A.A. Nazarenko

A.A. Nazarenko

Moscow State Technical University of Radio Engineering,
Electronics and Automation, 78, Vernadsky Prospect,
Moscow, 119454, Russia

RELIABILITY ENHANCEMENT OF THERMOELECTRIC COOLERS USING POLYMER VACUUM COATINGS

The effect of parylene protective coatings on the durability of miniature thermoelectric coolers (TECs) under high-temperature storage in the air and high humidity, and under the influence of aggressive solutions was studied. According to the results of research the type of parylene was selected and optimal thickness of parylene coating was determined. TECs were tested according to standard MIL-STD-883F methods, and it was established that parylene coatings increase TEC reliability, namely parameter stability under high-temperature storage (125 °C) and humidity is improved, structural elements are protected from the influence of aggressive media. It is shown that parylene coating does not noticeably change the thermophysical characteristics of TECs: for instance, the maximum temperature difference ΔT_{max} *of a single-stage TEC is reduced by only 0.3 °C as compared to the initial values.*

Key words: thermoelectric coolers, reliability, polymer coating, chemically active environment.

Introduction

Performance reliability of TECs is essentially restricted with use in the ordinary air atmosphere and aggressive media due to interaction of structural elements with the environment, which reduces the efficiency of module operation because of problems related to corrosion or moisture condensation with formation of “thermal bridge” between the hot and cold TEC junctions [1].

An efficient method of TECs protection from condensate formation is sealing by application of continuous polymer coating on the lateral surfaces of TECs (Fig. 1).

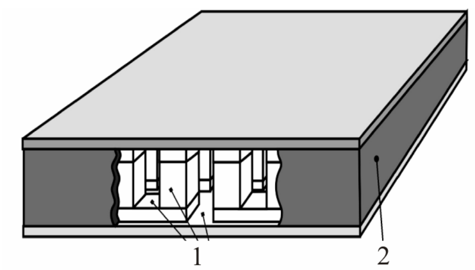


Fig. 1. TEC with double encapsulation by UR-231 varnish (1) and VGO-1 sealant (2).

For these purposes, multiple application of silicone, epoxy or varnish coatings is used to form a layer 50…80 μm thick, for instance, two-component coating of UR-231 varnish and VGO-1 silicone sealant [4]. However, such coatings can be destroyed on exposure to repeated temperature cycling. Moreover, heat losses along the perimeter reduce considerably TEC characteristics. In particular, the value of maximum temperature difference ΔT_{max} of a single-stage TEC is reduced by 3 to 5 K. For protection of miniature TECs this method is impractical.

Company RMT Ltd has developed and patented corrosion protection method for TECs, including miniature and multi-stage ones (Russian Federation patent № 41549). The internal and external surfaces of TECs are coated with a continuous parylene protective film (Fig. 2). However, this patent does not indicate the specific type of parylene coating and its thickness.

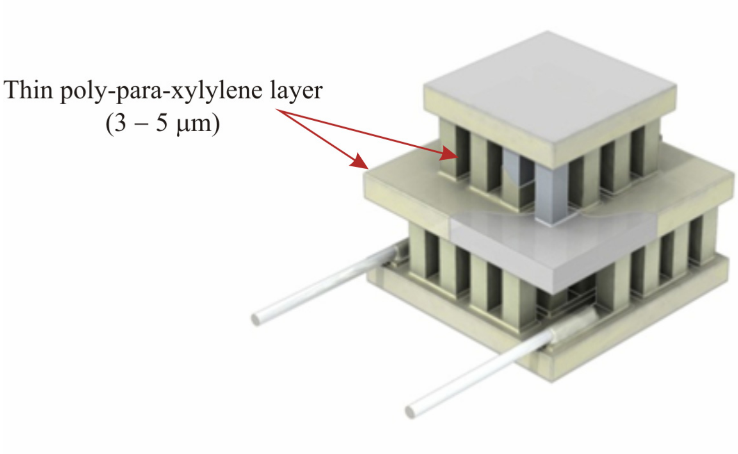


Fig. 2. Poly-para-xylylene polymer coating.

