Receiving sorption material from production waste

K V Katerinin, P A Sidyakin*, D M Shchitov, P S Chernov
Volgograd State Technical University, 1 Akademicheskaya str., Volgograd, 400074, Russia
E-mail: sidyakin_74@mail.ru

Abstract. The method of liquidation of the map of viscous production wastes of additives is developed. The special collector of waste is developed for selection of waste from the card. Complex influence of the ground of waste of the oil refinery including three sections, a pond evaporator, a pond store of synthetic fatty acids, a dump of solid industrial wastes, the map of viscous production wastes of additives on the environment is investigated. It is revealed that the main pollutant are oil products (oil hydrocarbons), a steady trend of their accumulation in the environment is noted.

The main fields of purpose of production wastes of additives are defined. They are applied as special additives at production of concrete and concrete goods and designs with increased requirements on water permeability, frost resistance, in quality of the plasticizing additives in concrete mixes, as the additive increasing elasticity and extensibility of bituminous coverings. Production wastes of additives in production of paints water and composite the general and special purpose are introduced.

Production wastes of additives are used for recultivation of the lands polluted by oil and also purification of oil-containing sewage.

A significant part of waste, generated at oil refineries, is not used; they are collected in storage tanks, taken to dumps, placed at landfills, which all leads to environmental pollution. It should be noted: after additional processing, they can be converted into valuable secondary raw materials. The presented materials in the article prove the relevance of research on this topic. The aim of the research was to obtain sorption material for the purification of water-containing products from the waste production of additives DF-11, EFO, AFC, VNIINP-360, VNIINP-370.

It is shown that the main polluting substances are petroleum hydrocarbon, which is explained by the production specifics and low degree of oil waste utilization, especially the production of additives. This waste is almost completely transferred to the viscous waste map of an industrial landfill, which has a limited volume, and this makes it necessary to look for ways to utilize additive production waste, as well as to develop ways to eliminate the map itself, as oil waste accumulates [22-25].

Additive production waste (OPP) is a multicomponent system, which includes both inorganic and organic components, the content of which depends on the feedstock purity and on the synthesis method of the main product. The composition of the OPP is not constant in time, the daily change in the content of different ingredients can vary up to three or more times a day. The composition and properties analysis of the OPP is aggravated by the fact that in these systems occurs the physicochemical interaction of the mineral and organic components at various temperatures and pressures.
The study of the OPP composition includes their separation into components and study each part, using a complex of physicochemical methods [1-5,8-10]. The content of components in the OPP was determined by spectral, atomic adsorption, X-ray fluorescence, and chemical analysis methods [2,4,6,9,11,12]. To determine the total organic material content in the OPP the UV and IR spectroscopy were used [1, 5,3,15,15].

Were researched following additives production wastes: DF-11, EFO, AFC, VNIINP-360, VNIINP-370, produced by “LUKOIL-VNP” LLC. Was determined the content of mineral and organic components, the mineral part chemical composition, as well as the group hydrocarbon composition of the organic part. The organic component was separated from the mineral by the extractive method [4,19,20,22], it consists of high molecular weight petroleum hydrocarbons of methane, naphthenic and aromatic series (table 1).

**Table 1.** Group chemical composition of the organic fraction of oil waste from the additives production

| Hydrocarbon group name | Content in additive, % |
|------------------------|------------------------|
|                        | VNIINP -360 | DF-11 | VNIINP -370 | EFO | AFC |
| Paraffin-naphthenic    | 14.9        | 22.2  | 26.7        | 36.0 | 17.4 |
| Light aromatic         | 13.2        | 5.3   | 14.7        | 11.0 | 11.7 |
| Medium aromatic        | 28.2        | 7.6   | 29.1        | -   | 37.8 |
| Heavy aromatic         | 14.6        | 40.8  | 9.2         | 2.8 | 8.0 |
| Aromatic Amount        | 56.0        | 53.7  | 53.0        | 13.8 | 57.5 |
| Resin 1                | 12.6        | 7.4   | 6.8         | 17.8 | 6.4 |
| Resin 2                | 12.5        | 6.8   | 11.3        | -   | 16.0 |
| Resin Amount           | 25.1        | 14.2  | 18.1        | -   | 22.4 |
| Asphaltenes            | 4.0         | 9.9   | 2.2         | 32.4 | 2.7 |

OPP contain oxygen-containing substances (acids and alcohols). Extraction of oxygen-containing compounds was carried out with methanol. The extracts output was (76-82)% depending on the amount of oxygen-containing compounds in the initial product. Fatty acids output were at (32-47.2)%, and neutral oxygen-containing compounds at (41-47)%. Table 2 presents data on the group composition of extracts, allocated from OPP, DF-11, VNIINP-360, VNIINP-370, EFO, AFC.

