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ULTRALIGHT SURFACE-ACTIVE SYSTEMS FOR PREVENTING LIQUID HYDROCARBONS EVAPORATION

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Abstract. Evaporation from the surface of hydrocarbon liquids without cover, at applying native glass microspheres cover, and coated with ultralight surfactant system including microspheres has been investigated. A series of ultralight surface-active systems that interact with the surface of the microspheres and prevent evaporation of hydro-carbon liquids by 98–99.6 % has been developed. For the first time it was found that native gas-filled glass microspheres of low density (200–410 kg/m^3) while providing excellent buoyancy do not protect but increase the evaporation of individual saturated hydrocarbons of homologous series C_5–C_{10}.

Keywords: evaporation of hydrocarbon liquids, spherical glass microspheres, fluorochemical surfactants, ultralight surface-active system.

1. Introduction

The pollution of land, air and water remains one of the most pressing problems. Some major environmental pollutants arise from the stored hydrocarbon liquids. On the way from the well to the gas station the annual hydrocarbons mass loss makes more than 1 % of the total production. During hydrocarbon liquids pumping, transportation and storage much of it is evaporated. The process is accompanied by the loss of the most valuable light fractions, mainly saturated hydrocarbons.

Improvement of fuel storage is therefore a major problem. Its solution, which requires systematic study and scientific research of the evaporation of hydrocarbon liquids process, will allow not only save fuel but also to prevent an occasional forming of explosive fuel-air concentrations that may lead to a complex emergency [1].

Fuels are multicomponent mixtures of hydrocarbons characterized by different boiling points. The lightest ones are car petrol (the beginning of boil is 308–313 K) and aviation gasoline (boiling above 313 K). When storing gasoline its quality deteriorates, mainly due to the evaporation of volatile hydrocarbons C_5–C_7, resulting in higher end-of-boiling temperature and increasing the density through making the fractional composition of fuel heavier.

Today many options to reduce the evaporation of hydrocarbon liquids are offered and used worldwide but none of them can completely stop the process.

Among the measures to prevent the natural loss of liquid hydrocarbons the greatest effect is achieved at using pontoons. Practical application of pontoons had shown that those which are made of synthetic materials have several advantages over metallic. On the one hand, these protective coats are unsinkable, flexible, of lower metal usage, simpler at installation, and their repair proceeds without fire dangerous welding. On the other hand, they possess weak antistatic and fire resistance properties, have narrow temperature range of application and short-term use.

Much less commonly known are coatings which are formed by special physical and chemical methods, and are applied on the surface of the stored oil product surfaces in the form of films, emulsions or foams [2-4]. As compared to other methods, they are simple, inexpensive, affordable, easy to use, and, therefore, deserve more detailed study. In work [5] protection of hydrocarbons from evaporation was performed by applying a fluorochemical surfactants (FSAS) on a carrier – loosened up bread grain (rice, wheat, corn), but such coating was effective for only 14 days and at the temperature no higher than 284 K.

2. Experimental

In our research we have used micro beads 25 microns in size, bulk density of 0.30 g/cm^3. The used hollow microbeads appear as white, thin-walled spheres, made of sodium borosilicate glass at JSC “Novgorod fiber plant” (Russia) according to the standard, type MS, group A_1, with the density of 240 g/cm^3 meeting hydrostatic compressing strength test of 8 MPa [6].

Surfactants (surface active substances, SAS) were: nonionic Tween-80, fluorosurfactant AFFF-3M, hydrophilic polymer polyvinyl alcohol (PVA) and stabilizer A 60731039.

The experiment was conducted as follows: evaporation cases were studied simultaneously by weighing method, namely by placing into thermostat cylindrical vessels with the volume of 100 ml at 298 K, which contained modeled samples of individual volatile hydrocarbon liquids C_5–C_{10} (gasoline constituents) with open surface area of 20 cm^2. For comparison research, microspheres were applied onto the same surface by monolayer and by such calculated number of layers that exceeded surface mirror area of hydrocarbons twice or three times. Research was conducted under the same conditions for 5 h and at weighing samples every 10 min. Also the evaporation of hydrocarbon liquids at application on its surface of ultralight surfactant system coating was investigated under the same conditions.