To the most efficient vacuum parylene coatings one can refer polymer coatings based on poly-para-xylylene (*Parylen N)*, poly-dichloro-para-xylylene *(Parylen D*) and fluoropolymers (*Parylen F*), that are deposited from gas phase (without passing through the liquid state) at normal or reduced (to 0 °C) temperature, and coating formation does not require curing. High thickness uniformity of coatings, including sharp edges and narrow (< 1 μm) gaps, make them indispensable for complex-contoured surfaces. These factors provide poly-para-xylylene coatings (in the range of thickness from 3 to 10 μm) with protective properties as good as or superior to coatings based on epoxy, silicone and polyurethane resins 50 to 80 μm thick. Vacuum coatings assure reliable operation of protected TECs under conditions of increased humidity, temperature variation in a wide range (from – 80 to + 100 °C), as well as the influence of biological, chemical and other factors [3].

The purpose of this work is to select the type of parylene coating and determine its optimal thickness according to the results of studying the resistance of miniature TECs to environmental impacts.

Selection of coating type and experimental procedure

Analysis of the physical properties of *Parylen N*, *Parylen D and Parylen F* polymers (Table 1) has revealed that the best parameters as compared to other poly-p-xylylenes are possessed by *Parylen F* which offers the lowest moisture permeability (< 0.0009 g/(cm^2·h)) and is the most thermally stable material (~ 400 °C in the air). However, high cost of material makes it economically unsound for use in large-scale production. Parylen *F* is reasonable to be used for encapsulation of high-temperature TECs, as well as for special missions requiring parameter stability under increased environmental impact.

Parylen N has the lowest thermal stability (80 °C) which restricts its application area and does not conform to test conditions.

Parylen D has moisture permeability 0.1 g/(cm^2·h) and thermal stability 150 °C which meets the requirements of test performed in the framework of this paper. Therefore, for studying the protective properties of coatings we fixed on *Parylen D*.

For protective polymer synthesis in low vacuum as the original substance we used di-chlorinated [2, 2]-paracyclofan which is a fine crystalline white powder with the density of 1.42 g/cm^3 and melting temperature ~ 310…330 °C [6].

As long as adhesion of poly-dichloro-p-xylylene (*Parylen D*) film to the surface of heterostructure to a large extent depends on the substitutes in the benzene ring of paracyclofan structure and the material of coated surface, in the formation of protective *Parylen D* layer the surface is pre-treated by silane vapours [5].

Table 1

Basic properties of poly-para-xylylene and poly-dichloro-para-xylylene

Parameter	Value		
	Parylen N	*Parylen D*	*Parylen F*
Dielectric permittivity at 60 Hz	2.65	2.84	2.28
Electric strength, kV/mm	240	145	141
Bulk resistivity under standard conditions, Ohm·m	10^{15}	$8 \cdot 10^{14}$	$6 \cdot 10^{14}$
Dielectric loss tangent at 60 Hz	0.0002	0.003	0.003
Melting temperature, °C	400	310 – 330	270
Vitrification temperature, °C	60 – 70	110	140
Tensile strength, MPa	63	42	42
Thermal stability in the atmosphere, °C	80 – 90	140 – 150	380 – 400
Water absorption during 24 hours, %	0.01	0.06	0.02
Moisture permeability, g/(cm^2·h)	0.3	0.1	0.009

Formation of *Parylen D* coating takes place during two-stage growth: application of intermediate silane adhesion layer 10 nm thick and deposition of basic poly-p-xylylene protective layer at constant sublimation temperature of paracyclofan original substance.

Parylen D coating was applied by gas-phase deposition method. The deposition took place at a pressure of 8 Pa in closed sublimator – pyrolysis reactor – deposition chamber system and device surface temperature ~ 40 °C for 45 min [5].

Thermoelectric coolers 1MD04-012, 1ML06-029 and 1MC06-060 manufactured by RMT Ltd, with their basic operating parameters given in Table 2, were used as experimental samples for the application of protective polymer coatings.

Table 2

Basic operating parameters of TECs

TEC type	ΔT_{max}, K	Q_{max}, W	I_{max}, A	U_{max}, V
1ML06-029-09	71	3.85	1	3.55
1MD04-012-07	72	0.38	0.8	0.85
1MC06-060-10	71	6.05	1.5	7.4

Criterion for estimation of the environmental resistance of thermoelectric modules is taken to be a change on environmental exposure in electric resistance R and thermoelectric figure of merit Z by not more than 5 % of the initially measured values. This criterion is used by RMT company and corresponds to reliability standards developed by Telcordia corporation. Requirements to TECs are formulated in Telcordia document GR-468-CORE (Generic Reliability Assurance Requirements for Optoelectronic Devices Used in Telecommunications Equipment) comprising general requirements to reliability of optoelectronic devices and components, as well as their test methods.

