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Improving the thermal insulation of nitrogen cryocontainers using the loop-shaped evacuation process

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The improvement of serial cryobiological Dewar containers with the use of the lowest thermal conductivity in calorimetric samples of screen-vacuum thermal insulation (SVTI) during storage of liquid nitrogen became possible after the development of fundamental methods for determining heat fluxes for each element of cryocontainers structure and the study of the peculiarities of heat transfer in SVTI. It is established that the deterioration of thermal insulation on cryocontainers by 7–8 times occurs from its gluing when they are heated during the manufacturing process. An additional decrease in the quality of thermal insulation by ~ 2 times during operation is due to the formation of cryocondensate from the pumped-out gas separation products in the cold layers of SVTI and an increase in radiant heat transfer. Eliminating the adhesion of the SVTI, as well as changing the direction of evacuating gas separation products towards the warm wall of cryocontainers through 35 perforated SVTI layers using an open loop-shaped evacuation process allowed to increase their service life by ~ 2 times (up to 145–148 days). However, it remains practically unchanged over 15 years of operation.

Keywords: cryocontainers, thermal insulation, liquid nitrogen, vacuum, service life.

1. Introduction

The successes of cryogenic technology in space, nuclear and military technology have stimulated their use in other areas, including the technology of the reproduction of highly productive cattle by the method of artificial insemination. It was proposed to store the stocks of the genetic materials in a cryopreserved form in liquid nitrogen in special cryobiological Dewar containers with a wide nozzle (50 to 120 mm in diameter). Screen-vacuum thermal insulation with the lowest heat-conductivity (on calorimetric samples) (SVTI) was used as thermal protection in these containers.

The previously developed technology for machine isolation of cryocontainers with SVTI layers was empirical and unoptimized, therefore the cryocontainers were of low quality. The reasons for this were not clear. In addition, there were no proven theoretical relationships, as well as reliable experimental methods for studying multidimensional processes of heat and mass transfer in the heat protection of a cryocontainer in order to identify deteriorating factors. Therefore, for a long time, cryobiological containers produced by tens of thousands remained of low quality.

At the Department of “Technical Cryophysics” NTU “KhPI” carried out research on the development of methods for improving cryobiological containers produced at the Kharkov plant of transport equipment.

This article presents new results of the development of a method for long-term protection of thermal insulation of nitrogen cryocontainers using perforated layers of SVTI and a loop-shaped process of evacuation of its degassing products.

2. Research methods

The studies were carried out on cryobiological containers X-34B (34 l capacity) with a fiberglass nozzle 60 mm in diameter and a polystyrene stopper 50 mm thick, schematically shown on the experimental stand (Fig. 1).

After insulating the cryocontainer tank with layers of SVTI, assembly and welding of its outer casing is carried out with checking the welded and glue seams for tightness. Thermal vacuum degassing of the cryocontainer is carried out by heating at a temperature of 380–390 K in a special electric furnace for 7 days with simultaneous evacuation of

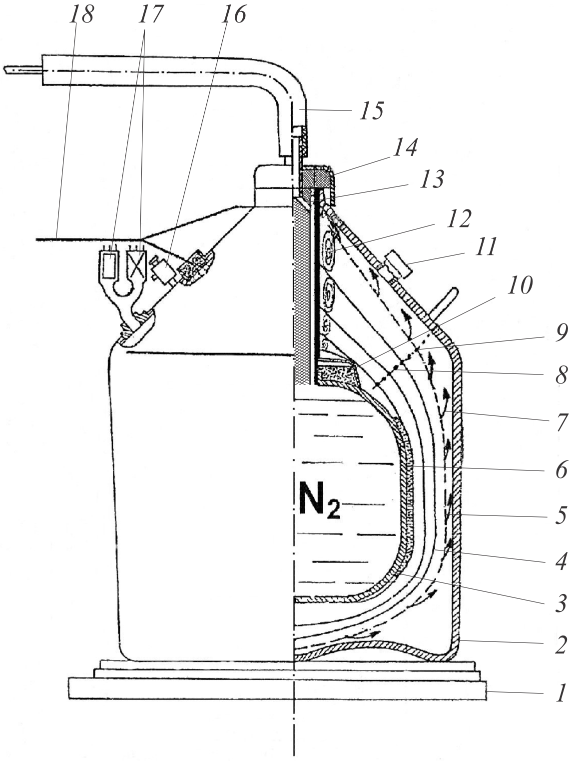

Fig. 1. Scheme of the experimental stand with the X-34B experimental cryocontainer: electronic balance (*1*); outer casing of the cryocontainer (*2*); internal reservoir (*3*); SVTI package (*4*); perforated layers of SVTI (*5*); adsorption vacuum pumps (*6*, *10*); loop-shaped direction of the process of evacuation of degassing products (*7*); thermocouple junctions (*8*); average integral thickness of the SVTI package (*9*); evacuation nozzle (*11*); winding layers (*12*); fiberglass nozzle (*13*); polystyrene plug (*14*); supply of evaporated nitrogen vapors to the gas meter (*15*); leak (*16*); pressure sensors (*17*); thermocouple wires to the measuring unit (*18*).

the insulating cavity, first with a fore-vacuum pump (for 4 days) and then with a steam-oil diffusion pump. After that, the evacuation nozzles of the cryocontainers were sealed with plugs, which were filled from above with a special sealant. It was believed that after filling with liquid nitrogen, in the package of thermal insulation of cryocontainers (manufactured using this technology), the optimal vacuum $P_0 \le 10^{-3}$ Pa will be established and maintained (using the adsorption vacuum pumps *6* and *10*), at which heat transfer through the thermal insulation along gas (Q_g) became negligible and is carried out mainly by radiant thermal conductivity (Q_{rad}) and thermal conductivity of the SVTI material (Q_{mat}).

