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Improving the operational reliability of membranes and bellows with fluorinated surfactants

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Abstract. One of the characteristic properties of organofluorine compounds is their low surface energy. In this regard, surfactants containing perfluoroalkyl groups, as a rule, are much more effective than their non-fluorinated analogues. The unique character of fluorinated surfactants is also determined by their pronounced oleophobic properties. Surfaces treated with fluorinated surfactants are not only water-repellent, as in the case of their hydrocarbon analogues, but also benzo- and oil-repellent. Fluorotensides are highly resistant to oxidants and aggressive substances (acids, alkalis, chlorine, etc.). They also have high temperature resistance, withstand oxygen shock, have a solidification temperature of up to -160 °C, do not change properties at a dose rate of up to 10^8 rad. The applications of surfactants are extremely diverse. One of the methods of increasing the wear resistance of friction pairs is the method of surface treatment of friction pairs with fluorotensides. Fluorotensides are multicomponent systems that include organofluorine surfactants in various solvents and regulatory additives. In Russia, brands of fluorotensides have been created that surpass foreign samples in many respects, which has significantly expanded the scope of their application.

1 Introduction

The condition for providing production with modern technology is the possession of the latest high-tech technologies, including those based on new physical and chemical-technical effects, and their combinations. Therefore, the ability to create them is relevant, while ensuring the conditions for their implementation in the industry of their country. Borrowing new scientific ideas and buying the latest technology is not always an alternative solution. The prospects of new technological directions are assessed taking into account the suitability of their use in various production areas, as well as the ability and ability to influence the progress of the industry. The most promising direction for obtaining the specified strength

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properties of existing alloys and for creating new high-strength alloys is the combination of several structural hardening mechanisms. The condition for providing production with modern technology is the possession of the latest high-tech technologies, including those based on new physical and chemical-technical effects, and their combinations. Therefore, the ability to create them is relevant, while ensuring the conditions for their implementation in the industry of their country. Borrowing new scientific ideas and buying the latest technology is not always an alternative solution.

Currently, in many countries of the world (Germany, Japan, China, Australia, England, USA), the task is to develop alternative fuels, which can be used as cryogenic fuels – liquefied methane, liquefied natural gas (LNG), consisting mainly of methane, and in the future liquid hydrogen (LH). In order to expand the scope of application and increase the efficiency of use, it is necessary to create technologies for the production, transportation and storage of such fuels, ensuring minimal product losses in all links of the producer-consumer chain. Natural gas fields are usually located far from the main consumers, so a significant part of the gas is still transported through main gas pipelines. Meanwhile, this method of gas supply is not always economically feasible. In some cases, it is more profitable to liquefy gas, transport it in this form by land or water transport to distribution points, where it is stored and, if necessary, gasified and supplied to the consumer in compressed form (pumped into cylinders at a pressure of 20-30 MPa) or at a small overpressure through local gas pipelines. Some researchers have focused on increasing the efficiency of LNG gasification processes, for example, by using various heat transfer fluids or improving the design of heat exchangers [1, 2]. Others have investigated the safety aspects of LNG storage and gasification, such as preventing overpressure in storage tanks and minimizing the risk of leaks or explosions [3, 4]. Overall, the development of LNG gasification technology is a complex and interdisciplinary field that requires collaboration between researchers, engineers, and industry professionals. By addressing the various challenges and tasks associated with LNG gasification, we can ensure the efficient and safe use of this important energy carrier in the future [5, 6]. Thus, along with the tasks of obtaining LNG, there is a need for its gasification. Liquefied natural gas based on methane is a cryogenic liquid and during its gasification it becomes necessary to solve a number of tasks: the choice and justification of the gasification method; development of gasifier heat exchangers, storage tanks and other cryogenic equipment; provision of long-term and drainage-free LNG storage, creation of a control system and safe operation of the cryogenic complex, disposal of excess vapor phase [7-9], in [10] a scheme of an automatic control system for gasification and cryofuel supply to the engine is proposed, in [11,12] the problems of creating an infrastructure scheme are studied the use of LNG and the basics of designing equipment for cryogenic raw materials.