TEC test methods set forth in Telcordia GR-468-CORE are based on the US military standard MIL-STD-883F. This standard formulates methods for testing microelectronic products for military and aerospace applications.

The measurements were performed on Z-meter of DX4165 series manufactured by RMT Ltd.

To estimate the proposed method of TEC protection from aggressive media and humidity, the following tests were performed:

– high-temperature storage in the air;
– exposure to chemical environment;
– humidity test.

Test results

Check of TEC thermophysical parameters. Prior to application of parylene coatings on 1MC06-060-10 modules, maximum temperature difference (ΔT_{max}) was measured in vacuum, in conformity with requirements of TU8420 001 34609988 12 “Performance specifications. TEC”, which was on the average 70.1 °C. Measurements were repeated after application on these TECs of *Parylen D* coatings 5 μm thick, which averaged ΔT_{max} = 69.8 °C, i.e. ΔT_{max} reduction made 0.3 °C.

High-temperature storage. To determine high–temperature durability of TEC with *Parylen D* protective coating 0, 3 and 5 μm thick, three lots of TEC 1MD04-012-07, 11 modules in each lot, were used. TECs were stored in the air at 125 °C for 1100 hours (accelerated test) instead of 85 °C/2000 hours recommended by Telcordia GR-468-CORE.

Prior to and after test the samples were subject to visual inspection and R and Z measurement. The results of measurement prior to and after test are represented in Table 3.

Table 3

Results of testing modules 1ML04-012-07 for storage in the air at 125 °C for 1100 hours

Coating thickness	Electric resistance R, Ω		Relative change, %	Thermoelectric figure of merit $Z \times 1000$, 1/K		Relative change, %
	Prior to test (R_1)	After test (R_2)		Prior to test (Z_1)	After test (Z_2)	
Without coating	1.61	1.66	3.11	2.67	2.60	–2.62
3 μm	1.62	1.65	1.85	2.67	2.63	–1.50
5 μm	1.62	1.65	1.85	2.66	2.63	–1.13

Figs. 3 and 4 show the plots of change in the basic parameters of thermoelectric coolers. For all TEC lots a change in *R* and *Z* as compared to the initial values did not exceed 5 % of criterion. From the plots it is seen that the output parameters of thermoelectric coolers with parylene coatings are more stable than parameters of modules without coating. Therefore, poly-dichloro-para-xylylene coating contributes to stabilization of module parameters in the process of high-temperature storage. Probably it is due to protection of thermoelectric materials and contact coatings from thermal oxidation.

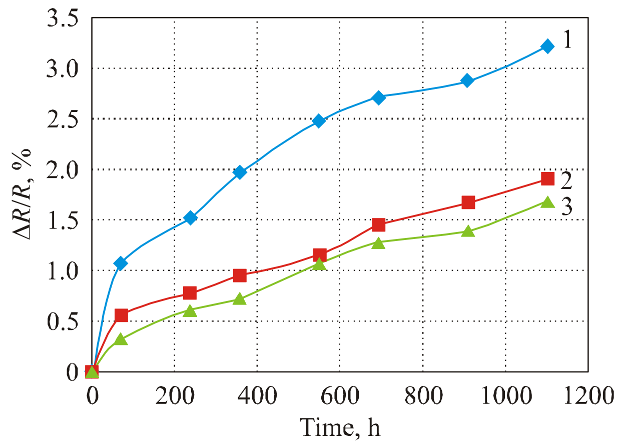


Fig. 3. Relative change in electric resistance with time.
Coating thickness: 1 – without coating; 2 – 3 μm; 3 – 5 μm.