Further, the manufactured cryocontainers (according to the technological regulations) are subjected to thermal tests with liquid nitrogen to determine their quality. To do this, the cryocontainers are filled with ¾ liquid nitrogen, kept for 2–3 days, after which they are weighed on a VLE-50 electronic balance and the mass M_1 is determined. After 2 days, the cryocontainers are reweighed and their mass M_2 is determined. Based on the results obtained, the average daily evaporation of liquid nitrogen is calculated with an accuracy of 7–8% in the test cryocontainers:

$$m = \frac{M_1 - M_2}{2}. \tag{1}$$

Evaporation can also be determined using a GSB-400 gas meter (by volume V). The results obtained make it possible to find the value of the total heat flux in the cryocontainer [1]:

$$Q_c = 24.62 \cdot 10^{-6} V \frac{P_{\text{bar}}}{T_g} \text{ [W]}, \tag{2}$$

where P_{bar} is the barometric pressure, mm Hg; T_g is the temperature of the evaporated nitrogen entering the gas meter, °C;

$$Q_c = mr \text{ [W]}, \tag{3}$$

where r is the heat of vaporization of liquid nitrogen (199.36 J/kg).

The measured evaporation value m is also used to determine the operating life of the cryocontainer (R), i.e., the storage time of liquid nitrogen in it (without refilling) until complete evaporation:

$$R = \frac{M}{m} \text{ [day]}, \tag{4}$$

where M = 28245 g is the mass of liquid nitrogen in a completely filled cryocontainer X-34B. The accuracy of determining the resource R is ± 1 day.

From the analysis of the construction of the X-34B cryocontainer (Fig. 1), it follows that the total heat fluxes Q_c in it are determined by heat transfer along the thermal insulation (Q_{ins}), nozzle (Q_{noz}), bung (Q_b) and gas slit ($Q_{g\,s}$) between the nozzle and stopper according to the relation

$$Q_c = Q_{\text{ins}} + Q_{\text{noz}} + Q_b + Q_{g.s} \text{ [W]}. \tag{5}$$

The method for determining these terms was developed in [2]. Its essence consists in measuring the temperature gradient ΔT (with an accuracy of ± 0.1 K) in the coldest areas of the cryocontainer nozzle, bung and gas slit with a height of $l \approx (5\text{–}7) \cdot 10^{-3}$ m, where the effect of longitudinal heat transfer between them becomes minimal. The measurement were carried out using calibrated (according to an exemplary platinum resistance thermometer) copper-constantan thermocouples. The results obtained made it possible to calculate heat fluxes along each thermal bridge of a cryocontainer and to determine the effective thermal conductivity coefficient (λ_{eff}) of its thermal insulation using the Fourier thermal conductivity equation [1]:

$$Q_{\text{noz}}(Q_b, Q_{g\,s}) = \frac{\lambda_m F \Delta T}{l}, \tag{6}$$

$$Q_{\text{ins}} = Q_c - Q_{\text{noz}} - Q_b - Q_{g\,s}, \tag{7}$$

$$\lambda_{\text{eff}} = \frac{Q_{\text{ins}}\delta_{\text{ins}\,m}}{F_m \Delta T_{\text{ins}}}, \tag{8}$$

where F is the thermal bridge cross section; F_m is the average surface of the thermal insulation layers on the cryocontainer X-34B (0.86 m^2); ΔT_{ins} is the temperature difference between the outer and inner surfaces of a cryocontainer filled with liquid nitrogen (219 K); λ_m is the average thermal conductivity of the thermal bridge in the measured area; $\delta_{\text{ins}\,m}$ is the the average integral thickness of the SVTI package over the entire surface of the inter-wall cavity of the X-34B cryocontainer (0.071 m).

It should be noted that in different places of the inter-wall cavity of the X-34B cryocontainer (as well as others) the SVTI heat-shielding package has a different thickness: 0.25 m near the nozzle; 0.04 m in the middle part; 0.086 m at the bottom. Depending on the accepted thickness of the SVTI package in Eq. (8), its thermal conductivity coefficient λ_{eff} in the cryocontainer can vary by ~ 6.3 times. In this regard, it was proposed to determine the true values of the thermal conductivity coefficients for SVTI on cryocontainers using their mean integral thickness $\delta_{\text{ins}\,m}$ over the entire surface of the insulating cavity. The coefficients of thermal conductivity λ_{eff} determined in this way in according with Eq. (8) are the true characteristics of the SVTI packages on various cryodevices to assess the efficiency of the used thermal insulation. The maximum error in determining λ_{eff} by this method is 3–5%.

The obtained characteristics for two low-quality cryocontainers X-34B with layers of SVTI made of the insulating composition PET-DA + SVTI-7 [polyethylene terephthalate film with double-sided aluminization PET-DA and interlining glass veil SVTI-7] are presented in Table 1.

The operating resources of the experimental cryocontainers 1 and 2 with liquid nitrogen [according to Eq. (4)] turned out to be equal to 80 and 75 days, respectively.

The effective coefficients of thermal conductivity λ_{eff}, determined from the heat fluxes Q_{ins} for the SVTI packages of cryocontainers, turned out to be 8.8–9.3 times higher than the values of this parameter for samples of similar thermal insulation on the calorimeter [equal to $3.1\cdot10^{-5}$ W/(m·K)].

According to [1], when a gas pressure in the thermal insulation made of SVTI exceeds the optimal value for them ($P_0 \le 10^{-3}$ Pa), thermal conductivity λ_{eff} should be carried out by radiation (λ_{rad}), contact-conductive method ($\lambda_{k\,k}$), as well as by residual gas molecules (λ_g):

$$\lambda_{\text{eff}}(T) = \lambda_{\text{rad}}(T) + \lambda_{k\,k}(T) + \lambda_g(T)\ [\text{W/(m·K)}]. \tag{9}$$

In this case, the radiant component can be determined by the equation [1]

$$\lambda_{\text{rad}} = 4\frac{\varepsilon}{2-\varepsilon}\frac{\delta_{\text{ins}\,m}}{N}\sigma T_m^3\ [\text{W/(m·K)}], \tag{10}$$

where ε is the thermal insulation screen blackness; σ is the Stefan–Boltzmann constant; N is the number of layers in the SVTI package; T_m is the average temperature in the thermal insulation area.

