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Short communication

New lead-acid battery for submersible vehicles

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ABSTRACT

In this paper a new design of a container is detailed for sealed lead-acid battery operating overboard of a submersible vehicle in conditions of increased ambient pressure. Such a container is both a battery jar and a pressure compensator. It has been shown that a mandatory requirement for such container use is an application of a gelled-electrolyte. Authors have offered a two-stage technology of filling of accumulators without using vacuum pumping.

1. Introduction

At the present time submersible vehicles have widespread applications for the investigation of a great number of important and demanding challenges. Submersible vehicles provide:

(1) complex oceanological scientific researches (geological, biological, hydrophysical and hydroacoustic etc.);
(2) salvage operations connected with the search of sunken objects, and help for their crews in raising and recovery of different objects;
(3) testing of marine engineering.

Modern submersible vehicles differ in:

(1) depth of submergence (shallow – down to 600 m, mid-water – down to 2000 m and deep-water – over 2000 m);
(2) manned or unmanned;
(3) method of underwater movement (floating, towed and moving over the bottom);
(4) method of power supply (autonomous and cable);
(5) method of data transfer (hydroacoustic and cable);
(6) method of provision of static condition (anchor, bottom and dynamically positioned).

The most perspectives are to be achieved by self-powered submersible vehicles having the highest level of operational efficiency and potential possibilities. The source of power of such vehicles is accumulator batteries. The main battery of a submersible has 50–160 kWh stored energy. Also on board there are auxiliary (10–20 kWh) and emergency current power sources. At the present time lead-acid batteries are used as the main and auxiliary accumulator batteries, and silver–zinc, nickel–zinc and nickel–cadmium batteries are used as emergency batteries. The application is known [1] of a lithium-ion battery as the main power source on board submersible vehicles. Also some interest is the application of nickel–hydrogen batteries having a durable metal case [2], thus being capable of operating outboard of submarine vessel. Modern nickel–hydrogen batteries can be operated at down to 300 m depths. Increase of operation depth would require increase of durable case thickness which would lead to a considerable decrease in the specific energy characteristics of such batteries.

Lead-acid accumulator batteries can be located either in a compartment of a submersible or outside which specifies their different application. The biggest advantage to be considered of external batteries is that it will allow increasing usable volume of submersible's compartments and efficiency of application of the latter one. However, use of lead external batteries requires implementation of measures to compensate for the effect of external hydrostatic loads, which in conditions of certain gas pressure in the battery can result in its destruction or entry of seawater use. In order to compensate the external hydrostatic load, modern lead-acid batteries use additional chambers with elastic walls and a valve filled with an electrolyte. Electrolyte from such chamber compensates the volumetric changes of electrolyte in a battery connected with compression and increase of solubility of gases in it. Another method of compensating the external hydrostatic load is based on the application of a dielectric liquid separating the accumulator electrolyte

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from seawater. In this case an battery is placed into a special container with the dielectric liquid. It is clear that both methods of compensation of external pressure decrease considerably the specific weight and volumetric characteristics of a lead accumulator and decrease its competitiveness in relation to other electrochemical systems.

At the present time the main tendency in lead accumulator development is to produce a leak-proof design. Application of such accumulators allows a considerable increase in the service life of an battery, eliminate limitations on its space orientation, practically exclude gassing, and to considerably reduce works required on its maintenance. By this, accumulators retain the lowest cost and high quality of energy. However, the relatively high gas occupancy of sealed lead-acid batteries does not allow their use as an external current source of a submersible as the external hydrostatic pressure will inevitably bring the destruction of their polymeric cases.

The purpose of the present work is the research of methods allowing the use of a sealed lead-acid battery as an external source of current for submarine vessels.

2. New sealed lead-acid battery for submersible vehicles

The authors of the present paper have proposed the use of a container made of thermoplastic elastomer for external accumulator which is simultaneously a case and a pressure compensator [3]. The walls of such a container can be considerably deformed by the effect of external hydrostatic pressure without their destruction.

Thermoplastic elastomers are thermoplastic rubber which, at ordinary temperatures, has the properties of rubber. Their nominal strength and percent elongation is, respectively, 6–9 MPa and 200–500%. In the present work thermoplastic elastomer "Armlen PP TEP-6" has been used, comprising of a polypropylene with a rubber having nominal strength and percent elongation, 9 MPa and 250%, respectively. Appearance of a container is shown in Fig. 1.