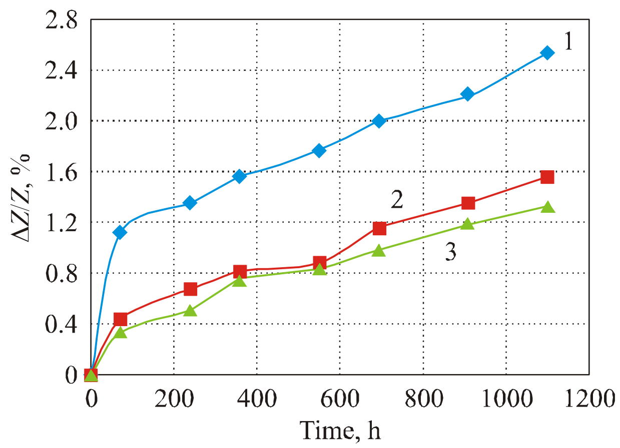
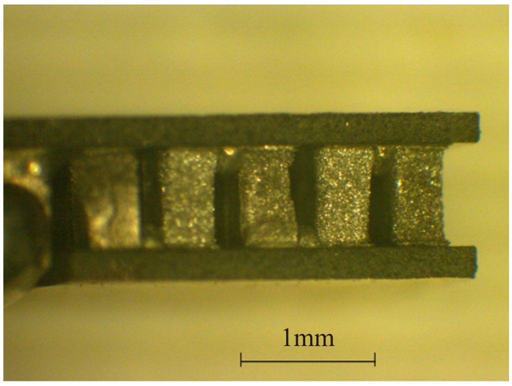


Fig. 4. Relative change in thermoelectric figure of merit with time.
Coating thickness: 1 – without coating; 2 – 3 μm; 3 – 5 μm.

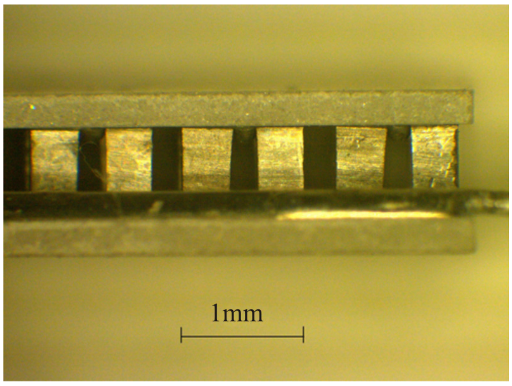
Exposure to chemical environment. Testing of TEC in chemically active environment was performed according to MIL-STD-883F, method 1009.8. To determine the efficiency of using poly-dichloro-para-xylylene coatings of various thicknesses for TEC protection, we used more severe conditions than in MIL-STD-883F: 10 % aqueous solution of *NaOH* instead of 3 %, test duration was increased from 240 to 336 hours. After testing, the samples were subject to visual inspection and parameter measurement by the criteria described above.

Testing was performed on TEC samples 1MD04-012-07 coated with vacuum films *Parylen D* 3 and 5 μm thick by holding in 10 % solution of sodium hydroxide (*NaOH*) for 336 hours.

The appearance of TEC after testing is represented in Fig. 5. It is seen that the legs of thermoelectric coolers without parylene were destroyed in *NaOH* solution. At the same time, the legs of modules with 5 μm vacuum coating had no defects.



a)



b)

Fig. 5. Appearance of TEC series 1MD04-012 on exposure to 10 % solution of sodium hydroxide (NaOH) for 336 hours: a) without coating, b) with Parylen D vacuum sealing coating 5 µm thick.

Results of measuring TEC parameters are represented in Table 4.

Table 4

Results of measuring parameters of 1MD04-012-07 modules prior to and after holding in 10 % NaOH solution

Coating thickness	Electric resistance R, Ω		Relative change, %	Thermoelectric figure of merit $Z \times 1000$ 1/K		Relative change, %
	Prior to test (R_1)	After test (R_2)		Prior to test (Z_1)	After test (Z_2)	
Without coating	1.11	2.97	167.57	2.53	0.96	–62.01
3 µm	1.17	1.75	49.57	2.52	2.10	–16.40
5 µm	1.11	1.17	4.98	2.49	2.38	–4.42

Figs. 6 and 7 represent plots of change in electric resistance and thermoelectric figure of merit of TEC in the course of holding in 10 % *NaOH* solution.

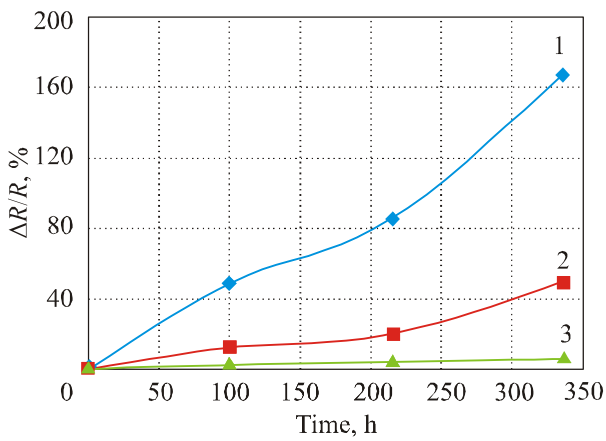


Fig. 6. Dependences of relative change in electric resistance R of thermoelectric coolers on the time of storage in 10 % NaOH solution. Coating thickness: 1 – without coating; 2 – 3 µm; 3 – 5 µm.