If the gas pressure in the SVTI layers is below 10^{-3} Pa, then heat transfer through the insulation is carried out mainly by radiant and contact-conductive components:

$$\lambda_{\text{eff}}(T) = \lambda_{\text{rad}}(T) + \lambda_{k\,k}(T). \tag{11}$$

Knowing the value of λ_{eff} [presented in formula (8)] and the radiant component λ_{rad} (10), it is possible to calculate the value of contact-conductive heat transfer in the SVTI package:

$$\lambda_{k\,k}(T) = \lambda_{\text{eff}}(T) - \lambda_{\text{rad}}(T). \tag{12}$$

It should be noted that the method developed by us for determining heat fluxes separately for all structural elements of cryocontainers (in order to assess their effectiveness) was later used by other researchers [3, 4].

To improve the characteristics of cryocontainers, the purpose of further research is to identify factors that worsen the thermal conductivity of the SVTI, as well as to develop designs and technologies for their elimination. It was assumed that studies on the mean integral thickness $\delta_{\text{ins}\,m}$ of the SVTI packages of temperature ($T_{\text{ins}}(\delta_{\text{ins}\,m})$ and pressure $P_{\text{ins}}(\delta_{\text{ins}\,m})$ profiles on low-quality cryocontainers would provide the necessary information about the deteriorating factors. However, there were no miniature temperature and pressure sensors necessary for such studies. Therefore, it was proposed to measure the temperature in the thermal insulation by junction of calibrated copper–constantan thermocouples, since they have a relatively large thermo-emf.

To study the distribution of gas pressure over the thickness of the thermal insulation (P_{ins}) on the cryocontainer, it was proposed [5] to use flat vacuum pipelines with a thickness of $(2.2–2.5)\cdot10^{-3}$ m, into which stainless steel

Table 1. Characteristics of experimental cryocontainers X-34B with liquid nitrogen (losses of liquid nitrogen m, total heat gain Q_c, thermal insulation Q_{ins}, nozzle Q_{noz}, bung Q_b, gas slit $Q_{g\,s}$, effective thermal conductivity coefficient λ_{eff})

Cryocontainer No.	m, g/day	Q_c, W	Heat gains by structural elements				λ_{eff}, 10^{-5} W/(m·K)
			Q_{ins}, W	Q_{noz}, W	Q_b, W	$Q_{g.s}$, W	
1	353	0.81	0.729	0.047	0.033	0.001	27.5
2	379	0.87	0.766	0.061	0.042	0.001	28.8

tubes with a diameter of $5\cdot10^{-3}$ m and a wall thickness of $1\cdot10^{-4}$ m are inserted. The open ends of such vacuum lines were fixed in those places along the thickness of the SVTI package, where it was necessary to measure the pressure. The upper end of each tube (of the same diameter $5\cdot10^{-3}$ m) was led out through the nozzle and connected to the PMT-2, PMI-2 and PMI-3-2 pressure sensors. The pressure sensors were calibrated and the calibration curves were plotted. The readings of the pressure gauges were recorded with an accuracy of no worse than ± 15%.

3. Studies of temperature and pressure fields in the thermal insulation of the cryocontainer

To study the temperature field, an experimental X-34B cryocontainer 1 was made with thermocouples in thermal insulation from the PET-DA + SVTI-7 composition, which had a high thermal conductivity of $28.2\cdot10^{-5}$ W/(m·K). The temperature profile measured by the mean integral reduced thickness (x/δ, where x is the current and δ is the total thickness) of the SVTI layers is shown in Fig. 2 by the dependence $T_{\text{ins}}(x/\delta)$. As can be seen at the temperature $T_k \approx 273$ K, an inflection formed on it (point A in Fig. 2) in the local section $x/\delta = 0.71$. The obtained characteristics for cryocontainer 1 are presented in Table 2.

According to the theoretical work [6], the appearance of an inflection on the temperature profile $T_{\text{ins}}(x/\delta)$ of thermal insulation indicates the presence of an increased gas pressure $P_{g\max}$ and heat transfer along it in this local section $x/\delta = 0.71$. Using the temperature value at the inflection point $T_k = 273$ K, an estimate of the magnitude of the increased pressure $P_{g\max}$ at the local section of the SVTI was carried out according to the formula proposed in [6]:

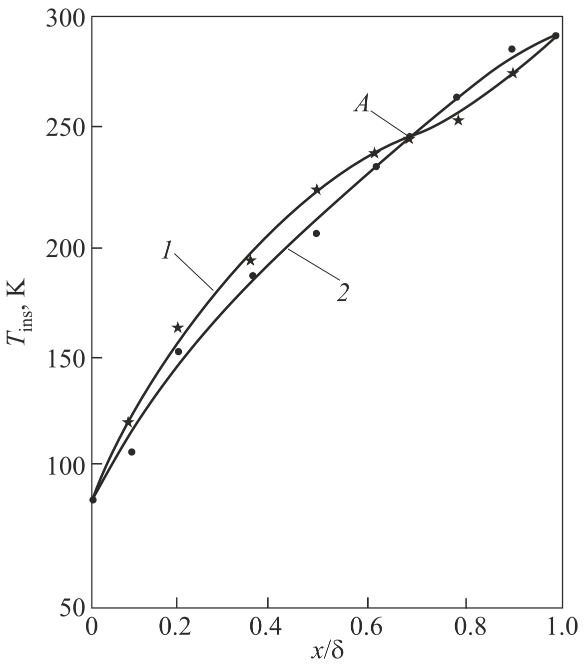

Fig. 2. Temperature distribution (T_{ins}) over the mean integral reduced thickness (x/δ) of PET-DA + SVTI-7 thermal insulation layers on a cryocontainer at boundary temperatures of 78–297 K: dependence $T_{\text{ins}}(x/\delta)$ with an inflection point (*1*); monotonic profile for SVTI layers (*2*); *A* is the inflection point.

$$P_{g\max} = \frac{4T_k^4\varepsilon_r\sigma}{[\alpha/(2-\alpha)][(\gamma+1)/(\gamma-1)]\sqrt{RT_k/2\pi M}}, \qquad (13)$$

where ε_r is the reduced emissivity of the SVTI screen at T_k at the inflection point on the dependence $T_{\text{ins}}(x/\delta)$ (0.043); γ is the ratio of isobaric and isochoric heat capacities (342); M is the molecular weight of air; α is the gas accommodation coefficient (0.8).