Sealed lead-acid battery with absorbed electrolyte has a relatively high free gas space (10–15%) and gaseous porosity of the electrode block elements. External pressure will result in considerable deformations of the container's walls and an undesirable effect on an electrode block. In order to eliminate this, it is necessary to have a big gap between the container's walls and electrode block, which will cause a decrease in the specific capacitance characteristics of a battery. It is possible to decrease the free gas volume of a battery by replacing the absorbed liquid electrolyte with gelled-electrolyte. In such a case gas channels between electrodes form a high efficiency closed oxygen cycle, which is not due to electrolyte limitation and its location in an electrode block only, but also due to the formation of cracks in the gelled-electrolyte in this interelectrode space. Thus, in sealed lead-acid batteries with gelled-electrolyte the total internal volume of a container outside an electrode block can be filled with electrolyte. This will decrease the free gas space and the extent of deformation of the container's walls. This will allow a minimum gap between them and electrode block and will provide a high volumetric energy density of an accumulator.

Fig. 1. Appearance of a container made of thermoplastic elastomer.

It should be noted that the deformation of the battery's walls by the external hydrostatic load on it will assist in the shutting of gas channels in the gelled-electrolyte which, in conditions of a discharge (by submarine vessel submersion), will decrease internal resistance of the accumulator and increase its discharge characteristics. By charging (in conditions of the absence of external pressure), the gas channels in the interelectrode space will be restored due to oxygen bubble pressure in the gelled-electrolyte and provide an efficient oxygen cycle.

Thus, a condition for the application of containers made of thermoplastic elastomers for accumulators of submersibles, is the use of a gelled-electrolyte.

Considering that the viscosity of a gelled-electrolyte is 5–6 times more than the viscosity of an ordinary liquid electrolyte [4], the filling of sealed lead-acid batteries with gelled-electrolyte is performed as a rule by vacuum pumping of a battery. However, the use of elastic containers creates problems by carrying out the operation of filling under vacuum as there is considerable deformation of the container's walls. On the other hand rejection of vacuum pumping does not allow quality filling of accumulators with gelled-electrolyte.

In order to increase the efficiency of electrode filling with electrolyte we have proposed a two-stage technology of filling accumulators without using vacuum pumping. At the first stage accumulators are filled with liquid electrolyte (sulfuric acid solution with specific gravity 1.28 g cm^{-3}). After the soaking of the plates liquid electrolyte is spilled out and accumulators are filled with gelled-electrolyte. Gelled-electrolyte is prepared by means of mixing sulfuric acid having 1.28 g cm^{-3} specific gravity with 5% aerosil (SiO_2) [5].

3. Experimental

The efficiency of two-stage technology filling was tested on the basis of carrying out comparative tests by means of a continuous cycle service of sealed lead-acid batteries with nominal capacity 110 Ah, made by using different technologies of electrolyte filling. Batteries were tested with gelled-electrolyte filling without vacuum pumping and filling on the abovementioned two-stage technology. Positive current collectors were molded from alloy Pb–1.5% Sb–1.2% Sn–0.02% Se, and negative ones – from alloy Pb–0.1% Ca. As a separator was used DARAK 2000.

Cycle service was performed by means of alternating four-stage charges and discharges by the current of 5-h mode during 3 h. The first-stage charging was carried out by the direct current 35 A at the voltage up to 2.40 V; the second-stage charging – by the current 11 A at the voltage up to 2.40 V; the third-stage charging – at the constant voltage 2.40 V within the period of 2 h. The fourth stage (5 A) is carried out at the limited overcharge 5%.

In every 20 cycles a monitoring discharge was performed by 10-h mode current until the end-of-discharge voltage of 1.75 V.

For the implementation of tests of sealed lead-acid batteries in containers from thermoplastic elastomer in conditions of high external hydrostatic load, sealed lead-acid batteries were made with a rated capacity of 170 Ah. Positive current collectors were molded from an alloy Pb–1.5% Sb–1.2% Sn–0.02% Se, and negative ones from an alloy Pb–0.1% Ca. As a separator was used DARAK 2000. A two-stage technology of battery filling with electrolyte was used. Gelled-electrolyte was prepared by means of mixing sulfuric acid having 1.28 g cm^{-3} specific gravity with 5% aerosol (SiO_2) [5]. There were 3 batteries tested.

