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Physicomechanical and Operational Properties Polyurethane Thermal Panels

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***Abstract:** Evaluation of consumer properties of polyurethane thermal panels is the goal of the work. Physico-mechanical and operational characteristics of thermal panels are determined to achieve the purpose of the work. Methods of IR spectroscopy and thermo gravimetric analysis were used to study the structure of the samples. Satisfactory consumer properties of the studied thermo panels are brought out: compliance of clinker with the DIN EN 121 standard; absence of visual defects and change of color of thermo panels after 50 cycles of freezing-thawing; absence of changing color of thermo panels after influence of UV of radiation with the wavelength of 240-320 nanometers within 607 hours 30 minutes; high values of coefficients of sound absorption in the frequency range from 600 to 1600 Hz; low heat conductivity of the FPU layer. The influence of UV-radiation on thermal stability of foamed polyurethane is valued. Thermal analysis methods and IR spectroscopy are used to assess the degree of UV - destruction of polyurethane foam. At destruction of foamed polyurethane there is a rupture of chemically weak communication and formation of alcohols, air, olefins. The results of IR-spectroscopy illustrate the beginning of the processes of destruction of samples of FPU under the influence of UV-radiation. Using the thermo gravimetric analysis the research of the FPU thermal properties under the influence of UV - radiations is conducted. It is established that compositions from FPU under the influence of UV- radiation have lower temperature of the beginning of decomposition, than initial material. The influence of UV-radiation on heat stability of the studied compositions is shown. The possible mechanism of destruction of FPU is confirmed in the research. The DSC method has estimated the resistance of FPU to the oxidizing influence characterizing the material operation time. The studied consumer properties of thermal panels show that they can be used in civil engineering as effective protection structures of buildings.*

***Keywords:** physical mechanical and operational properties, thermal analysis, IR-spectroscopy, thermo oxidizing destruction, front polyurethane panels.*

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I. INTRODUCTION

According to new standards of energy efficiency of buildings there is a need for the new system of warming and constructions [1, 2, 3, 4]. As heaters are used: basalt mats, "HIMFPEx" panels, foam plastic, etc. We apply the following facing materials: clinker, panel sandwich, timber, monolithic reinforced concrete walls, etc. The usage of dissimilar materials one for facing, others for isolation rises in the cost of construction. Today the domestic market of the materials destined for high-quality finishing of facades, one of the leading places is occupied by thermo panels. The main advantages of thermo panels are: effective thermal insulation; wide color scale; brick facing; ecological safety; reliable protection against atmospheric precipitation; there is no need in the additional bases; accuracy and purity of installation, irrespective of weather and season, in the minimum terms; long service life of 50-100 years; affordable price [5-8]. Facing of walls with thermo panels can be made at the stage of construction of the house and at reconstruction of buildings and constructions. When finishing thermo panels they completely exclude either frost penetration or penetration of moisture into the walls. They are quite suitable for frame houses too. The set of types of thermo panels is presented at the market of construction materials [9]: clinker thermo panels; thermo panels with a ceramic and granitic tile; thermo panels with a glazed tile. Available clinker thermo panels representing themselves as a flat multilayered product in which heater (expanded polystyrene or polyurethane foam) and the "carpet" out of clinker tile imitating a brick setting act as the main layer are the most popular. For reliability of the butting, achievement of the monolithic effect perimeter covering on the thorn groove system (figure 1) is provided.

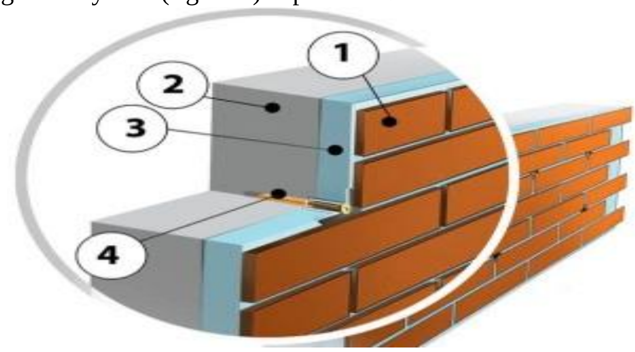

Figure. 1 - Layers of thermo panels [5]:
1. brick tile; 2. external wall;
3. heater-polyurethane foam layer;
4. assembly plugs

Evaluation of consumer properties of polyurethane thermal panels is the goal of the work. Physico-mechanical and operational characteristics of thermal panels are determined to achieve the purpose of the work.