This calculation showed that in the local section of the SVTI, the gas pressure from the gas separation products can reach ~ 1.5 Pa. This is four orders of magnitude higher than the optimal value of this parameter ($P_0 \le 10^{-3}$ Pa), which is necessary for the effective operation of thermal insulation from the SVTI layers on the cryocontainer. It became possible to check the theoretical prediction [6] after the development of a methodology for the simultaneous study of the peculiarities of the distribution of the temperature and pressure fields in the layers of thermal insulation. For this purpose, such an experimental cryocontainer 2 was manufactured with low-quality layers of SVTI with thermal conductivity $\lambda_{\text{eff}} = 28.6\cdot10^{-5}$ W/(м·K), close to the λ_{eff} of cryocontainer 1 (Table 2). Since the obtained characteristics x/δ and T_{ins} for the thermal insulation of cryocontainers 1 and 2 were practically the same (Table 2), the dependence $T_{\text{ins}}(x/\delta)$ for the SVTI layers of the cryocontainer 2 in Fig. 2 is not shown.

The pressure profile $P_g(x/\delta)$, investigated simultaneously for the thermal insulation of the cryocontainer 2, is shown in Fig. 3. As can be seen, it passes in accordance with the prediction of the theory [6], through a maximum at a pressure of $P_{g\max} = 2.1$ Pa (point *A*) on a local section of heat insulation with an inflection at $x/\delta = 0.72$ and $T_{\text{ins}} = 272$ K. The experimental value of the maximum pressure $P_{g\max} = 2.1$ Pa obtained in this case turned out to be close to the theoretical value of this parameter 1.5 Pa, according to Eq. (13). Thus, the theoretical prediction [6] about the possibility of the existence of local areas with increased pressure and heat transfer in gas in the layers of thermal insulation on cryocontainers was experimentally confirmed, as evidenced by the appearance of kinks in their temperature profiles $T_{\text{ins}}(x/\delta)$. The analysis showed that in this case the share of heat transfer by gas λ_g in thermal insulation can increase to 42% of the total value λ_{eff}, while maintaining the required optimal pressure $P_0 \le 10^{-3}$ Pa it will not exceed 2–4 %.

From the results shown in Fig. 3, it follows that in the thermal insulation of a cryocontainer, a local section with an increased gas pressure is formed during double-sided evacuation of gas separation products from it. In this case, the pumping process *2* is carried out towards its cold wall

Table 2. Characteristics of experimental cryocontainer X-34B (effective thermal conductivity coefficient λ_{eff}, breakpoint temperature T_k, reduced thickness of the SVTI package at the break point x/δ, maximum gas pressure at the break point $P_{g\,\max}$, gas pressure at the warm wall of the cryogenic container $P_{g\,w}$, diameter of the winding cords near the nozzle D)

Cryocontainer No.	λ_{eff}, 10^{-5}W/(m·K)	T_k, K	x/δ	$P_{g\,\max}$, Pa	$P_{g\,w}$, 10^{-3} Pa	D, mm	SVTI-7
1	28.2	273	0.71	–	2	2.0	with glue
2	28.6	272	0.722	2.1	3	2.0	with glue
3	14.1	–	–	–	2	2.0	with glue

(up to a pressure of $6\cdot10^{-5}$ Pa) with the help of vacuum adsorption pumps *6* and *10* mounted on it (Fig. 1). Another evacuation process *3* is carried out, as you can see, to a warm wall up to a pressure of $3\cdot10^{-5}$ Pa, where there are no vacuum pumps, and the evacuation nozzle *11* is closed and sealed. It was concluded that the only possible vacuum channel for pumping out the gas separation products from the local section of the SVTI towards the warm wall, and from it to the vacuum pumps *6* and *10* is a rarefied structure formed along the surface of the nozzle (during isolation) from the ends of the mounted strips of SVTI and winding harnesses *12* (20 mm in diameter) from SVTI-7 glass veil. The experimentally established process of evacuation of gas separation products from a local section of thermal insulation on a cryocontainer, the direction of which is difficult to change, was called loop-shaped.

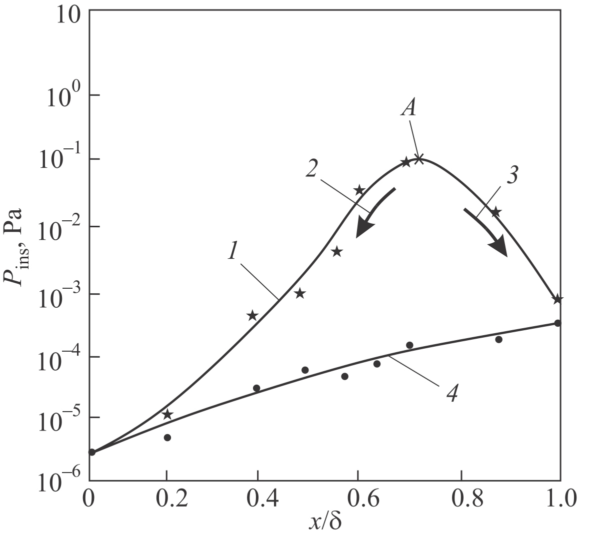

Fig. 3. Gas pressure distribution over the average integral thickness of the thermal insulation package on the X-34B cryocontainer with liquid nitrogen: pressure profile $P_g(x/\delta)$ for thermal insulation of a cryocontainer 1 with a kink at point *A* on the temperature profile $T_{\text{ins}}(x/\delta)$ (presented in Fig. 2) (*1*); direction of evacuation of gas separation products to the cold wall of the cryocontainer (*2*); pumping towards the warm wall of the cryocontainer (*3*); pressure profile $P_g(x/\delta)$ for thermal insulation of a cryocontainer 2 using an SVTI-7 cushioning glass veil without an adhesive base (*4*).

To identify the causes of the formation of local areas with an increased gas pressure in the layers of thermal insulation on cryocontainers, after the end of the research, the experimental cryocontainer 2 was dismantled. The analysis of the state of its thermal insulation carried out after that showed that it was a solid glued yellow-brown mass. The reason for this was the PVA adhesive emulsion, which is used in the manufacture of the SVTI-7 cushioning glass veil (for joining thin glass fibers).