2 Relevance

When analyzing the behavior of materials under load in accordance with modern concepts, it is necessary to consider, along with the macro and meso levels, also the nanoscale structural level of plastic deformation. In this case, the main mechanism of plastic deformation is local structural transformations (by the type of rearrangement of atomic clusters of various configurations) occurring in local zones of tensile normal stresses. Clusters are special metal structures — these are particles containing from 2 to 105 atoms connected to each other with a size from 0.5 to 100 nm. The use of LNG as a motor fuel for various types of vehicles (automobile, air, railway, water, etc.) provides energy and environmental advantages, as well as is more economically advantageous compared to traditional petroleum and other alternative types of motor fuels. The prospects of using LNG as an alternative motor fuel for motor transport have become obvious for most countries of the world. This trend in automotive technology is developing especially intensively in the USA. For example, the mayor of A decision has been made in New York to transfer all municipal transport to LNG in the near future. The production of LNG-powered mainline tractors is expanding. Thus, the company “Mack” Waste Managemtnt Inc. has been successfully engaged in the production of LNG engines for 20 years. The Mack CN/LNG truck tractor, powered by LNG, is the cleanest truck on American roads and has a large power reserve, which is over 1000 km. The situation is similar in Western Europe. Municipal transport is planned to be switched to LNG in many German cities. Italy has adopted an environmental program for the use of LNG in motor transport. The use of LNG in water transport is also expanding. Statoil has started mass production of LNG vessels in Norway. The first two vessels will be launched in 2003. The advantages of LNG compared to conventional bunker fuel from an environmental point of view are obvious: using it on only two ships during the year reduces emissions of nitrogen oxides to 420 tons. The Statoil initiative is actively supported by the Norwegian Minister of Oil and Energy, who considers it the beginning of a full-scale transition of ships to LNG. Experimental LNG vessels have been built and operated in the USA, Germany and a number of other countries around the world. The use of liquefied natural gas in railway transport is also expanding abroad. The long-term trouble-free operation of mainline and shunting diesel locomotives on LNG by the Burlington Northern, Morrison-Knudsen, Santa Fe, and Union Pacific railway companies speak about the objective advantages of this type of fuel. In the recent past, significant momentum has been given to developments in the field of production, storage and use of LNG by vehicles, due to a number of advantages of LNG over compressed natural gas (CNG). Such advantages include the fact that the LNG in the tank of the vehicle is at atmospheric pressure, unlike CNG, which requires high-strength cylinders, which are potentially dangerous objects; LNG provides higher explosion and fire safety, the density of LNG, compared with CNG, is higher, this entails an increase in the specific gravity of the transported fuel, and therefore the range of the vehicle.

3 Materials and methods

Fluorinated surfactants (fluoro-surfactants), fluorotensides, have become of great importance. Their use in electrochroming of various parts saves up to 30% chromium and significantly improves working conditions; foaming compounds of fluorinated surfactants are a radical means of fighting fires. Adding thousandths of a percent of fluorinated surfactants to gasoline slows its evaporation from the surface by 30*40%. Their application of fabrics made it possible to create oil-repellent workwear for workers in the oil and chemical industries.

The use of fluorotensides makes it possible to increase the wear resistance of mated parts and, as a result, improve the dynamics of machines, machine tools, industrial robots, various technological equipment, as well as cutting and other technological tools.

The following are the main advantages of fluorotenside treated surfaces:

- the surface energy of the material decreases sharply (approximately in 1 000 - 10 000 times; for metals: with 3 000 - 5 000 mN/m to 2-4 mN/m), this leads that the wear resistance of the mated parts increases. The coefficient of friction is reduced by about 10 times, and the moment of starting at rest is 10,000 times compared to untreated surfaces;
- retention of lubricant in the friction zone. It occurs due to the creation of a boundary layer that reduces the influence of the surface energy of a solid. This property determines the constant presence of a lubricating and cooling medium in the contact zone (friction), which, in turn, helps to increase the wear resistance of parts and cutting tools. The oil retention strength on the treated surface is about 30 times greater than that of the untreated surface;

- anti-adhesive properties. Fluorotenside films protect surfaces from contact interaction at the molecular level;
- antifriction properties. They appear both due to the retention of the lubricating medium and due to the formation of a coating with a low coefficient of friction;
- -prevention of micro-destruction of the contacting surfaces during the friction process. It is explained by the fact that during treatment with fluorotensides, micropores, microcracks, binding of atomic hydrogen and oxygen occur, contributing to embrittlement of the surface layer of the metal. Thus, micropores and microcracks are localized from the potential tendency to concentrate stress and be centers of destruction;
- reducing the gas permeability of materials. Fluorotensides, which have a high penetrating ability, fill all micropores, microcapillaries and microcracks, thereby reducing the gas permeability of the material.

As a result, its aging is prevented, the catalytic effect of metals on lubricants is reduced, their destruction and polymerization are prevented:

- surfactant films are resistant to low and high temperatures (they do not change their operating characteristics in the temperature range from -200° From up to +450°C and therefore can be used in space products), to pressure (specific load up to 3000 mN/mm^2), exposure to chemicals and radiation. The applied coating can only be removed from the surface by mechanical treatment.

Due to the above properties, when processing machine parts, machine tools and other technological equipment with fluorotensides, their service life, the positioning accuracy of actuators are increased, the purity of the surface treatment of parts using cutting, pressing and exhaust tools is increased, the wear resistance of the cutting tool, wear resistance and sealing ability of rubber sealing elements in movable joints, etc. are improved.

Fatigue destruction of the surface layer of the material under repeated action of the load leads to the nucleation and development of microcracks inside strongly deformed layers of the SC. In the case of multilayer SC, the presence of two types of fatigue wear is noted:

- the development of microscopic cracks from the surface of the SC, most often as a result of the Rebinder effect;
- the development of fretting wear between the layers of SC, associated with the presence of fretting friction between them.