II. PROPOSED METHODOLOGY

Pilot researches of the facade thermo panels consisting of: an external layer - clinker or polymer and sand tiles; a heat-insulation layer - foamed polyurethane, formed by reaction between polyol component "A" and isocyanates component "B"; an inside layer – the corrugated cardboard providing rigidity of the construction.

Physical and mechanical properties of facade thermo panels were studied:

- with a clinker tile of Houson of collections [10]: LM26218, DS62904, LM26253, LM26208, DS62901, LM26261;

- with a clinker tile of ADW Klinker of collections [11]: Beige Rustic Besandet, Lanzarote Glatt, Weiss struktur, Braun genarbt, Lanzarote genarbt, AntikMangan;

- with a polymer and sand tile of production of LLC NAMUS [12].

In pilot researches as the main components of urethane generative mix were applied [13]: polyol component "A" of Isolanbrand A 210-7; isocyanate component "B" of the Voratek brand of SD 100. For an external layer used class T23C corrugated fiberboard the sizes 1000x2000 [14].

The following researches have been conducted: water absorptions of a clinker tile under atmospheric pressure at the temperature of water (20±5) °C in accordance with the State Standard 7025-91 [15]; frost resistance of thermo panels at volumetric freezing in accordance with the State Standard 7025-91 [15];coefficient of sound absorption of thermo panels in accordance with the State Standard 16297-80 [16]; heat conductivity of thermo panels (λ) in accordance with the State Standard 7076-99 [17]; macrostructure research; determination of light resistance of a facing layer of facade thermo panels by a technique "JSC “GAZ”M 012.20.006-2001. Determination of light resistance".

We used the following test equipment: computing weighing scales GAS MWP-600 [18]; digital caliper of DC-I-150-0,05; climate cell MKT115of modeling of climatic conditions firm BINDER; ruler metal State Standard 427-75; acoustic pipe of Brühland Kjer of type 4206 [19]; microscope Altami MET 3MT [20]; electronic measuring instrument of heat conductivity IHC-MG4 [21]. For realization of the method of determination of light resistance we used the experimental installation developed by specialists of the Naberezhnye Chelny institute of KFU.

According to State Standard 16350-80 "Climate of the USSR. Division into districts and statistical parameters of climatic factors for the technical purposes" all the climatic zones of the former USSR are divided into 12 zones [22]. In case of using of products in the conditions of the midland of the Russian Federation it is necessary to use the climatic region of II5 (Moderate). A total dose of solar radiation of 300-400 nanometers taking into account losses per year of 148,10 MJ/sq.m. The stream of radiant energy makes P =128 W. Taking into account distance to examinees of samples (250 mm) hold time under a lamp about DRT 1000 power has made to equivalent 1 year 20 hours 5 minutes.

Thermal stability of samples was investigated by means of the thermo gravimetric analyzer "Netzsch TG 209 F1 Iris". Heating to 550 °C was carried out with the speed of 10 K/min. in the conditions of a steady argon pre gassing.

The Temperature of Oxidative Induction (TOI) and the time of oxidative induction (TOI) were fixed by means of the differential scanning calorimeter of a thermal stream by "Netzsch DSC 204 F1 Phoenix". For definition of TOI having heated to temperature of test carried out with a speed of 10 K/min. in the conditions of a constant purging with argon. On reaching the test temperature (230 °C) supply of inert gas stopped, began air supply with a speed of 50 ml/min. and registration of a signal of DSC. For definition of TOI having heated carried out with a speed of 10 K/min. On reaching 150 °C supply of inert gas stopped and began a purge air with a speed of 50 ml/min.

The research of functional structure and structure of samples was determined with the help of IK-Fourier of spectroscopy of "PerkinElmer Spectrum 100" by using of the FTIR-crystal of ZnSe.

III. RESULTS AND DISCUSSION

Water absorption researches have been conducted in accordance with State Standard 7025-91 [15] clinker plates of Houson [10] and ADW Klinker [11]. Results of the researches are presented in the Table 1.