Thus, the use of the SVTI-7 glass veil in the SVTI insulating composition on heated cryocontainers is ineffective. In connection with the absence of other cushioning materials, a technology was proposed for reducing the content of the adhesive base in the SVTI-7 by means of its preliminary heat treatment. In a special vacuum chamber, it was evacuated for 8 hours at a temperature of 370–380 K. The efficiency of thermal insulation using the SVTI-7 glass veil treated in this way was investigated on an experimental cryocontainer 3 with temperature and pressure sensors. The temperature profiles $T_{\text{ins}}(x/\delta)$ (Fig. 2) and the pressure $P_g(x/\delta)$ (Fig. 3), measured for the thermal insulation of the cryocontainer 3, turned out to be monotonic. This indicated the elimination of adhesion of the SVTI layers and the formation of local areas with increased pressure and heat transfer through the gas. Thus, an inflection on the temperature profile, measured by the average integral thickness of the SVTI layers, is formed only in the thermal insulation of a cryocontainer with glued layers, an increased gas pressure in them, and during a two-sided evacuation process.

The developed technology to eliminate the adhesion of the SVTI layers on the X-34B cryocontainers allowed to reduce the thermal conductivity of thermal insulation to $(14\text{–}14.5)\cdot10^{-5}$ W/(m·K) and, as a result, to increase the service life of the cryocontainer *R* with liquid nitrogen from 75–80 to 150–155 days (by 1.9–2 times). This technology began to be used in the serial production of cryobiological containers.

Cryobiological containers with stocks of genetic materials in liquid nitrogen are usually operated at breeding stations for artificial insemination for 10–15 years or more. In this regard, it was of interest to investigate their long-term thermal efficiency, given that the optimal temperature for their degassing process (equal to 380–390 K) is not always maintained. Often this technology is carried out at lower temperatures from 350 to 370 K.

4. Investigation of the thermal characteristics of cryocontainers with liquid nitrogen during long-term operation

Investigations were carried out on three experimental cryocontainers X-34B with layers of PET-DA + SVTI-7 without an adhesive base. They were manufactured using the same technology, with thermocouples according to the average integral thickness of the thermal insulation, but with different temperatures of the thermal vacuum degassing process (equal to 350, 375, and 390 K). The studies were carried out during 3 years of continuous storage in liquid nitrogen cryocontainers. Their thermal characteristics were determined by the gravimetric method on an experimental stand (Fig. 1). The results are shown in Table 3.

From the data Table 3, it follows that the initial thermal characteristics of the cryocontainers Q_c, as well as the pressure of gases P_g near their warm walls, turned out to be practically the same. The measured initial temperature profiles for the thermal insulation of the experimental cryocontainers were also the same and monotonic; therefore, in Fig. 4 they are represented by only one dependence $T_{\text{ins}}(x/\delta)$ (curve *1*).

Further investigations made it possible to establish that as the storage period of liquid nitrogen in cryocontainers increased, the temperature of the layers of their thermal insulation gradually, with varying intensity, increased. Especially in areas with a relative thickness x/δ from 0.15 to 0.4 (at temperatures from 120 to 210 K) (Fig. 4). Simultaneously, the evaporation of liquid nitrogen from cryocontainers increased. At the same time, with the highest intensity, the temperature of the thermal insulation T_{ins}, as well as the total heat fluxes Q_c, increased for the cryocontainer 3 with the lowest temperature of the process of its thermal vacuum degassing T_{deg} = 350 K (Fig. 4, Table 3). At the lowest rate, these characteristics changed for cryocontainer 1 with the highest heating temperature T_{deg} = 390 K.

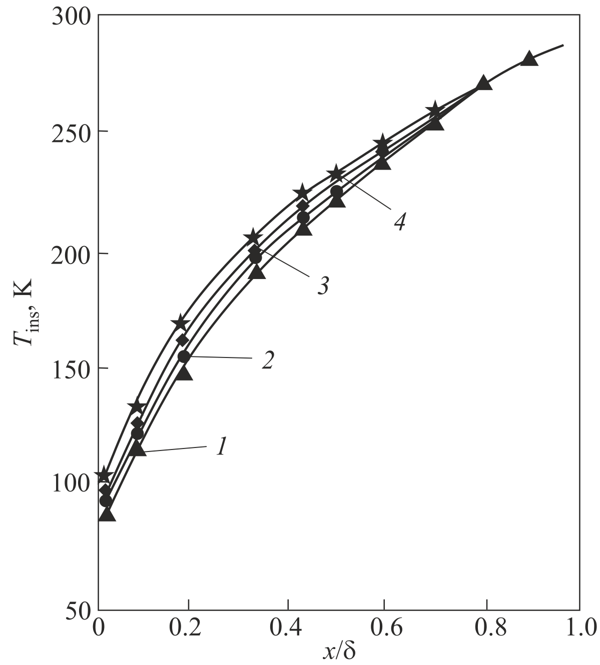

Fig. 4. Changes in temperature profiles $T_{\text{ins}}(x/\delta)$ according to the average integral thickness of the SVTI package on cryocontainers different temperatures of the conducted thermal vacuum degassing process after 3 years of storage of liquid nitrogen in them: initial temperature profile for thermal insulation of all experimental cryocontainers (*1*); temperature profile for cryocontainers 1 (*2*), 2 (*3*), 3 (*4*) after 3 years of storage of liquid nitrogen.