**Table 2.** The content of oxygen-containing compounds in OPP and extracts obtained from OPP

| Type of OPP | The content of oxygen-containing compounds in the OPP, % | The content of oxygen-containing compounds in the extract, % |
|-------------|------------------------------------------------------|--------------------------------------------------------|
|             | total       | solid acids | neutral acids | total    | solid acids | neutral acids | content of paraffin 1 and 11 |
| 1           | 2.0         | 3.0         | 4.0           | 5.0      | 6.0         | 7.0           | 8.0                  |
| DF-11       | 30.9        | 9.7         | 21.2          | 76.3     | 33.3        | 43.0          | 17.0                 |
| EFO         | 37.3        | -           | -             | 79.2     | 32.5        | 45.7          | 17.1                 |
| VNIINP -360 | 42.8        | 14.4        | 33.4          | 78.9     | 40.9        | 38.0          | 13.9                 |
It’s worth noticing, that in the OPP with a high content of paraffins (around 17%), the coagulation process intensifies, especially under the ultraviolet rays the influence. It is likely, that treatment of paraffin-containing systems with ultraviolet rays leads to the enlargement of paraffin crystals spatial aggregations at the initial stage of their formation, which is typical for lyophilic colloidal systems.

The inorganic part composition is shown in table 3.

**Table 3.** Mineral part composition of OPP

| Name of elements, substances | Content in additive, % |
|-----------------------------|-------------------------|
|                             | VNIINP-360 | DF-11 | VNIINP-370 | EFO | AFC |
| Ca^{2+}                     | -          | 1.93  | 14         | -   | 18.6|
| Mg^{2+}                     | -          | 1.2   | -          | -   | -   |
| Al^{3+},Al Cl_{1.3}         | -          | -     | -          | -   | 11.4|
| Al_{2}O_{3}                 | -          | 49.55 | -          | -   | -   |
| Ba^{2+},Ba(OH)_{2}           | 23.57      | -     | -          | 2.7 | -   |
| S^{2-}                      | 2.45       | 5.2   | to 8       | 3.42| -   |
| Zn^{2+}                     | 21.37      | 4.3   | -          | 13.4| -   |
| P^{5+}                      | 5.11       | 3.89  | -          | 2.7 | -   |
| Si^{4+},SiO_{2}              | -          | 8.1   | -          | -   | -   |

In all additives by technology uses mineral oil. Its content varies from 11 to 41%. When solving the issue on the OPP disposal, it should be not only determine the chemical composition of mineral oil in a particular waste, but also research changes in its composition as a result of the additives with mineral oil components interaction at high (300-400 °C) temperature. The study on the composition of the oil fraction during thermal action in the oil waste additives AFC, as well as in a mixture of OPP AFC, and AFC additive with a content of the last 5% mass, was conducted. The experiments were carried out on laboratory circulation micro equipment with the analysis of gaseous products. The results are shown in table 4.

To assess the chemical waste composition, were used indicators characterizing the structure of the average product molecule: resin forming ability coefficient; carbon fraction in aromatic rings. These indicators were determined by spectral methods [19-21]. The carbon proportion in aromatic structures for OPP AFC was 14.14, for the AFC additive, 22.57, and for their mixture - 15.98. Coefficients of resin forming ability turned out to be equal to 1.24; 1.66; 1.31 for OPP AFC, additives AFC and for their mixtures, accordingly.

**Table 4.** The composition of the oil fraction OPP AFC

| Indicator          | OPP AFC | Mixture of OPP AFC and AFC |
|--------------------|---------|----------------------------|
| 1                  | 2       | 3                          |
| Molecular weight   | 764     | 639                        |
| Basic composition, % mass. |        |                            |
| Carbon             | 85.94   | 87.1                       |
| Hydrogen           | 11.88   | 9.91                       |
A thermogravimetric study of the thermolysis of OPP AFC and its mixture with the AFC additive was carried out on a Paulik-Erden derivatograph in the non-isothermal mode with a linear heating rate of 10°C/min in helium medium.