The received results demonstrate that all samples of brick tiles of production Houson and ADW Klinker conform to the DIN EN 121 standard "Technical characteristics of a brick tile" and have water absorption: individual value on average ≤ 3%; maximum individual value ≤ 3,3%.

On three types of front thermo panels carried out tests of physic mechanical properties: with a brick tile of production Houson of the DS62901 collection; with a brick tile of production ADW Klinker of the Beige Rustic Besandet collection; with a polymer and sandy tile of production of LLC NAMUS. The layer of polyurethane foam heat insulation of front thermo panels was identical to all types. Thermo panels have been manufactured according to the same technology.

For control of frost resistance to the extent of damages have been selected 5 samples of each type of thermo panels. On initial samples there were no cracks, chips of edges and corners, other defects allowed by standard technical documentation on products of certain types. The number of freezing cycles - thawing of samples has got 50. After carrying out the required number of cycles of freezing-thawing made visual survey of samples on extent of damages and fixings of the appeared defects.

The received results demonstrate that all samples of thermo panels after 50 cycles of freezing-thawing have no visual defects and changing of color.

For determination of light resistance 3 samples of each type of thermo panels were selected. On samples of front thermo panels after the influence of the ultra-violet radiation (UV) with the wavelength of 240-320 nanometers during 607 hours 30 minutes (equivalent 30 years of operation) under a lamp like DRT 1000 defined change of color.

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The light resistance of the front layer of thermo panels should be considered as satisfactory because at visual assessment there are no changes of appearance and color of a detail in comparison with the samples of details which weren't subjected to the tests (the figure 2 - 3).

Table 1 - Water absorption of a clinker tile

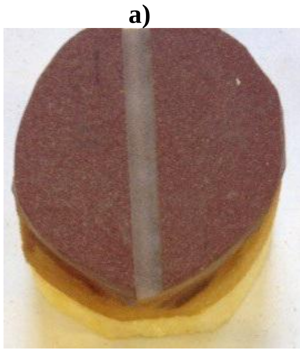
Sample	m, r	m1, r	W, %	Normality to DIN EN 121
ADW Klinker				
Beige Rustic Besandet	389,80	391,14	0,344	normality
Lanzarote Glatt	375,54	381,3	1,534	normality
Weiss struktur	346,58	349,42	0,819	normality
Braun genarbt	412,52	417,18	1,130	normality
Lanzarote genarbt	386,02	391,18	1,337	normality
Antik Mangan	384,68	388,36	0,957	normality
Houson				
LM26218	269,30	270,58	0,475	normality
LM26218	263,06	264,02	0,365	normality
DS62904	194,52	197,7	1,635	normality
DS62904	195,38	198,42	1,556	normality
LM26253	265,52	267,64	0,798	normality
LM26253	266,34	268,32	0,743	normality
LM26208	268,34	272,34	1,491	normality
LM26208	264,96	267,6	0,996	normality
DS62901	191,58	192,7	0,585	normality
DS62901	190,12	191,1	0,515	normality
LM26261	202,72	204,52	0,888	normality
LM26261	186,90	188,62	0,920	normality

a)

b)

Figure. 2 - Appearance of the front polyurethane foam thermo panel with a brick tile of production ADW Klinker of the Beige Rustic Besandet collection (x3): a) before influence of UV-radiation; b) after influence of UV-radiation (607 hours 30 minutes)

a)



b)

Figure. 3 - Appearance of the front polyurethane foam thermo panel with a polymer and sand tile of production of LLC NAMUS (x3): a) before influence of UV of radiation; b) after influence of UV of radiation (607 hours 30 minutes)

Considerable change of color of the foamed polyurethane layer (figure 4) is observed. FPU becomes fragile and breaking that is the sign of its thermo destruction and deterioration in physical and mechanical properties, including heat conductivity and rigidity.

a)

b)

c)

Figure. 4 - Appearance of FPU layer of the front thermo panel layer after influence of UV of radiation (607 hours 30 minutes) (x3):
a) with a clinker tile of production ADW Klinker of the Beige Rustic Besandet collection; b) with aclinker tile of production Houson of the DS62901 collection; c) with a polymer and sand tile by the production of the LLCNAMUS

The thermal analysis gives rather full information on the mechanism of destruction of materials, chemical transformations in the substance and other processes which are followed by a decrease of mass of substance endo- and exothermic reactions. This method allows to carry out the analysis of thermal decomposition of FPU on the obtained data.