Table 1
Effect of hydrostatic pressure on discharge performance of VRLA.

Cycle	Conditions of discharge	Capacity (Ah)		
		Battery no. 1	Battery no. 2	Battery no. 3
10	10-h discharge in normal conditions	168	170	173
11	10-h discharge by the outboard hydrostatic pressure 5.1 MPa	173	179	174
12	10-h discharge in normal conditions	169	169	171

Tests of batteries included the following stages:

(1) cycle service of batteries with the aim of taking capacity (9 cycles);
(2) carrying out of monitoring discharge by a current in normal conditions (10th cycle);
(3) carrying out of monitoring discharge in conditions of high hydrostatic pressure (11th cycle);
(4) carrying out of monitoring discharge in normal conditions (12th cycle);
(5) disassembling of batteries to examine the state of the electrode block after tests on effect of outboard pressure.

Charging was carried out in the four-stage mode. The first-stage charging was carried out by the direct current 50 A at the voltage up to 2.40 V; the second-stage charging – by the current 17 A at the voltage up to 2.40 V; the third-stage charging – at the constant voltage 2.40 V within the period of 2 h. The fourth stage (8 A) is carried out at the limited overcharge 5%. Discharges at the stage of capacity taking were carried out by 8.5 A current.

All monitoring discharges were carried out by 17 A current until the end-of-discharge voltage of 1.75 V.

Tests on the effect of external hydrostatic pressure were performed in a special hydro-pressure chamber. Pressure during monitoring discharge was 5.1 MPa.

4. Results and discussion

Fig. 2 shows the results of comparative tests of sealed lead-acid batteries with different technologies of electrolyte filling.

From the figure it is clear that application of two-stage technology of filling allows increased capacitive characteristics of sealed lead-acid batteries. It is connected with the increase in active mass efficiency due to the more qualitative filling of electrodes with electrolyte.

Fig. 3 indicates the values of end-of-charge voltage of batteries made using the different technology of electrolyte filling.

In the absence of the process of oxygen recombination end-of-charge voltage is determined by the potentials of two gas electrodes operating independently and is 2.70–2.75 V. By the formation of gas channels in the interelectrode space and passing of oxygen recombination process, the end-of-charge voltage decreases to 2.30–2.50 V, due to a depolarization of the negative electrode. The extent of the voltage decrease of a battery is determined by the rate of oxygen reduction at a negative electrode. From Fig. 3 it can be seen that, during the first 100 cycles, the formation of gas channels in the interelectrode space of batteries is insufficient. Later on, oxygen recombination is sufficiently efficient, as shown by the stable decrease of end-of-charge voltage. It is necessary to note that for accumulators filled with electrolyte by two-stage technology, the end-of-charge voltage is lower than for accumulators filled with gelled-electrolyte only. It shows that efficiency of the oxygen cycle for such accumulators is higher, which may be due to a less complicated exit of oxygen to outer boundary of an electrode, followed by the formation of gas channels.

Table 1 indicates the change of battery capacity shown when carrying out monitoring discharges nos. 10–12. From the table it is seen that batteries in a container made of thermoplastic elastomer retain their operating capacity even under high external hydrostatic pressure. It has been noted a certain increase of capacity for batteries discharged under pressure which is connected with decrease of gas filling of a battery and the increase of active mass use.

The energy-to-volume ratio of a battery in a thermoplastic elastomer container is 81.6 Wh dm^{-3}. The energy-to-volume ratio of an industrially manufactured battery with a rated capacity of 200 Ah provided to work externally on a submersible vehicle and having outer pressure compensator, is 65–70 Wh dm^{-3}. Thus, the use of

