Development of high-effective oil sorbents on the basis of microencapsulation/microgranulation techniques

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Abstract

The work was devoted to developing oil sorbents of novel type capable of forming a semisolid layer when taking up the spilled hydrocarbon in order that the resulting stuff could easily be picked up with mechanical devices and could firmly retain absorbed petroleum products. The work comprises three principal stages:
- choice and modification of dispersed solid carrier;
- study and choice of polymer ingredients;
- development of some appropriate microencapsulation (microgranulation) technology.

Expanded perlite (further perlite) and porographite have been selected for using as solid substrates for their further treating with polymers.

The general approaches to the design of discrete polymer shells for the composite absorbing materials (CAM) have been developed. It is proposed that polymer as a CAM component should provide the following principal functions:
- to be highly swellable in hydrocarbons, but not to dissolve in them;
- to ensure a possibility of microencapsulation or microgranulation of porous sorbent;
- to bind CAM particles together when swollen in spilled hydrocarbons.

From the above considerations, loosely cross-linked acrylic low-polar rubbers have been chosen.

A set of laboratory tests have been performed and shown the above concept to be highly promising for its further practical implementation.
1 Introduction

The work was devoted to developing oil sorbents of novel type capable to form semisolid layer when taking up the spilled hydrocarbon in order that the resulting stuff could be then easily picked up with mechanical devices and could firmly retain absorbed petroleum products. The work comprises three principal stages:
- choice and modification of dispersed solid carrier;
- study and choice of polymer ingredients;
- development of some appropriate microencapsulation (microgranulation) technology.

The work is a further extension of the authors' earlier developments in the area of oil products storage and operating safety [1].

2 Choices and Modification of Dispersed Sorbents for Manufacturing CAM

The sorbents used for localization and/or cleanup of oil and oil products in cases of their accident spills are divided into three basic groups: organic (of vegetable origin), non-organic (of mineral origin) and synthetic materials (e.g., [2 - 4]).

The principal parameters, which determine the choice of one or another sorbent are as follows:
- retention capacity of the sorbent in relation to oil and oil products (sorption power, liquid retention capacity, adsorption, absorption);
- oleophily (hydrophoby);
- floatability, including floatability after taking up oil or oil products from the water in the course of clean-up;
- liquid retention and capacity for squeezing out;
- cost;
- availability.

The sorbents examination was conducted in two principal directions:
- studying the kinetics of oil products sorption process with sorbents of various types;
- studying the porous sorbents structure.

To study the kinetics of dispersed sorbents sorption process there was adapted the previously developed original method in which a loosely poured layer of sorbent is capillary impregnated with liquid (oil products) accompanied by continuous automatic registration of the mass of liquid impregnating the layer.

On the whole, more than 50 dispersed sorbents of the three main types were studied: non-organic, organic, and synthetic. The following oil products were used as impregnating (sorbed) ones: diesel fuel oil of summer and winter types, as well as kerosene and crude oil.

Fig.1 and Fig.2 display examples of sorption curves for various sorbents.
The study of sorption kinetics showed that liquid retention capacity of various sorbent types have values in the range from fractions of 1 (river sand) to 40 (porographite) depending on the nature, structure, dispersity degree of a particular sample. The character (kinetics) of oil products sorption also considerably differs. Thus, under conditions of the experiment on the capillary impregnation of various sorbents, the time needed for equilibrium sorption of a certain product varied by an order of magnitude and more.