Carrying out the thermo gravimetric analysis gives important information on heat stability of substance and his behavior when heating.

The thermal analysis is defined the following changes in the process:

- the mass of the studied sample depending on temperature of its heating; - speed of loss of mass of a sample depending on the temperature of its heating.

It is possible to obtain rather full information on kinetics of destruction of the studied material on the basis of the analysis of the specified parameters [23].

Initial information on influence of preliminary UV-influence was obtained, analyzing stages of the process of destruction of material on TG-curve (figure 5).

From thermo grams of initial FPU (sample 1), FPU after radiation UV-during 550 h (sample 2) and 606 h (sample 3) (table 2, figure 5), are defined temperatures of the beginning of the decomposition of the samples, temperatures are characteristic for 5% of mass loss, loss of weight (Δm) at the time of achievement of the temperature of the maximum speed of decomposition (Tmax), material rest size at 550 °C, the maximum speed of decomposition (table 2). Apparently from the Table 2 and the Figure 5 falling of weight of all samples takes place in several stages of different intensity.

Analyzing data by TG and the results of their processing (table 2, the figure 5), it is possible to note that the low-temperature I stage for FPU is characterized by area of 150-260 °C, and previously UV-irradiated samples 2 and 3 begins practically with 30 °C and is explained by already proceeding processes of decomposition of polyurethane on an isocyanate and polyatomic alcohol. At the same time samples 2 and 3 lose about 12-14% of weight, and the sample of FPUlosesonly 7%.

The second stage of process is characterized by intensive disintegration in the field of temperatures of 270-550 °C, considerable loss of mass of all samples (up to 43%) with the maximum speed of weight falling 0,2 mg/min. at 347 °C that indicates active course of processes of thermo destruction and decomposition. And the speed of decomposition of samples 2 and 3 is twice higher, than a sample 1 that is explained by acceleration of these reactions thermo destruction products.

Thus, compositions out of FPU under the influence of UV-radiation have much lower temperature of decomposition, than initial material. So, for FPU as a result of UV-radiation the speed of the first stage of destruction of the material is twice higher, and the beginning of the thermal destruction decreases from 150 °C to 30 °C in comparison with a standard sample of FPU.

For stability assessment in the oxidizing medium of the samples we used indicators of temperature and time of oxidizing induction. The resistance of FPU to oxidizing influence is one of the important parameters, the characterizing material, as in use it should maintain the destroying influence of oxygen and thermal loading [24]. It is known that assessment of stability of FPU at the storage time and operation can be estimated by means of the DSC method. Comparison of oxidation of samples of initial FPU (sample 1) FPU after UV-radiation during 550 h is also model (sample 2) and 606 h (sample 3) (table 3, figure 6) have shown that reaction of oxidation at the temperature of 230 °C of sample 1 has begun after 87,7 min. and after 63,1 min., 61,4 min. for samples 2 and 3 respectively. It is obvious that the firmness of the sample 1 to oxidation is much higher, than FPU after UV-radiation. It confirms the fact that the more time prior to destruction, the more stable is the sample to oxidation and the longer operational service life of the material. Therefore, the FPU samples after 505 h UV-radiation lose physical and mechanical properties; the term of their further operation is reduced.