Research of ultralight surfactant containing systems (USCS) efficiency in preventing evaporation of model mixture imitating composition of gasoline and gasoline A-95 itself was carried out at our experimental installation using chromatographic analysis.

The model mix in the amount of 100 ml was placed into the experimental cell (glass cylinder diameter of 50 mm and height of 100 mm). Onto the layer of model mixture of gasoline A-95 (Table 1) inverted lightweight surface-active systems of composition as shown below were applied; these systems formed floating columns with the height up to 10 mm.

Insoluble in hydrocarbons inverted lightweight surfactant systems were prepared by gradual addition of aerated hydrophilic surfactant solution FSAS (fluortenside), Tween-80 and PVA to the preliminary prepared solution of major SAS (Emultal, Oleodin, Fosfatydin) in a hydrocarbon solvent, followed by stirring for 10 min, using ultrasonic dispersant. To obtain emulsion-suspension systems gas-filled microspheres were added by small parts into already prepared highly structured inverse emulsion at constant stirring for 7–10 min. According to preliminary research, such time was sufficient to establish equilibrium adsorption of surfactant molecules and to obtain the stable suspension-emulsion composition.

3. Results and Discussion

The carrier should be chemically inert and mechanically strong, and the system in which it is composed should be resistant to hydrocarbon liquids, totally impermeable to liquids and gases and have low thermal conductivity, resistance to cracking, satisfactory adhesion, and low cost.

The density of protective coating shall not exceed the density of petroleum products, *i.e.* to be not more than 0.6 g/cm^3.This requirement is mandatory for the use of a floating cover on the surface of oil products.

The objective of this work was the following: development of ultralight surfactants systems to prevent evaporation of hydrocarbon liquids through determination of physical and chemical properties of the components and features of the interaction between them, which is essential for correct combination of the best properties of the components and for creation of composite systems with fundamentally new properties; comparison of evaporation rate from undisturbed hydrocarbon liquids surfaces – first from uncoated, secondly from covered with native glass hollow microspheres and finally from the ones coated with our developed ultralight surface active substances containing systems with hollow glass microspheres in their compositions. By using the high buoyancy of microspheres their protection ability at application in different amounts on the model surface (liquid individual hydrocarbons C_5–C_{10}, which volatile components with the greatest capacity for evaporation are the most problematic at storage) has been evaluated. Experimental results of C_5–C_{10} evaporation kinetic study from clear surface (for reference) and from the one covered with microbeads demonstrated that after application of microspheres on the surface of hydrocarbon liquids the evaporation increases as compared to clear unprotected surface of hydrocarbons. Also, with increasing the number of microspheres layers, the evaporation rate grows, the phenomena that is connected probably with microspheres thermal motion, its rotation resulting in increased evaporation surface area.

To investigate the insulating ability of continuous layer of microspheres against the area of hydrocarbon liquids surface we have layered a variable number of microspheres (Fig. 1): from the partially covered area at 15 % (*line* 2) and at 60 % (*line* 3) to the monolayer 100 % (*line* 4) and up to double – 200 % and triple – 300 % self-excess of hollow microspheres surface calculated relative to the surface mirror evaporation area (*lines* 5 and 6, respectively).

After formation of continuous monodispersed 2- or 3-fold excess microspheres monolayers, relative to the hydrocarbon surface mirror (*lines* 5 and 6), the evaporation is continuing to grow. It was also observed that in the process of hexane evaporation due to adhesion a part of microspheres stuck hanging on the walls of the glass vessel forming a continuous layer which increases surface area and through capillary interactions also increases evaporation.

Similar patterns were observed for other homologs of saturated hydrocarbons such as octane, nonane and decane.