One of the most important characteristics of sorbents is their microstructure. The scanning electron microscopy method is a unique one allowing visualization of those structures which considerably facilitates the correct choice of sorbents, and gives a chance to observe them in the process of their modification and ageing. Electron microscopic study of oil sorbents morphology was carried out with scanning electron microscope JSM-35, Jeol make. It was established that vegetable-originated sorbents represent porous cellulose fiber stuff the structure and dimensions of which depend on the structure of a parent plant. Generally, these are fibrous or laminated materials featuring various pores and ducts of 1 - 30 μ width sometimes partly filled with resinous substances.
Fig 2: Kinetics of diesel fuel sorption by various sorbents of vegetable origin
1 - pine bark, treated at 300 °C; 2 - native pine needles (extracted), treated at 296 °C; 3 - pine bark; 4 - native pine needles (extracted), treated at 296 °C <300 µ; 5 - native pine needles (extracted); native pine needles (extracted), <300 µ

From the group of mineral sorbents, expanded perlite, kieselguhr and vermiculite were investigated. Expanded perlite represents hollow spheres of irregular shape of 10 - 500µ in size with thin walls of 1 - 0.5 µ thick. Spheres of 300 - 500 µ in size are usually split. Small spheres of 10 - 50µm in size remain intact (Fig. 3a). Kieselguhr - dispersed material consisting of particles 1 - 30 µ in size and having through pores ~ 1 - 2µ in diameter. Vermiculite - laminated particles of 5 - 150µ in size. Pores of 0.1 - 1µ in diameter. Porographite, the artificial sorbent, represents the "bellow-type" morphological structure with cross-section of 100 - 300 µ and length of up to 1mm. The folds with walls of < 1µ thick are shut or loosely shut. Gaps between folds vary in range from 1 to 50µ. (Fig.3b).
Summarizing the results of microscopic studies of oil sorbents, and comparing these data with their liquid retaining capacity data, it can be preliminary concluded that the most effective are the sorbents made of highly oleophilic materials with pores of 10 - 100 \( \mu \) in size and walls of \( \leq 1 \mu \) thick. Sorbents of various nature with pores less than 5\( \mu \)m in diameter are less efficient for oil products.

The sorbents properties taken together served as a basis for choosing expanded perlite (further perlite) and porographite for development of basic composition and for production of CAM. These sorbents have the highest sorbing capacity, good floatability, they are chemically inert and resistant. Porographite is a highly hydrophobic and oleophilic sorbent. Perlite has good wettability for oil products but it needs hydrophobization which is possible in the process of its microencapsulation. Both sorbents are industrially produced and available in the market. The need of microencapsulation (microgranulation) of perlite and porographite is determined by their low density (especially in case of porographite) and high degree of dispersity which fact makes their application in pure form as oil sorbents practically impossible. The sorbents are very dusty substances, easily scattered by wind in the air, and by waves and currents on the water which makes very difficult their delivery to the accident location (spill), and their recovery after they have picked up oil products.

3 Study and choices of polymer for manufacturing CAM

Ensuring the efficiency of sorbents with polymer coating in localization and pick-up of accident spills of oil and oil products involves maximum use of sorbing capacity of both sorbent and polymer coating.
Polymer as a CAM component should fulfil the following principal functions:
- to be thermodynamically highly compatible with hydrocarbons (oil products), to achieve high degree of swelling in them, but not to dissolve in them;
- to ensure a possibility of microencapsulation or microgranulation of porous sorbent;
- to fulfil the role of a binding agent, i.e., elastically bind particles of sorbents, forming agglomerates and thus increasing liquid sorbency of material; and after retaining the oil product, to bind those swollen agglomerates to each other, forming coating of a float type;
- to raise hydrophoby of CAM.

On the basis of the above considerations, we suggested slightly cross-linked, hydrocarbon or acrylate, low-polarity rubbers in latex form as a component of CAM for coating sorbent particles. Latex form of rubbers allows one to organize the technologically efficient and safe process of microencapsulating sorbents without use of organic solvents. The techniques were mastered for measuring mass contents of rubber in latex, degrees of equilibrium rubber swelling in hydrocarbons, gel-sol fraction contents in rubber.

Sorbing capacity of rubber in respect to oil products - swelling degree - depends, in addition to external factors (temperature, moisture, etc.), on two principal inherent factors: cross-linking density and rubber polarity which is determined by its chemical nature, i.e., its monomer composition [5]. Therefore, a well-founded choice of rubber component represents an important stage in development of an effective oil sorbent.