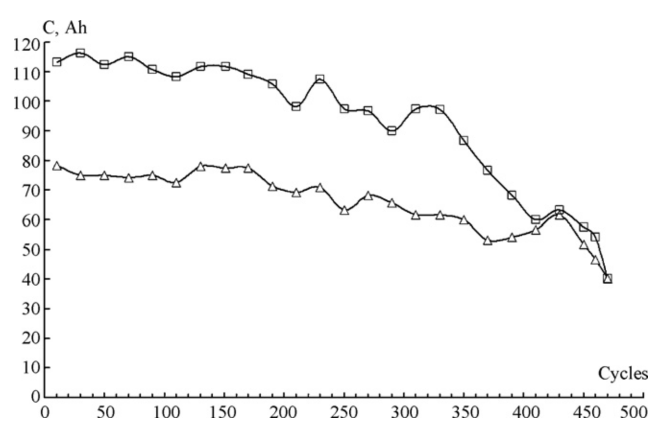

Fig. 2. Change of capacity (*C*, Ah) at 10-h mode of discharge in process of cycle service of sealed lead-acid batteries with different technologies of electrolyte filling: filling with gelled-electrolyte without vacuum pumping (△); two-stage technology of filling (□).

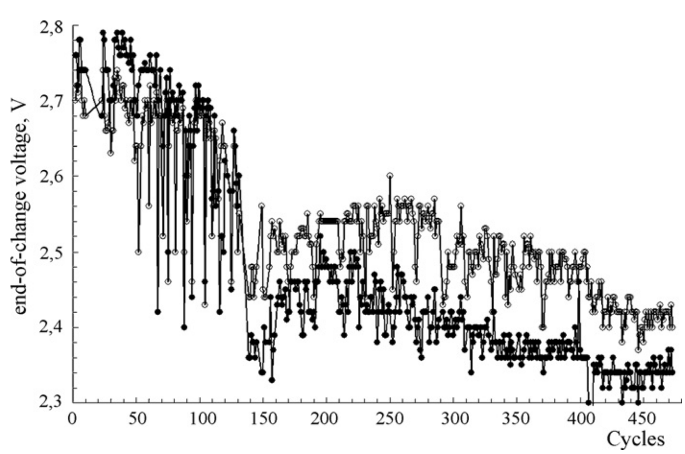

Fig. 3. Change of end-of-charge voltage in process of cycle service of sealed lead-acid batteries with different technology of electrolyte filling: filling by gelled-electrolyte without vacuum pumping (○); two-stage technology of filling (●).

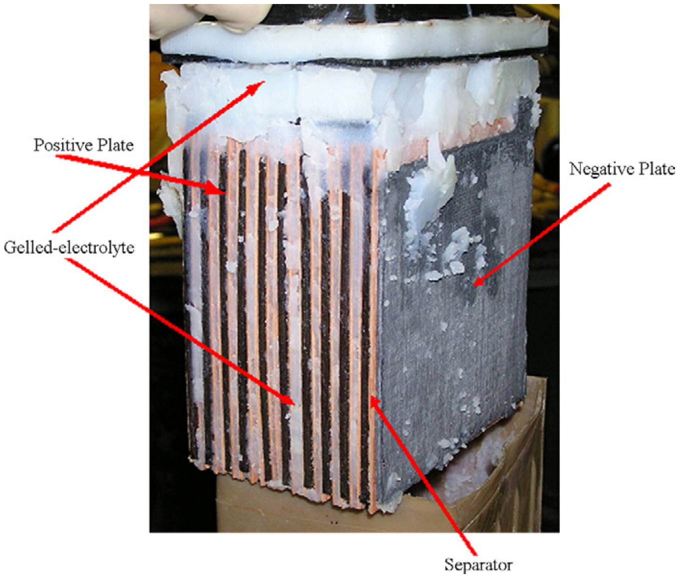

Fig. 4. Appearance of a battery electrode block with a container of thermoplastic elastomer after tests on the effect of outboard hydrostatic pressure.

a container made of thermoplastic elastomer shows an increased energy-to-volume ratio of a battery by 11–16%.

Fig. 4 shows the electrode block of a battery with a container of thermoplastic elastomer after tests on the effect of external hydrostatic pressure.

Examination of an electrode block has indicated absence of any deformations and destructions.

5. Conclusion

In the work a possibility has been shown for the use of thermoplastic elastomer containers for sealed lead-acid batteries operating externally on submersible vehicles. Application of such containers allows the elimination from battery design of external compensating devices and, correspondingly, increasing of their per-unit-volume characteristics.

It has been shown that the application of thermoplastic elastomer containers requires the use of gelled-electrolyte in a battery which provides a decrease of free gas space.

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