Unlike for pure hydrocarbons model, in case of gasoline (Fig. 2) evaporation is reduced after partial (*curve* 2), continuous (*curve* 4) and two time microspheres monolayer excess relative to the surface of hydrocarbon liquid mirror (*curves* 5 and 6).

From the kinetics of evaporation of gasoline A-95 after application on its surface of a layer of glass microspheres reducing of evaporation was observed compared with a free surface case. Probably, the sorption of normally existing in fuels more hydrophilic compounds as compared to paraffinic hydrocarbons (*e.g.* oxygenates) leads to their sorption on the surface of the glass microspheres surface and thus increases interaction of the microspheres with hydrocarbon solvent removing push off interaction between the microspheres, which slows down rotation and, consequently, reduces evaporation.

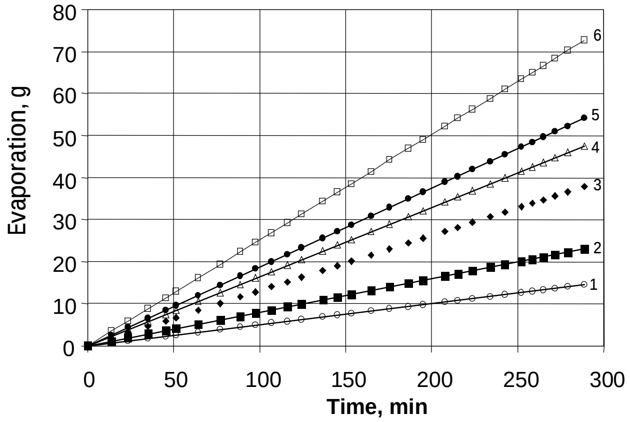

Fig. 1. Kinetics of evaporation of hexane without coating (1) and at layering with glass microspheres, in % of the evaporation area: 15 (2); 60 (3); 100 (4); 200 (5) and 300 (6)

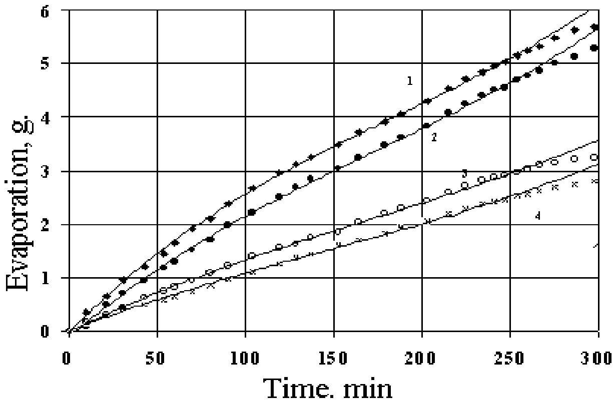

Fig. 2. Kinetics of gasoline A-95 evaporation without cover (1) and covered with glass hollow microspheres in % of evaporation surface area: 60 (2); 200 (3) and 100 (4)

Table

Model mix vapor concentration measurement in air above the protective coating

Hydrocarbons	The content of hydrocarbons		The reduction of evaporation, %
	In vapor, without coating, vol %	In vapor, above coatings, vol %	
n-Pentane	4.93	0.094	98.1
2.3-Dimethylbutane	0.88	0.018	98.0
3-Methylpentane	2.86	0.029	99.0
n-Hexane	7.86	0.031	99.6
Methylcyclopentane	4.4	0.048	98.9
Benzene	1.66	0.015	99.1
Cyclohexane	2.17	0.026	98.8
2-Methylhexane	1.69	0.017	99.0
2,3-Dimethylpentane	1.66	0.083	95.0
1-*trans*-2-Dimethylcyclopentane	1.65	0.025	98.5
n-Heptane	1.7	0.008	99.5
Pentadiene-1.2	11.9	0.155	98.7
1,1,2-Trimethylcyclopropane	8.62	0.215	97.5
Cyclopentane	3.18	0.038	98.8
2,3-Dimethylbutane	1.16	0.015	98.7
1,1,2-Trimethylcyclohexane	3.63	0.047	98.7
n-Nonane	3.08	0.031	99.0
2-Methylheptane	1.07	0.012	98.9
3-Methylheptane	0.74	0.008	98.9
n-Octane	6.26	0.031	99.5