The solid residues obtained after thermal decomposition were analyzed on a X-ray diffractometer DRON-2. The interlayer distance \(d_{002}\) was used as an indicator degree of crystallites ordering. It was found that the addition of AFC additive at 450°C does not affect the crystallites structure. With an increase in the temperature decomposition to 475°C, \(d_{002}\) decreases from 3.508 to 3.481 A, the crystallite size increases from 27 to 29A.

Therefore, with an increase in temperature, occurs enhanced resin formation waste, which can be converted to a solid residue by adding an additive in (up to 5% mass.).

The composition and properties of the OPP, subjected to prolonged heat treatment analyzed. The studies were carried out on oil waste samples taken from technological plants for the production of additives EFO and VNIINP-370 after heat treatment at a temperature of 300°C for 10 hours.

The group carbon composition was determined by a combination of rectification and chromatography methods [4, 13-18, 21]. The results are shown in table 5.

**Table 5.** The oil fraction composition of additives EFO, VNIINP-370 after heat treatment

| Indicators                          | Type of OPP   |
|------------------------------------|---------------|
|                                    | EFO | VNIINP -370 |
| Density, kg/m³                      | 921 | 923          |
| Sulfur content, %                   | 0.35 | 0.90        |
| Fractional composition, distillation to,°C |     |              |
| 350                                 | 17  | 4            |
| 400                                 | 42  | 20           |
| 450                                 | 67  | 43           |
| 500                                 | 82  | 58           |
| 525                                 | 86  | 65           |
| Group hydrocarbon composition,%     |      |              |
| Paraffin- and naphthene-based       | 55.6 | 41.4        |
| Aromatic: Light                     | 5D  | 10.8         |
| medium                              | 10.8 | 11.4        |
| heavy                               | 158 | 23.0         |
| resin                               | 11.0 | 116         |
| asphaltenes                         | 11.7 | 2.0         |

- **Group hydrocarbon composition, % mass.**

| Group   | Paraffin- and naphthene-based | Aromatic: Light | Medium | Heavy | Resin | Asphaltenes |
|---------|-------------------------------|----------------|--------|-------|-------|-------------|
|         | 44.9                          | 6.6            | 8.3    | 3.6   | 16    | 20.5        |
| Aromatic: Light | 8.3                          | 6              |        |       |       |             |
| Medium  | 3.6                           | 10.2           |        |       |       |             |
| Heavy   | 16                            | 41.4           |        |       |       |             |
| Resin   | 20.5                          | 28.5           |        |       |       |             |
| Asphaltenes | 6.7                          | 7.3            |        |       |       |             |
The studied samples were subjected to vacuum distillation with the selection of narrow fractions, boiling within °C: n.k.-350; 350-370; 370-400; 400-425; 425-450; 450-475; 475-475-k.k. The group hydrocarbon composition of the obtained narrow fractions of oil wastes was studied by liquid-displacement chromatography (table 6).

The data analysis of the studied OPPs chemical showed the composition dependence on temperature. With increasing boiling limits of narrow fractions, their group carbon composition changes, decreases the proportion of paraffin-naphthenic hydrocarbons, simultaneously, the content of heavy aromatics and resins increases. The asphaltene, contained in the oil waste, during the vacuum distillation are concentrated in the residual fraction boiling above 475 °C.