After 3 years of storage of liquid nitrogen in cryocontainer 1, the temperature of the SVTI layers in the section x/δ = 0.2 increased by 2 K, which can be seen from a comparison of the graphs of temperature profiles *2* and *1* (Fig. 4). The total heat flux Q_c also increased in this cryocontainer by 15%, and its service life, as a result, decreased from 152 to 130 days (Table 3). For cryocontainer 3, during this time at a similar section of the SVTI layers, the temperature increased by a large value — 5 K (Fig. 4, curve *4*), and the total heat fluxes Q_c by 20% (Table 3). As a result, the service life of this cryocontainer decreased from 153 to 123 days. In this case, the gas pressure P_g near the warm wall in the experimental container remained practically unchanged (Table 3), which ruled out the assumption of a possible deterioration in the characteristics of the cryocontainer due to gas leakage. In addition, it should be noted that the experimental cryocontainers during the experiments were not subjected to displacements and shaking, which excluded the deformation of their SVTI layers and a possible increase in thermal conductivity along the thermal insulation material. It is concluded that an increase in the total heat fluxes Q_c in experimental cryocontainers can occur only as a result of an increase in the radiant thermal conductivity λ_{rad}, which, in turn, should cause [see relation (10)] an

Table 3. Characteristics of experimental cryocontainers X-34B with liquid nitrogen (total heat fluxes Q_c, service life R, gas pressure near the warm wall P_g, temperature of the process of thermal vacuum degassing in electric furnaces T_{deg})

Cryocontainer No.	T_{deg}, K	After stabilization of thermal equilibrium (after 10 days)			After 3 years of storage of liquid nitrogen		
		Q_c, W	R, day	P_g, 10^{-3} Pa	Q_c, W	R, day	P_g, 10^{-3} Pa
1	390	0.410	152	2.5	0.472	130	3.1
2	375	0.407	153	3.2	0.483	127	3.4
3	350	0.409	153	2.8	0.492	123	3.2

increase in the thermal insulation temperature T_{ins} (which takes place) from an increase in the emissivity of the SVTI screen material. The analysis made it possible to conclude that the only source of an increase in the emissivity of screening materials for thermal insulation is the formation of gas separation products on cold layers of cryocondensate from the gas separation products pumped out from the outer warm layers of SVTI. According to [7], the products of gas separation from insulating materials consist mainly of H_2O and CO_2 molecules. Other lower boiling gases are also present in small quantities. From this it follows that the above-described technology of thermal vacuum degassing of the insulating cavity of the manufactured cryocontainers does not provide a sufficiently complete removal of dissolved gas molecules from the thermal insulation. The results of the studing the long-term evacuation process for structural and heat-insulating materials used in cryogenic systems showed that even after 10 years of continuous evacuation, gas separation from them does not stop, but only slows down by 1.5–2 orders of magnitude [8].

Let is estimate the degree of deterioration of the thermal characteristics of cryocontainers with liquid nitrogen due to an increase in radiant heat transfer in thermal insulation during their long-term operation (for 5, 10, and 15 years). From the experimental data obtained for cryocontainers during 3-year storage of liquid nitrogen (Table 3), the average monthly values of the decrease in the service life of cryocontainers (ΔR, day/month) were determined, which made it possible to calculate the required characteristics. The results obtained in this way are shown in Fig. 5 and Table 4.

From the results obtained, it follows that in a cryocontainer 1 with a temperature of thermal-vacuum degassing $T_{\text{deg}} = 390$ K, only due to an increase in the radiant component of thermal conductivity, the service life over 15 years of operation can decrease by 47%. For cryocontainer 3 with the lowest temperature of this process $T_{\text{deg}} = 350$ K, a larger volume of nonevacuated gases remained in the structure of its heat-insulating materials. As a result, during the operation of this cryocontainer, thicker (in comparison with cryocontainer 1) layers of cryocondensate and with the highest degree of emissivity (ε) are formed from the evacuated gas separation products on cold screens. This contributed to the greatest increase in temperature for the layers of thermal insulation in this cryocontainer, as well as radiant heat transfer λ_{rad}. As a result, the service life of the cryocontainer R is reduced by 82%. To check the reliability of the results obtained (Table 4), cryocontainers with long service life by serial numbers were found and investigated at the artificial insemination stations. After 12 years of operation, one of these cryocontainers had a service life of 98 days. Another, with a life of 16 years with liquid nitrogen, had a resource of 76 days. These cryocontainers underwent the process of thermal vacuum degassing in an electric furnace with a heating temperature of 380–390 K. Comparison of the results for the cryocontainers with the data presented in Table 4 shows a satisfactory agreement between them. Cryocontainers with less work resources were not found because after a short time they were rejected and taken out of service.

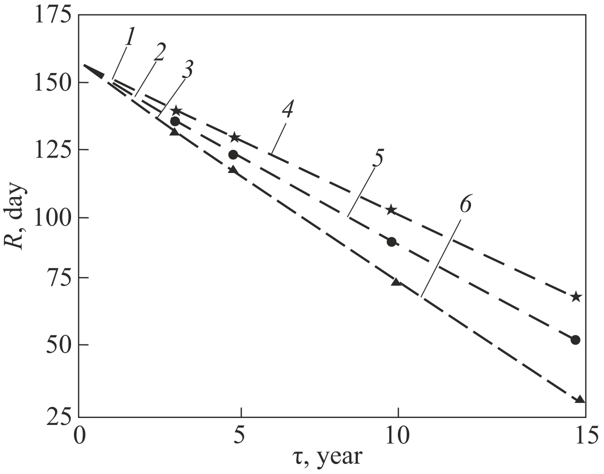

Fig. 5. Results of the study of changes in service life (R) for cryocontainer X-34B with liquid nitrogen during long-term operation (τ): experimental data (*1–3*); calculated dependences (*4–6*); results for cryocontainers with degassing temperature $T_{\text{deg}} = 390$ (*1*, *4*), 370 (*2*, *5*), and 350 (*3*, *6*) K.

The revealed significant deterioration of the thermal characteristics of cryocontainers with liquid nitrogen during long-term operation set the task of developing the design of the thermal protection package of the SVTI and the evacuation process, excluding the implementation of considered processes. For this purpose, in a cryocontainers it was proposed to pump out the gas separation products from the outer warm layers of the SVTI not through the cold layers of heat insulation, but in the opposite direction, to its outer warm wall, by perforating them for this, and also using a new loop-shaped the process of evacuation.

