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PROPERTIES, APPLICATION AND PROSPECTS OF HIGH-TEMPERATURE ORGANIC HEAT MEDIA DEVELOPMENT

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At present the problem of creation of competitive domestic civil marine engineering is very actual. A federal target-oriented programme «Development of civil marine engineering» for the years 2009-2016 was developed to solve this problem. According to this programme, it is necessary to overcome scientific, technical and technological lag of Russia from industrially developed countries, as well as to develop industrial potential of shipbuilding industry.

One of the many directions of the programme is the development of creation technologies of heat supply system with use of high-temperature organic heat media (HOHM) for ice ships, Arctic icebreakers and platforms.

The purpose of this work is to review existing HOHM and their properties and also consider application and prospects of new high-temperature organic heat media creation.

High-temperature organic heat media are synthetic and mineral oils, resistant to high temperatures. They consist of higher dialkylbenzol. HOHM are applied both in liquid and vaporous states in the interval of temperatures from – 60 °C (gas oil) to 400 °C. These fluids almost do not corrode structural materials. They are all combustible and explosion-proof. HOHM can be almost non-toxic and highly toxic substances. When operating the heater unit must meet high requirements in the point of tightness. Hazard class of used HOHM should be no less than 3-4 class (hazardous and low hazardous substances) in accordance with GOST 12.1007-76 «Harmful substances. Classification and general safety requirements».

Use of HOHM is limited by their thermal resistance, and in nuclear power engineering it is also limited by their radiation resistance.

Thermal resistance is the ability of heat medium to keep its composition and physical properties during the thermal impact. A measure of the thermal resistance is the temperature at which decomposition of the heat medium with change of its composition and physical properties starts. Indicators of the HOHM relative thermal resistance are the formation rate of gaseous, low-boiling (LB) and high-boiling (HB) products of fluid decomposition.

Radiation decomposition, or radiolysis, is the process of initial heat medium chemical transformations under the influence of ionizing radiation. Radiolysis is determined by two factors – radiation resistance (the ability of initial fluid to withstand chemical transformations, caused by the effect of radiation) and the ability of formed active particles (ions and radicals) to react with each other and with the molecules of initial heat medium. A measure of the relative radiation resistance is radiation-chemical output, which is equal to the number of generated or dissociated molecules of the substance to 100 eV absorbed energy.

High-temperature organic heat media are divided into single-component (single-component HOHM) and multi-component (multi-component HOHM). In the form of molecules single-component HOHM are divided into two subgroups: with symmetrical and with flat molecules.

Currently used in practice single-component HOHM with symmetrical HOHM are glycerin and ethylene glycol.

The experience of the use of glycerin as a liquid heat medium shows, that it can be applied to the temperature threshold of + 220 °C. With the help of glycerin uniform heating of heat-energized devices is achieved. In these devices temperature fluctuations do not exceed +\ - 1,5 °C. Glycerin is non-poisonous and non-explosive. During the operation of the heating installation in case of glycerin leakage into the atmosphere it does not inflame, because its auto-ignition temperature is equal to + 393 °C. Pure glycerin does not corrode structural materials, except tin.

Ethylene glycol is used for engine cooling, working in the intense heat mode. Thermal decomposition occurs at a temperature from + 500 to + 520 °C. Ethylene glycol causes corrosion of metals, especially iron. However, by adding inhibitors into ethylene glycol, corrosion can be excluded.

Single-component HOHM with flat molecules are aromatic hydrocarbons: naphthalene, substituted benzol and substituted naphthalene. Among substituted benzol as a high-temperature heat media the following compounds are used: diphenyl, diphenyl ether, diphenylbenzol (terphenyl), monoisopropyldiphenyl, ditholilmethane, tetraisopropyldiphenylmethane and isopropylterphenyl. All mentioned heat media are thermally resistant up to + 300 °C, have

negative melting temperature (except naphthalene, diphenyl ether and isopropyldiphenyl) and high boiling temperature. The properties of the mentioned HOHM are given in the table.

The main physical properties of some one-component HOHM with flat molecules.