**Table 6.** The composition of the narrow oil fractions in waste additives of EFO, VNII NP-370 after heat treatment

| Narrow fractions boiling range, °C | Paraffin- and naphthen-based | Aromatic | Resins | asphaltenes |
|-----------------------------------|-------------------------------|----------|--------|-------------|
|                                   |                               | light    | medium | heavy       | benzene | benzene-alcohol |
| 1-2                               |                               | 3        | 4      | 5           | 6       | 7               |
| EFO                               |                               | 64.7     | 8.4    | 8.7         | 11.7    | 1.9             | 46 | - |
| 350-370                           |                               | 49.4     | 16.7   | 8.2         | 12.6    | 2.5             | 10.6 | - |
| 400-425                           |                               | 60.0     | 9D     | 9.0         | 13.1    | 1.45            | 7.4 | - |
| 425-450                           |                               | 66.9     | 8.8    | 3.9         | 12.9    | 2.4             | 5.1 | - |
| 450-4756                          |                               | 56.3     | 11.3   | 5.5         | 16.0    | 4.2             | 6.7 | - |
| Above 475                         |                               | 25.3     | 4.4    | 1.9         | 31.6    | 13.8            | 20.6 | 2.4 |
| VNII NP-370                       |                               | 57.6     | 6.5    | 13.7        | 5.3     | 0.9             | 16 | - |
| 326-350                           |                               | 58.1     | 7.4    | 11.9        | 9.0     | 1D              | 12.5 | - |
| 350-375                           |                               | 51.5     | 12.0   | 15.3        | 16.0    | 1.7             | 2.6 | - |
| 375-400                           |                               | 48.2     | 12.2   | 13.3        | 12.8    | 2.1             | 11.4 | - |
| 400-425                           |                               | 95.1     | 13.9   | 7.9         | 14.6    | 4.7             | 23.8 | - |
| 425-450                           |                               | 38.1     | 14.4   | 8.8         | 24.3    | 2.7             | 11.7 | - |
| Above 475                         |                               | 13.9     | 6.0    | 2.3         | 39.8    | 16.2            | 18.0 | 3.8 |

Consequently, based on the above, next conclusions are formulated:

- researched the composition of waste production additives DF-11, EFO, AFC, VNII NP-360, VNII NP-370.
- the content of mineral and organic components, the chemical composition of the mineral, the group composition of the organic part have been established.
- the content of oxygen-containing compounds is established.
- a study of the oil fraction composition during thermal action in oil waste additives production was conducted.
- it was found that with increasing temperature there is an enhanced resin formation of the waste, which can be converted to a solid residue by adding an additive.
References

[1] Seregina I F, Okina O I, Distanov A A 1999 Spektrofotometricheskoe opredelenie nefteperekandy dlya pochev Analiticheskaya himiya 54 (4) 434-440.

[2] Skug D, Uehst D 1980 Osnovy analiticheskoi himii (Mir, Moscow) 30.

[3] Fryazinov V V, Kolbin M A, Vasileva R V 1977 Issledovanie spekral'nymi metodami molekul'nykh struktur otnostych nefteperekandy Sb. nauchnyh trudov BashNIIHP, Ufa NIINPD977 5-15.

[4] Shatalov A Ya, Marshakov I K 1968 Praktikum po fizicheskoi himii (Vysshaya shkola, Moscow) 224.

[5] Figurnovskij N A 1968 Sedimentacionnyj analiz (Goskhimizdat, Moscow) 205.

[6] Kuz'mina Eh F 1977 Spektrofotometricheskaya metodika opredeleniya koksoobrashuyushchej sposobnosti neftyannykh otnostych Sb. nauchnyh trudov BashNIIHP, Ufa, NIINPD977 29-35.

[7] Posobie po proektirovaniu polygonov po obezrevzhiyuniyu i zahoroneniyu toksichnyh promyshlennyh othodov (SNiP 2.01.28-85), Moscow, Central'nij institut tipovogo proektirovaniya, 46.

[8] Puzanova N V, Bachernikova S G, Enskova N P, Mihal'kova A I 2002 Preventivnye sredstva na otnove netkanych materialov dlya predotvrashcheniya popadaniya othodov proizvodstva v okruzhayuschuyu sredu Aktual'nye problemy sozdaniya i ispol'zovaniya novyih materialov i ocneni ih kachestva (CHErkizovo, MGU) 177-179.

[9] Samojlenko N N, CHErkashina A N, Gurenko L P 2000 Modeli prognozirovaniya zagryzheniya okruzhayushchej prirodnoj sredy pri ispol'zovaniy vtorichnyih resurso Gntegrov. tekhnol. ta energoberezhenie 4 26-30.

[10] Sulejmenov R A 1997 Sravniiteli'naya harakteristika vybruvkov o atmosferu predpriyatij neftekhimicheskoi i neftepererabatyvayushchej promyshlennosti (Gigiena i sanitariya) 1 8-10.