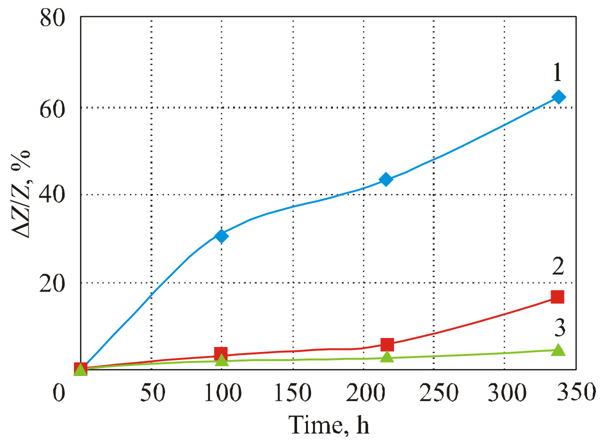


Fig. 7. Dependences of relative change in thermoelectric figure of merit Z of 1MD04-012-07 modules on the time of storage in 10 % NaOH solution. Coating thickness: 1 – without coating; 2 – 3μm; 3 – 5 μm.

Results of visual inspection and electrical measurement show that TECs without parylene coating did not withstand this test. Parameters of thermoelectric coolers with *Parylen D* coating proved to be more stable, and changes in both parameters (R and Z) of TECs with 3 μm *Parylen D* coating exceeded 5 % criterion, and with 5 μm did not go beyond the limits of criterion.

During the second part of testing for resistance to chemical environment we estimated the influence of 10% *NaC* aqueous solution on TEC under electric load. Testing was performed on TEC samples MC06-060-10 without coating and with *Parylen D* coating. The samples were placed into a vessel with a salt solution, and voltage 3.7 V (½ U_{max}) was applied for 336 hours. The results of testing are represented in Table 5.

In the course of testing the legs of modules without coating were destroyed completely. Parameters of thermoelectric coolers with vacuum polymer coating 3 μm thick went beyond the limits of 5 % criterion, while those with coating 5 μm thick remained within 5 %.

Table 5

Results of testing 1MC06-060-10 modules for resistance to 10 % NaCl solution at 3.7 V

Coating thickness	Electric resistance R, Ω		Relative change, %	Thermoelectric figure of merit $Z \times 1000$, 1/K		Relative change, %
	Prior to test (R_1)	After test (R_2)		Prior to test (Z_1)	After test (Z_2)	
Without coating	1.15	–	–	2.56	–	–
3 μm	1.14	1.23	7.89	2.58	2.40	–7.16
5 μm	1.15	1.20	4.34	2.55	2.43	–4.71

Humidity test. This test was performed in conformity with MIL-STD-883F, method 1004.7, with a view to determine the efficiency of TEC humidity protection with *Parylen D*. For testing, as before, we selected 3 lots of samples 1MD04-012-07, with *Parylen D* coating 3 μm, 5 μm and without coating. Graphic representation of humidity resistance test is shown in Fig. 8.

