1 - m_2}{m_1 - m_0} 100,$$

Mass fraction of volatile substances removed by burning was calculated by the same procedure:

$$X_{550} = \frac{m_1' - m_2'}{m_1' - m_0'} 100,$$

where m_0' , m_1' , m_2' – the masses of the empty glass and the glass with a batch before and after burning (g), accordingly.

For determination of the water-soluble substances 25 cm³ of water was added to 0.5 g of inorganic substances; the solution was boiled for at least 30 min under watches glass. Then the solution was evaporated, added 25 cm³ of water, brought to boiling temperature, cooled, placed in a volumetric flask of 250 cm³, driven up to the mark and then filtered through a filter under temperature 105°C.

Mass fraction of water-soluble substances X_{ws} was calculated using the formula:

$$X_{ws} = \frac{m_1^d - (m_f^d - m_f)}{m_1^d} 100,$$

where m_1^d , m_f^d , m_1^d – mass of sediment taken for water-boiling, the weight of the filter residue after boiling and filter weight (g), respectively.

Determination of the mass fraction of acid-solved substances X_{as} was carried out after the batch of inorganic sediment of 0.5 g having been boiled for 30 min in a mixture of concentrated nitric and hydrochloric acids (ratio 1 : 3 – “aqua regia”) followed by concentrated hydrochloric acid added and evaporated. The calculation was performed as follows:

$$X_{as} = \frac{m_1^{as} - (m_f^{as} - m_f)}{m_1^{as}} 100,$$

where m_1^{as} , m_f^{as} , m_f – the masses of the batch taken for boiling with acids, the mass of the filter residue boiling and filter weight (g), respectively.

Measurement of a metal mass fraction in the filtrate was carried out by atomic - absorption spectrophotometers AAS-1N and C-115.

Metal content C_{Me} (mkg/g) in the sample was determined such as:

$$C_{Me} = \frac{(C_{Me}^1 - C_{Me}^0)VF}{m} 100,$$

where C_{Me}^1 , C_{Me}^0 – metal concentrations in an analyzed sample solution and the test solution (mkg/cm³), respectively;

V – volume of the sample solution, cm³;

F – dilution factor of the solution (in the case of the dilution of a test solution during measurement);

m – petroleum product sample taken for analysis (g).

3. Results and discussions

The composition of petroleum, which causes deposits formation is given in Table 1.

Table 1. Characterization of petroleum

Fraction	Yield,% vol.
Up to 200 °C	16.0
Up to 360 °C	45.0
Up to 500 °C	75.0
Fraction residue 350–420 °C	12.3
Fraction residue 420–500 °C	15.3
Fraction residue > 500 °C	24.0
Sulfur content	0.5
Content of asphalts (A)	0.34
Wax content(W)	8.27
Tar (T)	5.25
Ratio P / (A + T)	1.48
Ratio P / (A + T)	1.48
Ratio S / (P + A)	0.61

The table shows that the ratio $W / (A + T) > 1$, which can be attributed to the pre-wax type [Oil Chemistry...1984].

Results of deposits analysis presented in the Table 2.

Fractional composition of petroleum and deposits is shown in Figure.

It can be seen that the true boiling temperature (TBT) curve for deposit lies in the higher temperature range than petroleum TBT. This is understandable, since the deposits forms from the most high temperature part of the hydrocarbons.

Results of elemental analysis of inorganic deposits are presented in the Table 3.

While analyzing samples from cooling towers it was found that petroleum deposits are contaminated with mechanical impurities, glass wool, sand and water. Atomic absorption method revealed that the inorganic fraction of the product is represented by compounds of iron, sodium, calcium, magnesium, manganese, zinc, copper, potassium and silicon.

The organic fraction represents petroleum product which boils at the temperature range between 312–497°C and contains 57.43% wt. of n-alkanes and iso-alkanes. Naphthenic hydrocarbons are forming petroleum-naphthenic “hump” (42.57% wt) at the chromatogram. Melting point of the petroleum product purified from water and mechanical impurities is +47°C, and refraction coefficient at the temperature 50°C is 1.4548. Apparently, it describes the fraction of 350–420°C contaminated with waste petroleum, wax, water, corrosion and salts.