It is known that the linear polymer solution density and equilibrium degree of cross-linked polymers swelling have an extremum character of dependence on solubility parameter of solvents, and their maximal value is found in the area of vicinity or coincidence of these latter with parameters of rubber solubility. Oil products, and especially crude oil, represent complex multi-component system for which, in contrast with ordinary mixture of solvents, it is practically impossible to calculate the solubility parameter, the value of which would allow one to theoretically select a suitable rubber.

Solubility parameters of rubbers have been evaluated by two techniques - equilibrium swelling in a range of organic solvents and with the use of inverse gas chromatography (IGC). An example of the appropriate experimental dependency for 2-ethylhexylacrylate (EHA) rubber is displayed in Fig.4. Solubility parameters of oil products have been determined from the data of equilibrium swelling of some previously tested cross-linked elastomers taken as a standard.

It was experimentally established that solubility parameters of a number of the most interesting oil products lie within the interval of 16.0 - 16.4 (J/cm$^3$)$^{1/2}$. So it would be naturally to use a rubber having a solubility parameter of the same value. But the final choice can only be based on a complex of properties including price, a possibility to control the cross-linking density, acceptable rate of oil products sorption, and swollen gel properties. EHA is technologically
available product, and latexes on its basis can be comparatively easily modified. Their modification (cross-linking, monomer composition) was carried out with the aim to give them optimal properties in respect to sorbency, suitability for microencapsulation, and ability to form thixotropic gels. An effective method of three-dimensional structuring of chosen acrylic rubbers in latex form is $\gamma$- or chemical cross-linking, which allows

![Swelling degree vs. solubility parameter of solvent](image)

**Fig.4: Equilibrium sorption of EHA vs. solubility parameter of solvent**

one to produce highly elastic loosely cross-linked polymers with, assigned density of cross-linking.

We produced and studied a considerable number of EHA-latex samples with various acrylonitrile contents (0-23% by mass) and with various degrees of cross-linking, i.e., with various contents of gel-fraction which is determined by irradiation dosage. The best results were obtained for EHA with acrylonitrile content of 5-10% by mass and gel-fraction of 0.7-0.85 which ensure swelling degree of 15-25 with rather good gel solidity making possible, in our opinion, to effectively pick up swollen sorbent. Electron micrographs of coated perlite and porographite are displayed in Fig.5.
4 Investigation of CAM sorbing capacity

For investigating the CAM sorbing capacity, some CAM samples were manufactured on the basis of perlite and porographite with various sorbent/polymer ratio in tableted form.

The results of investigations presented in Table. 1 showed that CAM on the basis of porographite (PG) is characterized by a decrease of sorbing capacity with an increase in polymer share in CAM composition, and there is a direct dependence of CAM sorbing capacity on the density of liquid being sorbed. The effect of liquid hydrocarbon nature on sorbing capacity for CAM on the basis of porographite is insignificant. The obtained data prove that in hydrocarbon sorbing the determining factor for these CAMs is the high capillary absorbing capacity of porographite. The polymer largely serves as a binder.

Table 1. CAM sorbency as measured by the capillary impregnation method

<table>
<thead>
<tr>
<th>Substance name</th>
<th>CAM composition, weight parts</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>PG/HA* -3/1</td>
</tr>
<tr>
<td></td>
<td>sorbency degree, g/g</td>
</tr>
<tr>
<td>octane</td>
<td>19,85</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>21,47</td>
</tr>
<tr>
<td>toluene</td>
<td>25,55</td>
</tr>
<tr>
<td>gasoline A-76</td>
<td>21,13</td>
</tr>
<tr>
<td>diesel oil</td>
<td>23,90</td>
</tr>
</tbody>
</table>

*HA - hexylacrylate rubber
CAMs on the basis of perlite, on the contrary, display a growth of sorbing capacity with an increase in polymer share, the degree of sorption for these CAMs depends on the nature of liquid being sorbed, especially in case of high polymer share in CAM composition. In this case the degree is higher when the affinity of polymer and liquid being absorbed is better. The effect of liquid density becomes significant only in case of low polymer content. Thus, for CAMs on the basis of perlite the decisive factor in hydrocarbon sorption is absorption processes, i.e., swelling of polymer component in hydrocarbons. Perlite which has relatively low liquid retaining capacity ensures CAM floatability and fast access of the liquid being absorbed into the volume of granule (tablet) and consequently fast enough liquid absorption by CAM (90% over 15-30 min). Perlite also gives the material the required rigidity.