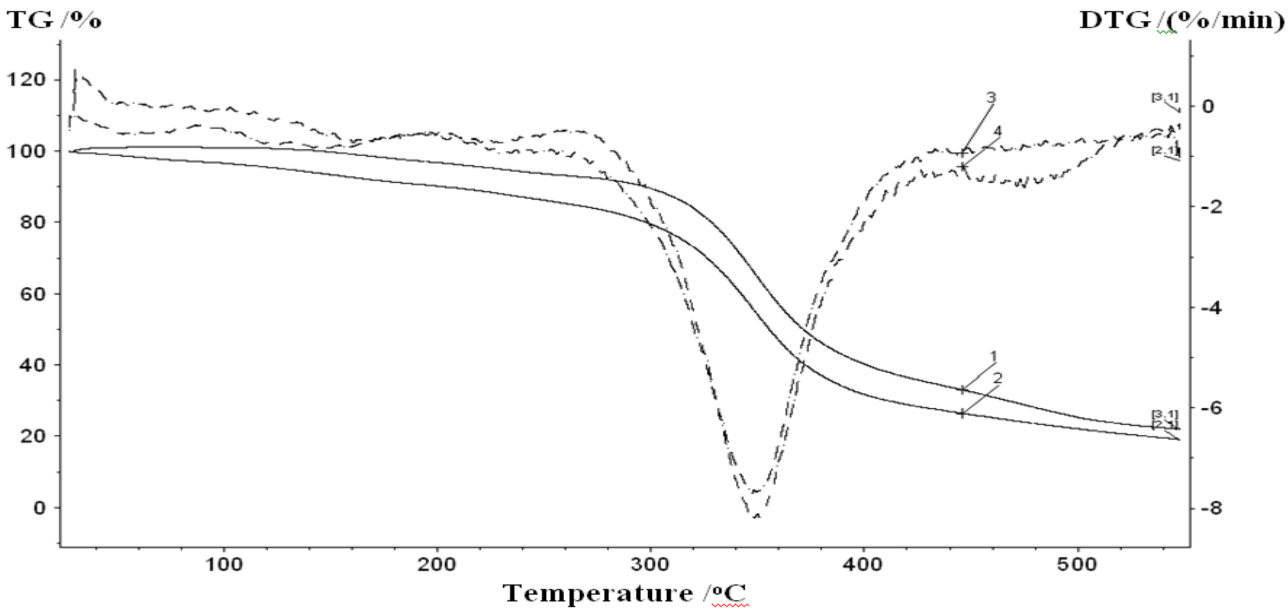


Figure. 5 - The thermo gravimetric analysis of initial FPU (curve TG-1, curve DTG - 3) is also samples of FPU after radiation UV-during 606 h (curve TG-2, curve DTG-4)

Table 2 - Results of thermo destruction of the studied FPU samples

Sample	Tн decomposition, °C	T 5% massloss, °C	Tmax decomposition, °C	Maximum speed of the decomposition, mg/min	Tmax mass loss under decomposition	Residual mass at 550 °C, %
1	150	228	350	0,1	32,9	22,0
2	30	142	347	0,2	41,6	20,3
3	30	127	347	0,2	43,2	19,0

Table 3 - Temperature and time of oxidizing induction of the studied FPU samples

Sample	Temperature of oxidizing induction, °C	Time of oxidizing induction at 230 °C, min.
1	250	87,7
2	244	63,1
3	244	61,4