Based on experimental studies, we have developed compositions which components capable of forming the systems of surfactants. Qualitative and quantitative ratio of these components determines the stability of the system on the surface of liquid hydrocarbons and its influence on evaporation [7]. Fluorotenside containing aerated hydrophilic film-forming coating were applied to the surface of liquid hydrocarbon compounds, their effectiveness in preventing evaporation was determined by measuring the concentration of leaked hydrocarbon vapors in air above the protective coating [9] at chromatographic experimental setup [8].

The results of the model mix vapor concentration measurement in air above the protective coating and composite efficacy of coating usage are shown in the Table.

4. Conclusions

It was found that the hollow spherical glass microspheres containing coatings increase the evaporation of liquid individual hydrocarbons C_5–C_{10}.

The increased evaporation can be explained by the growth of the efficient surface area due to the rotation of microspheres within adsorption layer as a result of thermal motion and due to adhesion that is responsible for formation a continuous layer around the perimeter of test vessels.

With the growth of hydrocarbon radical length the evaporation rate decreased and abnormal impact of microspheres is invalidated. For technical mixtures of hydrocarbons (gasoline, diesel) evaporation decreases proportionally to the number of microspheres layers; that can be attributed to sorption and increased interaction of fuels with the naturally hydrophilic surfaces of microspheres.

Therefore, analysis results indicate that hollow microspheres should not be used separately but as a significant component for ultralight technology systems in combination with surfactants. The stability and toughness of these systems largely depends on proper selection of components, concentrations and the carriers. First of all it concerns SAS, their chemical structure and behavior in solutions of different polarity and scientifically grounded selection of the composite, which has shown to be significantly more effective than at using of individual SAS substances. The developed hydrophilic coating composition comprising a polymer, nonionic surfactants, binder, and water maximizes electrical attraction between mixed micelles of SAS and polymer without causing deposition of coating. Inclusion of gas-filled microspheres, that are able to provide excellent buoyancy for ultralight technology systems (UTS), and their high structural and mechanical properties increase the reliability of the protective barrier for vapor diffusion during storage and ensure high mechanical strength and fire safety. Thus, knowledge of physicochemical properties of components and features of the interaction between them is essential not only for the correct combination of the components best properties, but also allows to create compositions and systems with fundamentally new properties. We have developed a series of ultralight surface-active systems that interact with the surface of the microspheres and allow to create barriers to prevent evaporation of hydrocarbon liquids by 98–99.6 %.

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НАДЛЕГКІ ПОВЕРХНЕВО-АКТИВНІ СИСТЕМИ ДЛЯ ЗАПОБІГАННЯ ВИПАРОВУВАННЮ ВУГЛЕВОДНЕВИХ РІДИН

Анотація. *Проведено порівняння випаровування вуглеводневих рідин з вільної поверхні, при заповненні цієї поверхні скляними мікрокульками та при нанесенні на поверхню надлегкої поверхнево-активної композиції зі скляними мікрокульками. Показано, що самі скляні газонаповнені мікрокульки, завдяки низькій густині (200–410 кг/м^3) забезпечують плавучість, але не тільки не захищають, а й підвищують випаровування індивідуальних насичених вуглеводнів гомологічного ряду C_5-C_{10}. Розроблено низку надлегких поверхнево-активних систем, що взаємодіють з поверхнею мікросфер і запобігають випаровуванню вуглеводневих рідин на 98–99,6 %.*

Ключові слова: *випаровування вуглеводневих рідин, фтортензиди, скляні сферичні мікрокульки, поверхнево-активна система.*