On the whole, we can make a conclusion that in respect to their sorbing character the suggested CAMs are classified as different types of oil sorbents. CAMs on the basis of porographite are largely adsorbents, they are characterized by very fast and high sorption (up to 30 g/g) and they are capable, under certain conditions, of desorbing (releasing) oil products which can be used again. CAMs on the basis of perlite are largely absorbents. They are characterized by very active retaining of oil products, their slower absorption. Their retaining capacity is up to 20 g/g.

Experimental modeling of oil products spills and pick up was carried out on water, and sand. The bulk of work was carried out on water as it is the most dangerous, complex, and frequent case of accident spills of oil products. The tests on water were carried out using CAM made on the basis of porographite as that material meets principal requirements for application of sorbents on water, namely: high sorbency, floatability, hydrophoby, oleophily, high rate of sorption and ecological safety.

Water tests were conducted with CAM tablets 6 cm in diameter and 1.5 cm thick. The tablets were weighed to 0.0002 g accuracy, placed on the surface of oil product spot, kept there for 5 min, picked up and weighed again. As sorbent in the process of sorption can pick up water, it was necessary to determine content of water in sorbed liquid mass, as well as the efficiency of removing oil product from water. To that purpose an original technique was developed which made it possible to measure both mentioned parameters. The results are presented in the Table 2. As can be seen, the obtained results of tests with CAM made on the basis of porographite showed high efficiency of sorbents.

A situation of possible land oil spill clean-up can be conventionally divided into two problems. The first is picking up free (excessive) oil product from soil surface or any other solid surface and from various holes. The second is prompt localization of spill in the soil volume and preventing oil product penetration into soil and then subsoil water.

The first problem is effectively solved with help of CAM made on the basis of porographite. In so doing, the sorbency factor for diesel fuel was about 30 g/g, duration of pickup is a few minutes.
The second problem is considerably more complicated. To solve it, we used CAM of the second type made on the basis of perlite and 2-ethylhexylacrylate rubber. That type contained 50% by mass of rubber and is mainly an absorbent. The laboratory tests were conducted on river sand. After introduction of CAM into the volume of sand which was wetted in equilibrium manner with diesel fuel (while fuel content was about 20% by mass), we could achieve sorption of 50% of fuel, i.e., to extract fuel available among the particles of soil (sand) and so to prevent its further diffusion.

Table 2: Absorption of summer diesel fuel from water by CAM on the basis of porographite (PG/EHA = 5/1)

<table>
<thead>
<tr>
<th>Thickness of diesel oil film, mm</th>
<th>Fuel removed, %</th>
<th>Water content in CAM, % by mass</th>
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<tbody>
<tr>
<td>0,1</td>
<td>89</td>
<td>65</td>
</tr>
<tr>
<td>1,0</td>
<td>97</td>
<td>40</td>
</tr>
<tr>
<td>2,5</td>
<td>99,7</td>
<td>32</td>
</tr>
<tr>
<td>3,6</td>
<td>99,7</td>
<td>7,8</td>
</tr>
<tr>
<td>5,8</td>
<td>99,0</td>
<td>0,88</td>
</tr>
</tbody>
</table>

It should be noted that for ecologically sensitive areas it is expedient to use CAM on the basis of perlite for spills on soil as this material possesses high retaining capacity in respect to oil products. Thus, while simulating a spill at sea shore area (wet sand) we managed to pick up more than 90% of spilled summer diesel oil (CAM on the basis of perlite in proportion of perlite/EHA equal to 1/1).

References