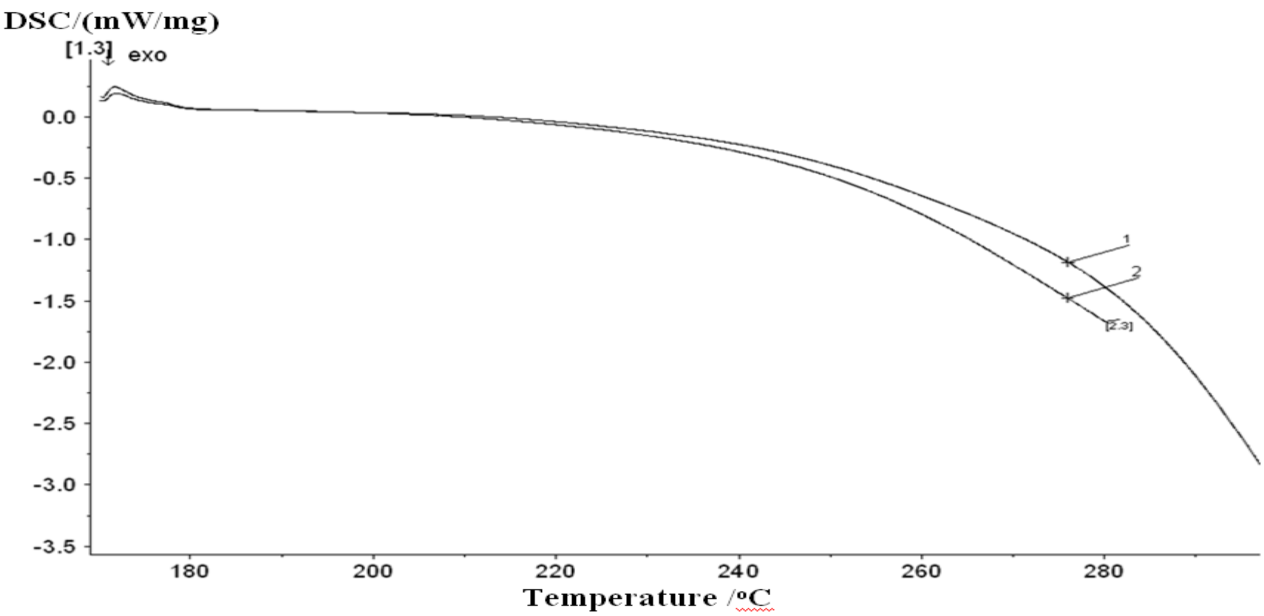


Figure. 6 - TOI of samples of initial FPU (1) and FPU after 550 h UV-radiation (2)

In the article [25] it is shown that reaction of oxidation under the temperature proceeds through the formation of peroxide radicals at interaction with molecular oxygen in the conditions of heating. Then, these peroxide radicals turn into hydro peroxides because of the hydrogen separation from the chain. Decomposition of hydro peroxides on alkoxyl and hydroxyl radicals is reaction with considerable energy of activation. Therefore if temperature increases the speed of reaction increases, besides, in our case, it is accelerated with UV-radiation.

As TOI of an initial sample of 150 °C, and samples after UV-radiation of 144 °C, therefore, can be assumed that at the UV-radiation stage on air in samples 2 and 3 peroxide radicals are formed. At the testing of the reaction of oxidation at the temperature in samples 2 and 3 additional peroxide radicals are formed. As a result, the speed of the reaction of oxidation of the samples 2 and 3 is higher, than initial FPU (sample 1) (table 3, figure 6).

For the researching of the functional structure and the structure of the foamed polyurethane the method of molecular spectroscopy in the IR area is the most expedient. Infrared ranges give the chance to find existence in substances of oxygen-containing (hydroxyl, carbonyl, carboxyl, radio), nitrogen-containing functional groups; aliphatic and aromatic hydro carbonic fragments. The lack of the method of the IR-spectroscopy (X) is the complexity of the differentiation of same structure [23].

In all ranges of the researched FPU samples, the bandwidth of 2926 cm-1, 2854 cm-1 connected with valence vibrations of CH2, CH3-group and a strip 1460 sm-1, 1375 sm-1, connected with deformation fluctuations of the same groups (figure 7) [26] are traced.

On the spectrum of the initial foamed polyurethane is well observed that it is received on the basis of simple polyether as on the spectrum of the bandwidth of 1080-1090 cm-1that belongs to C-O-C of communication of simple polyether is observed. The spectrum of UV-activated samples keep strips, characteristic of polyurethane: in the field of 1720 cm-1, belonging to absorption of C=O of urethane group, a strip in areas 1590 of cm-1 and 1515 cm-1, belonging to absorption of N-H-groups (Amide I, Amide II) and also a strip in the field of 1100 cm-1 – C-O-C of simple ether (figure 7) [26].

On the spectrum of samples 2 and 3 the intensity and the contour of strips in areas 3200-3600 of cm-1 and 1100 cm-1 demonstrating that new communications of C-OC are formed changes and IT is groups. There is more intensive strip in the field of 910-920 cm-1, characteristic of deformation fluctuations of H-C = C-N group (figure 7).