Table 4. Changes in the service life (R) of the X-34B cryocontainers with liquid nitrogen, depending on the long-term operation (τ) and the degassing temperature (T_{deg})

Cryocontainer No.	T_{deg}, K	ΔR, day/month	τ = 5 years		τ = 10 years		τ = 15 years	
			R, day	%, from initial	R, day	%, from initial	R, day	%, from initial
1	390	0.56	127	85	101	63	81	53
2	370	0.67	122	80	88	57	43	28
3	350	0.78	110	73	69	45	27	18

5. Development and research of energy-efficient thermal protection for cryocontainers

The implementation the proposed method for protecting cold layers of SVTI on cryocontainers is possible only if a lower hydraulic resistance for the evacuated gas separation products is provided through the layers of thermal insulation in the direction of the outer wall of the cryocontainers and further along the vacuum channel along the nozzle to adsorption pump on a cold wall in comparison with pumping through cold layers of SVTI. For this, it was proposed to increase the gas permeability of the thermal insulation layers near the warm wall for gas separation products by perforating screen films (holes $2 \cdot 10^{-3}$ m in diameter with a degree of perforation of ~ 8%) in the used heat-shielding composition PET-DA + SVTI-7.

To reveal the effectiveness of the proposed evacuation technology, experimental studies of the thermal characteristics for five cryocontainers were carried out during 3 years of storage of liquid nitrogen in them. These cryocontainers were made with the same number (100) of SVTI layers and a thermal vacuum degassing temperature of 390 K. Perforated PET-DA screens were not used in the thermal insulation in cryocontainer 1. In other cryocontainers (2–5), a different number of SVTI layers with perforated PET-DA films were used in thermal insulation near their outer walls. The results are presented in Table 5.

From the results obtained, it follows that as a result of the use of 20 layers of SVTI with perforated screens in the thermal insulation of cryocontainer 2, its initial service life (after stabilization of the thermal field after 10 days) was 153 days, which is 2 days less in comparison with the cryocontainer 1 (without perforated thermal insulation layers). The reason for this was an increase in radiant heat transfer in the thermal insulation of the cryocontainer 2 by 0.06 W through the perforation holes.

After 3 years of storage of liquid nitrogen, the service life of the cryocontainer 2 decreased from 153 to 141 days as a result of the deterioration of the thermal characteristics of thermal insulation from cryocondensation of gas separation products in it. However, the resulting service life R in it turned out to be 9 days longer in comparison with cryocontainer 1. This happened because part of the gas separation products in the cryocontainer 2 was pumped out to the outer wall. As a result, cryocondensation of gas separation products, the degree of blackness of the screens, as well as radiant transfer by 0.013 W in comparison with cryocontainer 1 decreased in its old layers of SVTI.

An increase in the number of layers with perforated screens in the cryocontainer 3 to 28 contributed to a decrease in the initial resource to 151 days, which was 4 days less in comparison with the cryocontainer 1 as a result of an increase in radiant heat transfer through the perforation holes by 0.011 W. After 3 years, the service life of cryocontainer 3 turned out to be 145 days, which became 13 days longer than cryocontainer 1 as a result of a decrease in radiant heat transfer by 0.032 W from cryocondensation of gas separation products and a decrease in the degree of emissivity.

In this series of experiments, cryocontainer 4 was also investigated, in the thermal insulation of which an even larger number (35) of SVTI layers with perforated PET-DA screens were used. As a result, the initial service life in it became equal to 148 days, which is 7 days less compared to cryocontainer 1. After 3 years of storage of liquid nitrogen, the service life of the cryocontainer remained the same, which is 15 days higher than the service life of the cryocontainer 1. This was achieved due to the even greater protection in the cryocontainer 4 of the cold layers of SVTI from cryocondensation of gas separation products and deterioration (as a result) of thermal characteristics.

The initial service life of cryocontainer 5 with 42 layers of perforated screens, equal to 144 days, became 4 days lower in comparison with cryocontainer 4 and remained the same after 3 years of liquid nitrogen storage. In this cryocontainer, the degree of deterioration of thermal characteristics by the exclusion of the “poisonous” action of cryocondensate layers becomes significantly lower in comparison with the simultaneous increase in radiant thermal conductivity λ_{rad} from the use of 42 layers with perforated screens.

In Fig. 6, the results obtained are presented in the form of the dependence of the service life of the cryocontainer on the number of perforated layers (N) used in its thermal

Table 5. Changes in the characteristics of cryocontainers with PET-DA + SVTI-7 layers (total heat fluxes Q_c, service life R, gas pressure P_g) depending on the number of layers in SVTI (N) used with PET-DA perforated screens near a warm wall during storage of liquid nitrogen for 10 days and 3 years

Cryocontainer No.	N	After 10 days			After 3 years		
		Q_c, W	R, day	P_g, 10^{-3} Pa	Q_c, W	R, day	P_g, 10^{-3} Pa
1	–	0.417	155	2.5	0.472	132	3.1
2	20	0.423	153	3.2	0.459	141	3.3
3	28	0.428	151	2.9	0.440	145	3.9
4	35	0.437	148	3.6	0.437	148	2.7
5	42	0.452	144	2.8	0.456	144	3.4

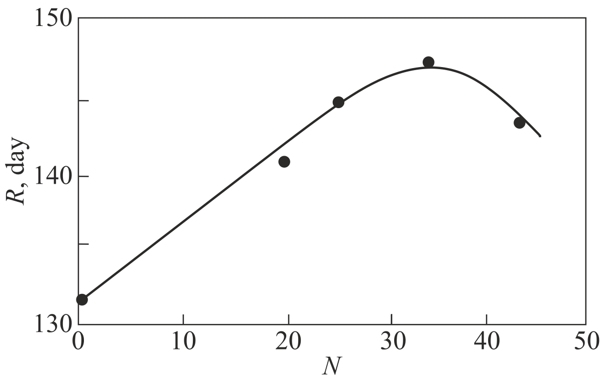

Fig. 6. Dependence of the service life of the cryocontainer X-34B (R) on the number of layers with perforated screens (N) in the heat-shielding package.

insulation. As can be seen, the $R(N)$ dependence passes through a maximum for thermal insulation with 35 perforated layers, at which the maximum service life of $R = 148$ days is reached.

Obtaining these results became possible due to the development of a heat-shielding structure on a cryocontainer with an optimal number (35) of perforated layers. This made it possible to reduce the hydraulic resistance and direct the evacuation of gas separation products through them using a loop-shaped evacuation process in the direction opposite to the cold layers. It should be noted that the evacuation towards the warm wall of the cryocontainer occurs from the SVTI layers with perforated screens with a temperature higher than 210 K. At lower temperatures, gas separation practically does not occur, because the partial pressure for the main products of gas separation (H_2O and CO_2 molecules), which are in a dissolved state in materials, becomes less than 10^{-3} Pa [9].