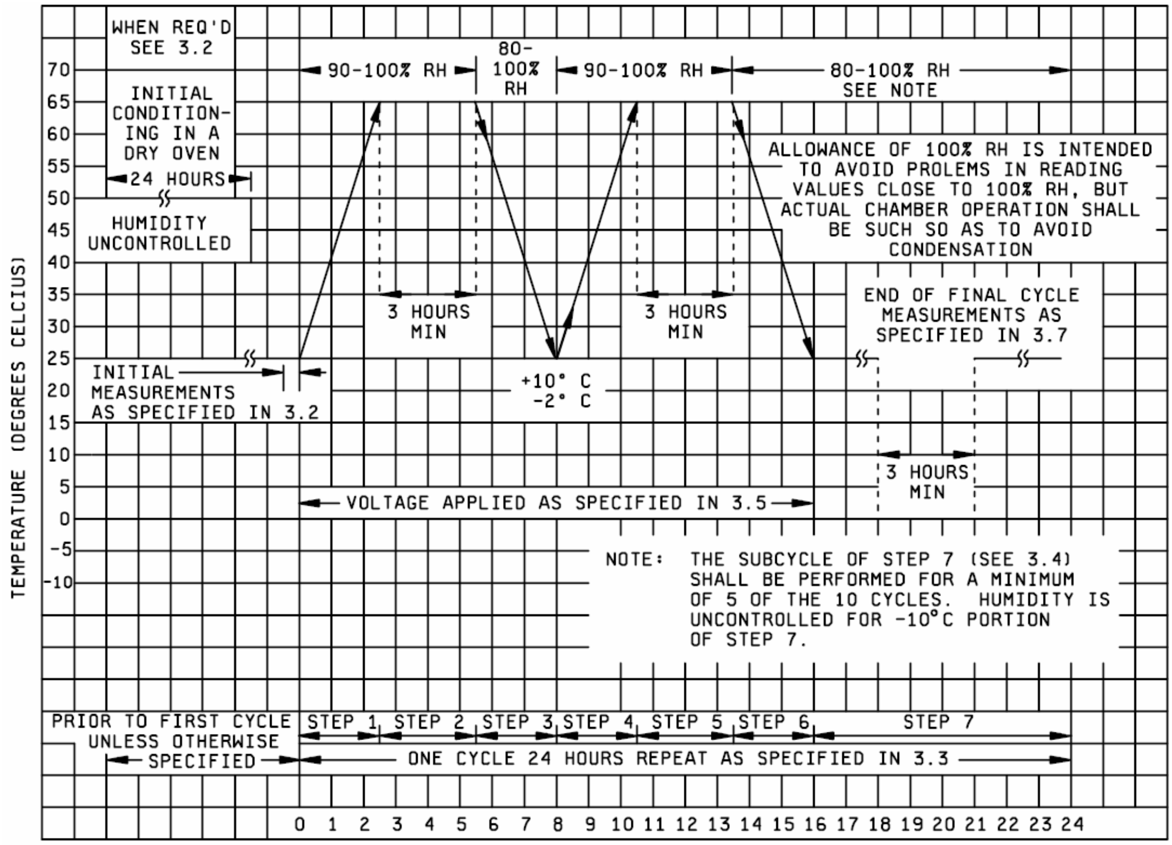


Fig. 8. Graphic representation of humidity test.

Results of TEC humidity test are represented in Table 6.

Table 6

Results of humidity test of 1MD04-12-07 modules

Coating thickness	Electric resistance R, Ω		Relative change, %	Thermoelectric figure of merit $Z \times 1000$, 1/K		Relative change, %
	Prior to test (R_1)	After test (R_2)	$(R_2 - R_1)/R_1 \cdot 100$	Prior to test (Z_1)	After test (Z_2)	$(Z_2 - Z_1)/Z_1 \cdot 100$
Without coating	1.12	1.14	1.79	2.58	2.54	–1.62
3 µm	1.15	1.16	0.79	2.52	2.49	–1.15
5 µm	1.15	1.157	0.61	2.59	2.57	–0.74

From the test results it follows that all the modules have passed the test and their parameters have remained within 5 %. It should be noted that TECs with *Parylen D* coating have more stable parameters as compared to modules without coating.

Conclusions

The durability of TECs with *Parylen D* coating under high-temperature storage in the air has been investigated. It has been shown that, unlike TECs without coating, the basic parameters of thermoelectric coolers with poly-dichloro-paraxylylene remain more stable under long (over 1000 hours) high-temperature storage (125 °C).

It has been established that thermoelectric coolers without protective coatings undergo strong destruction on exposure to aggressive media (10 % *NaCl*, 10 % *NaOH*). It has been noted that poly-dichloro-paraxylylene coating can protect TECs from chemical attack with coating thickness 5 μm.

TECs have been tested for reliability under humidity conditions, and it has been noted that parameter divergence of all the coolers does not exceed 5 %. In so doing, the greatest stability of properties is shown by coolers with a coating 5 μm thick.

Parylen D coating has no essential effect on the thermophysical properties of TECs, in particular, the value of maximum temperature difference ΔT_{max} of a single-stage TEC is reduced by 0.3 °C.

Based on the results of the research it can be concluded that for the efficient protection and stabilization of TEC parameters the thickness of *Parylen D* coating must be 5 μm.

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