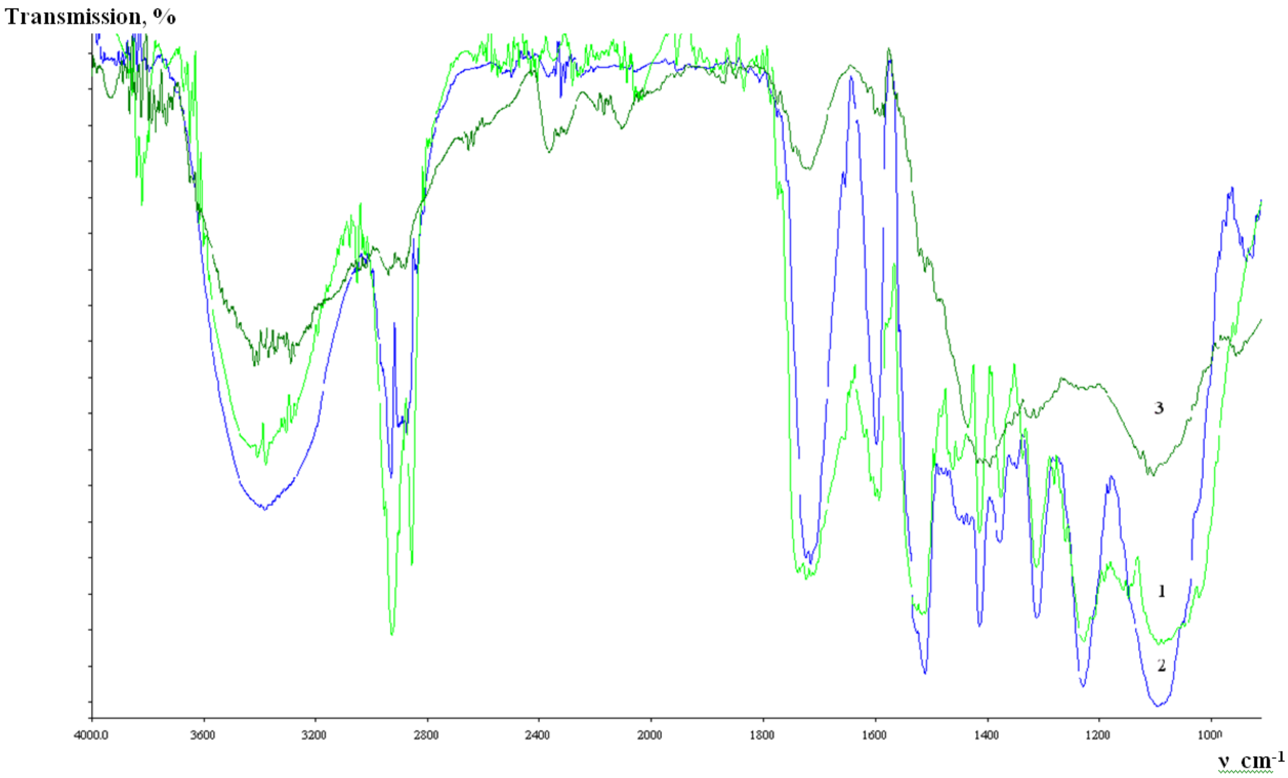


Figure. 7. IR spectrums of initial FPU (1), FPU after 606 h UV-radiation (2), FPU sample after reaction of oxidation at 230 °C (3)

In the spectrum of products of thermo oxidizing destruction the strips characteristic of formation of carbon structures in areas 1400 of cm-1 and 1100 cm-1 appear. The strips of 1720 cm-1 and 1590 cm-1 characteristic for the urethane groups, become less intensive that demonstrates their reduction and intensive release of nitrogen from samples, the strip in the field of 910-920 cm-1, characteristic of double communications (figure 7) is also observed [26].

The obtained data correspond with the results of the researches, presented in the review [23] where it is specified that an initial stage of destruction of polyurethane is the rupture of the weakest communication of C-NH. In ranges of products of thermo oxidizing destruction the strip in the field of 1510 cm-1 is practically not shown in difference from initial FPU. The destruction mechanism presented in the review is described by four types of reaction (figure 8).