[11] Sokolov L I, Tomilov A B Tekhnologiya obezrevzhiyuniyu neftesoderzhashchih osadkov Mezdunarodnaya nauchno-tekhnicheskaya konferenciya "Problemy ehkologii 4 18-21.

[12] Halilov V Sh, Gapurov R R 2001 Tekhnologiya utilizacii nefteghashchih osadkov v okruzhayuschej sredy Mezdunarodnaya konferenciya po voprosam effektyvnosti yanov i svojstv otnostych othodov (SIBIKO, Moscow) 270-271.

[13] Shatalov A A, Pluzhnikova Z A, Agentov V V, Nekrasov Yu F 2000 Obsepchenie bezopasnosti skladirovaniya othodov i stokov predpriyatij himicheskoi, neftekhimicheskoi i neftepererabatyvayushchej promyshlennosti Bezopasnost' truda v promyshlennosti 3 25-27.

[14] Andushkin K N 1997 Issledovaniya po sozdaniyu ehkologicheskoi chast' sredstva ochistki polov otn zagryzheniya nefteperekandy Neftyanaya i gazovaya promyshlennost'. Seriya Zashchita ot korozii i ochkani okruzhayushchej sredy 3 17-19.

[15] A Koolaj-feldlogozfs romyeyet-vedelmi kerdesei a 16. Koolaj Vilagkon- gressz. Deak Gyula MOL szak.tud/orzl/ 2001 31 15-18.

[16] Myroso A R 2000 Voprosy sozdaniya polygonov po obezrevzhiyuniyu i zahoroneniyu toksichnyh othodov Doklady mezhdunarodnogo ehkologicheskogo kongressa "Novoe v ehkologii i bezopasnosti zhiznedeyatel'nosti "t. 1 (SPb: BTGU) 524—526.

[17] Mymrin V A 1997 Utilizacii promyshlennyh othodov v stroitel'stve kak reshenie chasti ehkologicheskoi problem SMkologii promyshlennogo proizvodstva 1-2 22-27.

[18] Cleaning of petroleum or its derivatives on soil. № 1116785 EPV, MPK7 S//D 1/820 Fina Oleo Chemicals N., Pinon Cristian, № 00100831.

[19] Hugo Achim, Neumann Peter, Schmidt Klaus, Gthrard Baumgarten Diana Grenzttin 2000 und Mog-lchkeiten eines anlagenbezogenen Umweltmonitorings, Chem- Ing.-Techn, 72 (9) 952-953.

[20] Jiang Pei-hua, Zhong Zing, Shuan Xiaojuan, Dai Wei 2001 Shiyou huayong gaodeng xuebao xuebao J.Petochen. Univ. 14 (4) 27-30.

[21] Fishe K, Norman V S, Chemosphere 1999 Studies of the Behavior and Fats of the polymer additives octadecyl-3 (3,5-di- T-buty-4-hydroxyphenyl) propionate and tri(2,4-di-t-butyphenyl) phosphite in the environment 39 (4) 611-625.
[22] Moskvicheva A V, Tregubov A Y, Sakharova A A, Moskvicheva E V, Puhov M V 2018 Sorption purification of underground sources water Journal of the Volgograd State Architectural and Construction University. Ser.: Construction and architecture 51 (70) 160-169.

[23] Moskvicheva E V, Yuryev Yu Yu, Batmanov V P, Prikhodchenko A V, Fomin A A 2016 Processing product scopes galvano-and the SOZH-containing sewage the Messenger the Volgograd state. architectural and construction un-that. It is gray. Construction and construction 44 (1) 84-92.

[24] Moskvicheva E V, Strepetov I V, Batmanov V P, Doskina E P, Khanova E L, Suvorova M A 2016 Filtration process using loading from oil waste Journal of the Volgograd State. Architectural and Construction un-ta. It is gray. Construction and construction 44 (1) 74-83.

[25] Moskvicheva E V, Sakharova A A, Gonchar Y N, Ignatkina D O, Kuzmina T A Waste water treatment using mixed reagent obtained from oil waste Journal of the Volgograd State Architectural and Construction University. It is gray. Construction and architecture 34 (53) 114-120.