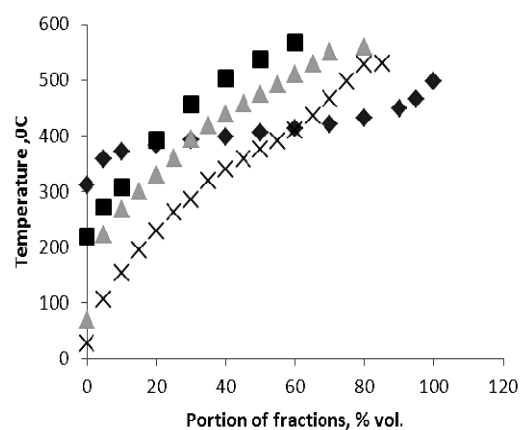
The deposit formed in wagon tanks looked like dark viscous asphalt residue. Toluene dissolved 93.44 wt% of organic substances that evaporated at the temperatures 220–634°C. The content of inorganic substances is 6.56 wt% (the part insoluble in conventional mineral acids is 4.19%). The latter is completely soluble in hydrofluoric acid and looks like sand (probably aluminum-silicates). Inorganic compounds are represented by the compositions of the silicon, aluminum, sodium, calcium, iron, vanadium and other metals that were found in small quantities.

Table 2. Results of deposits analyzes taken from refinery equipment

Indicators	In-water-cooling tower	Wagon tank	Reservoir
Organic substances % weight	87.54	93.44	98.92
Inorganic substances % weight	12.46	6.56 (4.19% solutions HF)	1.08
Water	11.0	-	-
Mechanical impurities	1.47	-	1.08
Substances removed at the temperature of (550 ± 25)°C, %	-	94.16	99.05

Table 3. The content of cations in the deposits, weight%

Element	In-water-cooling tower	Wagon tank	Reservoir
Iron	0.08	0.043	0.17
Zinc	0.003	0.002	0.02
Copper	0.002	0.001	0.001
Manganese	0.005	0.001	0.005
Calcium	0.015	0.068	0.07
Magnesium	0.005	0.009	0.01
Sodium	0.0015	0.083	0.03
Potassium	0.001	0.001	0.004
Silicon	Traces	Traces	0.02
Vanadium	-	0.018	0.01
Aluminum	-	0.01	0.01



TBT of oil and organic part of deposits:

- ◆ – cooling tower;
- – cistern;
- ▲ – vessel;
- × – oil

Dark viscous residue with a melting point 53°C was formed in reservoir. Deposits contain 2.08% of sulfur and mechanical impurities (Table 2). High content of iron, nickel, zinc, aluminum, calcium, sodium, magnesium and silicon was notified. The organic part (98.92%) contained 70% n-alkanes and iso-alkanes. Deposit has lost of 99.05% of its matter at the temperature 550°C. After combustion, residue had reddish-brown color which is the evidence of increased iron content due to corrosion product accumulation.

Bottom deposits from the reservoir contained naphthenic hydrocarbons and wax(s) from C₆ (boiling temperature is 6°C) to C₅₉ (boiling temperature 613°C).

Micro-elemental composition of bottom deposits is the same as in the original petroleum. It includes iron, nickel, zinc, aluminum and typical corrosion products, as well as calcium, sodium, magnesium, silicon, typical for this sort of deposits.

Metals are included also in compounds that resin and asphalts are produced from. These compounds have surface-active properties and influence the beginning of crystallization and wax crystals growth. Cooling of petroleum with high wax content increases the deposit thickness due to extensive crystallization and formation of strong macro-crystalline structure. This causes the formation ARWD profiles with a constant increase of thickness. Particles of sand, clay and other mechanical impurities in petroleum act often as crystallization centers that strengthen the ARWD.

Sludge and deposits are extremely harmful for environment because of their hard solubility. As usual, oil-slimes after accumulation and dehydration are transported to industrial waste landfills. At the same time, refinery deposits from cooling towers can be accumulated in oil-separators available at every block of water purification and then mixed

with a wide oil fraction at the rising temperature for a further rectification. Depositions from the wagon-tanks and reservoir have approximately the same fractional composition which is seen from Figure, so they can be warmed up and mixed with petroleum and processed to Air-Vacuum Pipe Heater (AVPH).

4. Conclusions

1. The analysis of deposits from in -water-cooling towers, cistern, wax petroleum storage tanks was done. Significant portion of deposits is proved to be hydrocarbon compounds. In-water-cooling towers deposits of light color (mainly wax) were found; in other vessels dark foul-smelling asphalt - wax deposits were formed during wax-paraffinic petroleum transportation and storage.

2. Further usage of deposits was proposed in depending on their fractional composition: light color deposits from in-water cooling towers can be reheated and mixed with broad-rate-petroleum fractions; dark color deposits can be also heated and processed to the AVPH.