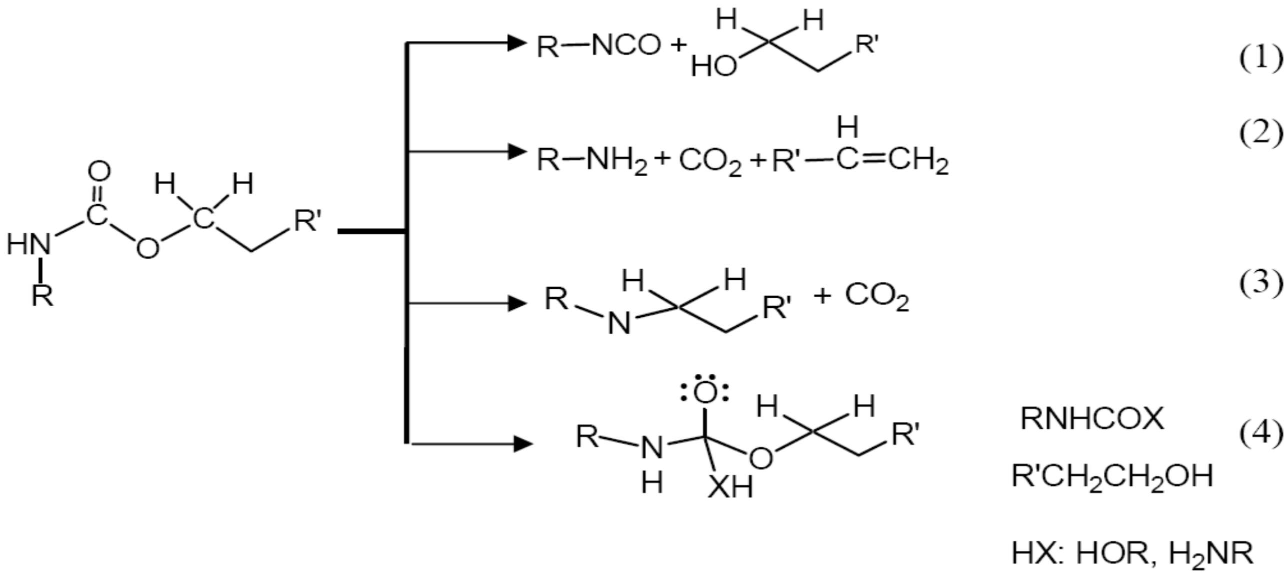


Figure. 8. Mechanism of the urethane segment destruction

Thus, at a temperature of thermo oxidizing destruction of 230 °C most likely course of process of destruction of FPU on the basis of simple polyether and the aromatic diizotsionat on the 1 and 2 mechanism of reaction (figure 8).

The conducted researches have revealed need isolation of FPU from action of UF of radiation in the course of installation by special polishing pastes.

For determination of coefficient of sound absorption have selected 3 samples of each type of thermo panels. For all studied thermo panels change of coefficient of sound absorption from 0,2 to 0,8 in the frequency range from 600 to 1600 Hz is observed.

Defined heat conductivity of a layer of FPU 20 mm thick with a density of 60 kg/m3 in accordance with State Standard 7076-99 [17] which has made 0,035±0,005 W / (m*0s) that corresponds to average values of front thermo panels [5-9].

IV. CONCLUSION

The analysis of experimental data has revealed satisfactory consumer properties of the studied thermo panels: compliance of clinker to the DIN EN 121 standard; lack of visual defects and change of color of thermo panels after 50 cycles of freezing – thawing; absence change of color of thermo panels after influence of UV of radiation with the wavelength of 240-320 nanometers within 607 hours 30 minutes; high values of coefficients of sound absorption in the frequency range from 600 to 1600 Hz; low heat conductivity of a layer of FPU.

The conducted researches have shown that process of thermal destruction of FPU proceeds in three stages. At the first stage there is a destruction of a rigid segment to formation of isocyanate, alcohol, olefin, and for FPU as a result of UV-radiation the speed of the first stage is twice higher and the beginning of thermal destruction decreases from 150 °C to 30 °C in comparison with a standard sample of FPU.

The received results will be coordinated with data of IR-spectroscopy. An initial stage of destruction of FPU as a result of UV-radiation is the rupture of the weakest connection of S-NH with formation of alcohols, air and olefins.

The DSC method has determined the values of induction time of oxidation allowing to predict terms of operation of products from polyurethane foam. So, after 550 hours of UV-radiation that makes 27 years of operation, material destruction already begins practically at the room temperature. The possible mechanism of course of thermo oxidizing destruction of FPU is confirmed.

Taking into account that the received figures are recommended for using front thermo panels in civil engineering as the effective protecting constructions. Thermo panels have high heat-insulating properties, light resistance, frost resistance, low water absorption of a facing layer, attractive appearance.

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