The efficiency of the developed optimized heat-shielding structure with perforated screens has been confirmed by the characteristics of cryocontainers with long service life. For example, after 10 years of operation, one of these cryocontainers had a storage life of liquid nitrogen of 140 days, the second, 13 years after production, 142 days, and the third, 15 years later, 144 days. As can be seen, the results obtained for cryocontainers from the field of operation are in satisfactory agreement with similar parameters for experimental cryocontainers (Table 5).

Conclusions

The improvement of nitrogen cryobiological Dewars for use in cryomedicine, cryobiology and scientific research became possible after the developed fundamental methods for determining heat fluxes for each element of their structure, studying the temperature and pressure profiles, as well as the peculiarities of heat and mass transfer in the layers of thermal insulation.

The temperature profile along the average integral thickness of the heat insulation on a low-quality cryocontainer turned out to be bent. According to the theory, this indicates the presence of a local area in it with increased pressure and heat transfer through the gas. The pressure profile measured according to the developed method confirmed the presence of such a section with a gas pressure increased by 4 orders of magnitude (equal to 2.1 Pa).

It was found that the pumping out from the local area is carried out in two directions: to the cold wall of the cryocontainer through the SVTI layers, and also partially to its warm wall, and then along the open vacuum channel along the nozzle surface in the form of a loop-shaped vacuum process in the direction.

The thermal insulation on the cryocontainer after the experiments is a continuous glued mass. The reason for this was the PVA glue base, which is used in the manufacture of insulating cushioning glass veil SVTI-7. It was developed for use in thermal insulation of cold space cryostats. When SVTI-7 is used in the heat insulation (which heats up to 380–390 K in the process of thermal vacuum degassing), the adhesive base in the glass veil softens, which causes the SVTI layers to stick together and an increase in their thermal conductivity by 7–8 times.

The use of that SVTI-7 glass veil (specially pretreated to reduce the content of the adhesive base) in the thermal insulation of cryocontainers made it possible to reduce its thermal conductivity from $(27–29)\cdot10^{-5}$ to $(14–14.5)\cdot10^{-5}$ W/(m·K) and increase their service life with liquid nitrogen from 75–80 to 150–155 days. The temperature profile investigated for such thermal insulation turned out to be monotonic without kinks.

Long-term studies of cryocontainers with liquid nitrogen to reveal the efficiency of the technologies used for their manufacture allowed to establish that, due to cryocondensation on the cold layers of the SVTI of the evacuated gas separation products, there is a gradual increase in their emissivity, temperature and radiant heat transfer. As a result, after 15 years of operation, their resource decreases to 70–80 days.

A technology has been developed to protect the layers of SVTI on cryocontainers from the formation of “poisonous” cryocondensate. For this, it is proposed to change the direction of pumping in the opposite direction, reducing the hydraulic resistance of the thermal insulation, by using a certain optimal number (35) of perforated layers and an open loop-shaped vacuum process in the direction. As a result of the use of perforation in thermal insulation and an increase in radiant heat transfer through it, the initial resource of cryocontainers decreases by ~ 5% to 145–148 days, which remained practically constant over 15 years of operation.

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1. M. G. Kaganer, *Heat and Mass Transfer in Low-Temperature Structures*, Energy, Moscow (1979) (in Russian).
2. G. G. Zhun, A. G. Podolskiy, and V. I. Shalaev, *Cryogenic Systems: Development and Research*, Naukova Dumka, Kiev (1984) (in Russian).

3. S. B. Milman, M. G. Velikanova, and Yu. M. Zavyalov, *Chemical and Oil Engineering* **4**, 21 (1989) (in Russian).
4. S. B. Milman and M. G. Velikanova, *IFZh* **59**, 216 (1990) (in Russian).
5. G. G. Zhun, *Aerospace Engineering and Technology* **27**, 94 (2002) (in Russian).
6. R. S. Mikhalchenko, V. F. Getmanets, and B. Ya. Sukharevsky, *IFZh* **18**, 481 (1970) (in Russian).
7. R. S. Mikhalchenko, V. F. Getmanets, and V. S. Gaidamaka, *Gas Dynamics and Heat Exchange in Cryogenic Systems*, Naukova Dumka, Kiev (1977) (in Russian).
8. G. Zhun, *Integrated Technologies and Energy Saving* **2**, 115 (2001) (in Russian).
9. M. P. Malkov, *Handbook of the Physical and Technical Foundations of Cryogenics*, Energoatomizdat, Moscow (1985) (in Russian).

Поліпшення теплоізоляції азотних кріоконтейнерів за допомогою петлеподібного процесу вакуумування

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Удосконалення серійних кріоконтейнерів Дьюара для зберігання рідкого азоту з використанням екранно-вакуумної теплоізоляції (ЕВТІ), що має найменшу теплопровідність в калориметричних зразках, уможливлено шляхом розробки фундаментальних методів визначення теплопритоків по кожному елементу конструкції кріоконтейнера та вивчення особливостей теплообміну в ЕВТІ. Встановлено, що погіршення теплоізоляції на кріоконтейнерах в 7–8 разів відбувається внаслідок її злипання при нагріванні в процесі виготовлення. Додаткове зниження якості теплоізоляції в ~ 2 рази при експлуатації обумовлено утворенням кріоконденсату з продуктів газорозділення в холодних шарах ЕВТІ та збільшення променевого теплопереносу. Усунення злипання ЕВТІ, а також зміна напрямку відкачування продуктів газорозділення в напрямку теплої стінки кріоконтейнерів через 35 перфорованих шарів ЕВТІ з використанням відкритого петлеподібного процесу вакуумування дозволило збільшити їх ресурс роботи в ~ 2 рази (до 145–148 діб). При цьому ресурс роботи залишається практично незмінним протягом 15 років експлуатації.

Ключові слова: кріоконтейнер, теплоізоляція, рідкий азот, вакуум, ресурс роботи.