References

- Ahmetov, A.F.; Gerasimova, E.V.; Nurizdanova, V.F. 2008. *Analysis of laboratory tests effectiveness for dissolution of asphalt-resin-wax deposits*. Bashkir Chemical Journal. Vol. 15. N 1: 65–67 (in Russian).
- Ivanova, L.V.; Burov, E.A.; Koshelev, V.N. 2011. *Asphalt-resin-wax deposits in oil production, transportation and storage*. Electronic scientific journal "Oil and gas business". P. 268–284. Available from Interenet: <http://www.ogbus.ru/authors/IvanovaLV/IvanovaLV_1.WSF>. (in Russian).
- Oil Chemistry*. 1984. Ed. by Z.I. Syunjaev // I.Yu. Batueva, A.A. Gaile, Yu.V. Pokonova. Leningrad, Chemistry. 360 p. (in Russian).

Received 16 October 2013.

Н.В. Бондар¹, А.М. Денисюк², Ю.Ю. Симонов³, О.В. Тертишна⁴, Л.О. Сніжко⁵. Аналіз асфальто-смоло-парафінових відкладень на нафтопереробному обладнанні

^{1,2}ПАТ "Укрнафта", вул. Свіштовська, 3, Кременчук, Україна, 39610

^{3,4,5}Український державний хіміко-технологічний університет, 8, просп. Гагаріна, Дніпропетровськ, Україна, 49005

E-mails: ¹bondar@ukrtatnafta.com; ²denisiuk@ukrtatnafta.com; ³simonov13@yandex.ru; ⁴t_elena2000@bigmir.net; ⁵lsnizhko@mail.ru

Проведено аналіз асфальто-смоло-парафінових відкладень, відібраних із градирні, вагоноцистерни і резервуару, в якому зберігалася парафініста нафта. Показано, що до складу відкладень входять органічна (> 90%) і неорганічна частини – перша збагачена високомолекулярними алкановими вуглеводнями, друга – механічними забрудненнями. Запропоновано методи утилізації відкладень.

Ключові слова: аналіз; асфальто-смоло-парафінові відкладення; склад.

Н.В. Бондарь¹, А.Н. Денисюк², Ю.Ю. Симонов³, Е.В. Тертышная⁴, Л.А. Снежко⁵. Анализ асфальто-смоло-парафиновых отложений на нефтеперерабатывающем оборудовании

^{1,2}ПАТ “Укрнафта”, ул. Свиштовская, 3, Кременчуг, Украина, 39610

^{3,4,5}Украинский государственный химико-технологический университет, 8 просп. Гагарина, Днепропетровск, Украина, 49005

E-mails: ¹bondar@ukrtatnafta.com; ²denisiuk@ukrtatnafta.com; ³simonov13@yandex.ru; ⁴t_elen2000@bigmir.net; ⁵lsnizhko@mail.ru

Выполнен анализ асфальто-смоло-парафиновых отложений, отобранных из градирни, вагоноцистерны и резервуара, в которых хранилась парафинистая нефть. Показано, что в состав отложений входят органическая (> 90%) и неорганическая составляющие – первая обогащена высокомолекулярными алкановыми углеводородами, вторая – механическими загрязнениями. Предложены методы утилизации отложений.

Ключевые слова: анализ; асфальто-смоло-парафиновые отложения; состав.

Bondar Nadejda. Head of the Oil Laboratory.

PAT “Ukratnafta”, Kremenchug, Ukraine.

Education: Donetsk State University, Donetsk, Ukraine (1982).

Research area: oil investigations.

E-mail: bondar-nv@ukrtatnafta.com

Denysyuk Anatoliy. Deputy Chief Technologist.

PAT “Ukratnafta”, Kremenchug, Ukraine

Education: Lviv Politechnik, Lviv, Ukraine (1971).

Research area: oil refining.

E-mail: denisiuk@ukrtatnafta.com

Simonov Yuriy. Engineer.

Education: Ukrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine (1995).

Research area: oil refining.

Publications: 4.

E-mail: simonov13@yandex.ru

Tertyshna Olena. Candidate of Engineering. Associate Professor.

Fuel Engineering Department, Ukrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine.

Education: Ukrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine (1985).

Research area: oil refining.

Publications: 12.

E-mail: t_elen2000@bigmir.net

Snizhko Lyubov. Doctor of Chemistry. Professor.

Head of Fuel Technology Department, Ukrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine.

Education: Ukrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine (1973).

Research area: electrochemistry, oil refining.

Publications: 82.

E-mail: lsnizhko@mail.ru