№	Name	ρ , kg/m ³ at 20 °C	temperature, °C		viscosity, H*s/m ²		c_p , kJ/(кг*degr ee) at 20 °C
			melting	boiling point	$\mu \cdot 10^5$	at t, °C	
1	Naphthalene	1150	80,2	218,0	88,58	90	2,010*
2	Diphenyl	1006	69,5	255,6	155,2	70	1,758
3	Diphenyl ether	1080 ^{2*}	27	258,5	273,7	50	1,671
4	Monoisopropyldiphenyl	979	- 47	290,0	1410	20	1,725
5	Ditholilmethane	982,6	- 30 – - 36	296,0	532,7	20	1,553
6	Tetraisopropyldiphenyl methane	927,8	-8	384,0	26316	20	1,331
7	Isopropylterphenyl	1013	7-15	346- 374	6259	50	1,158

* At 100 °C. ^{2*} At 60 °C

Multi-component HOHM are divided into three subgroups: eutectic, non-eutectic mixtures and mineral oils. If the technological process provides generation of chemically different organic substances with particular composition, such fluids are HOHM mixtures. They can represent both eutectic and mechanical mixtures. The former can be applied both in the form of liquid, and in the form of steam, the latter, generally, in the form of non-boiling liquid. HOHM mixtures melting temperature always is below at least one high-boiling component, but for eutectic mixtures it is below all components, comprising the eutectic mixture. From the binary eutectic mixtures DDM (28 % of diphenyl and 72 % of diphenylmethane) and diphenyl mixture have practical importance.

Diphenyl mixture is the most studied HOHM. This heat medium, which is used both in liquid and vaporous states, is thermally resistant for continuous operation up to + 380 °C, and in short-term up to + 400 °C. As the experience of diphenyl heating installations work shows, fire danger for them is excluded in the correct installation and use. Diphenyl mixture is almost non-toxic. Possibilities of diphenyl mixture application are very large. Use of the diphenyl mixture properties can be developed in the following directions [3]: implementation of heating by

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diphenyl mixture in the processes, that takes place at temperatures up to + 350 °C, where the decisive technological factor is the stability of temperature; efficiency increase in the chemical equipment work by replacing smokes, water vapour and other fluids with diphenyl mixture; rise of the power plants efficiency: diphenyl mixture can be used as the intermediate heat medium to obtain water vapour.

DDM, along with a diphenyl mixture, is a eutectic mixture. Significant heat medium thermal decomposition begins at the temperature of + 350 °C, so DDM can be used as HOHM up to this temperature.

Quite important is the question of increasing the HOHM thermal stability and boiling temperature. To achieve this goal it is appropriate to use mixtures of terphenyl isomers with diphenyl naphthalene as HOHM. Such mixtures are called santovakses. Among all known at the present time HOHM terphenyl mixtures are the most thermally and radiation resistant heat media: the thermal decomposition beginning temperature is below + 420 °C. They have extremely low corrosive effect on structural materials. As all HOHM they are combustible and explosion-proof. Flash temperature is in the range from + 120 °C to + 200 °C, and the auto-ignition temperature from + 550 °C to + 1000 °C. Melting temperature of all terphenyl mixtures is lower, than that of their components. Eutectic terphenyl mixtures composed of chemically pure components do not have low melting temperatures.

Among known at present HOHM mineral oils are the cheapest heat media, but at the same time the most thermally unstable. In addition, they are the only explosive HOHM and therefore should be applied in airtight assemblies, that do not permit fluid leaking, and at the temperatures below the auto-ignition temperature, which are generally lower than + 300 °C. Oil heat media are divided into two subgroups: non-aromatic mineral oils, or simply mineral, and aromatic oils. Thermal resistance of mineral oils depends on the chemical composition of the oil and the degree of its purification. The operation experience of mineral oils shows, that when heated to a temperature close to the flash temperature, there is marked thermal decomposition and oxidation. Due to this carbon forms on the heat transfer surface, and this carbon dramatically worsens heat transfer. Hence, the use of mineral oils for heating purposes is limited to temperatures, somewhat lower than flash temperature, which is in the range from + 215 °C to + 310 °C. Practically, as a rule, oil heating is applied to + 230 °C.

As regards the application of HOHM in the ice ships and Arctic icebreakers, it is necessary to note a number of requirements: low melting temperature (below – 35 °C), heat medium thermal resistance up to 200 °C. The following fluids meet all these requirements: gas oil and ethylene glycol mixed with water.

Gas oil is a purified from sulphur gas oil fraction of the distillation of geolines nafteno-aromatic basis. Gas oil is completely thermally stable up to + 250 °C. The radiation thermal cracking beginning temperature lies in the range from + 300 to + 330 °C. The results of the radiation-thermal stability of gas oil research in the conditions of its work in the circulation circuit show that the heat medium can work in a nuclear reactor up to + 330 °C.

Preliminary design calculations of counterflow shell-and-tube heat exchanger were made in the framework of the implementation of a course project on the subject of «Heat exchangers». Creation of experimental model of heat exchanger is planned after the completion of calculations.

Materials of this work will be used in the preparation of the article to the conference ASME (American Society of Mechanical Engineers) International Mechanical Engineering Congress and Exposition which will be held from 15 to 23 November 2013.

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