In order to prevent the development of cracks in metal SC, it is important to closely monitor the material for any signs of microscopic defects and address them early on. This can be done through regular inspections and maintenance of the material, as well as ensuring that it is not subjected to excessive stress or strain. Additionally, using high-quality materials and proper fabrication techniques can also help reduce the risk of crack development in metal SC.

During the third stage, the crack continues to propagate and eventually leads to complete mechanical destruction of the SC layer. This results in leakage of the sealed medium and can cause catastrophic failure of the system. It is important to monitor the condition of SC layers and detect any signs of crack development early in order to prevent this stage from occurring. Proper maintenance and inspection procedures can help prolong the lifespan of the IC system and prevent costly repairs or replacements [3, 11].

The VR rate is influenced by various factors, including the material properties, loading conditions, and environmental factors. For example, higher loading frequencies and amplitudes can increase the VR rate due to increased stress levels. Additionally, environmental factors such as temperature and humidity can also affect the VR rate by influencing the material properties and the rate of crack propagation.

Understanding the VR rate is crucial in predicting the durability and reliability of multilayer SC structures. By studying and controlling the factors that influence the VR rate, we can improve the design and performance of these structures and ensure their longevity in service [3, 9]. This is a complex process that includes: fretting, friction, fatigue and much more.

The phenomenon of fretting can significantly reduce the benefit from the use of multilayer SC, while the efficiency of the SC is largely determined by the parameter γ = VF / VR, which characterizes the ratio of the cyclic rate of fretting wear to the cyclic rate of microcrack development. In addition to the parameter γ, it is convenient to use the coefficient $\beta = \gamma/(1+ \gamma)$. Using the above logic of the development of the SD process in the SC, we will build a mathematical model that corresponds to the functioning of the SC until the moment of failure; that is, for cyclic TR of the SC.

Unfortunately, Figure 1 is not provided in the text. For further understanding, it is suggested to refer to the original source or document to view the schematic diagram of the M-layer IC device.

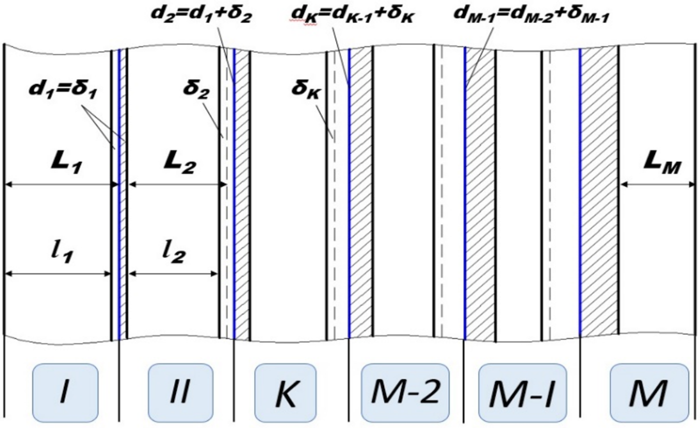

Fig. 1. Geometric and physical parameters of a multilayer bellows.

We introduce: l_K – the depth of growth of the microcrack in layer k during its complete germination over the entire thickness of the layer; δ_K – the amount by which the sublayer fretting wear has grown during the growth of the microcrack inside the k-th layer of the SC; $\underline{d_K}$ – the total thickness of the sublayer fretting wear at the k-th boundary of the SC at the time of loss of tightness by layer k. Additionally, we introduce the total value L_K of microcracks and fretting wear formed inside the k layer after the previous SC layer lost its tightness. It is calculated by the formula:

$$L_K = l_K + \delta_K. \qquad (1)$$

The above scenario of the development of the SD process in the UK leads us to a set of recurrent formulas for all layers of the UK, which determine the functioning of the UK until the moment of failure:

Layer (1):

$$\delta_1 = D\,\beta;\;\; l_1 = D/(1+\gamma);\; L_1 = D;\; d_1 = \delta_1. \qquad (2)$$

Inner layer (k), k = 2, . . . M-1:

$$L_K = D - 2{\cdot}d_{K-1};\; \delta_K = \beta{\cdot}L_K;\; l_K = L_K/(1+\gamma);\;\;\; d_K = d_{K-1}+\delta_K. \qquad (3)$$

Layer (M):

$$L_M = l_M = D - d_{M-1}. \qquad (4)$$

The resulting set of formulas (2) - (4) allows us to establish the dependence of the functioning of the IC on the technological and design parameters of the IC.

Practically, to characterize the functioning of the SC, the cyclic TR SC N (cycle) is used, which is the sum of N00 and the total (for all layers) value of the fatigue crack L_R:

$$N = N_{00} + L_R / V_R.;\ L_R = \sum_{K=1}^{M} l_K \qquad (5)$$

To assess the effectiveness of the functioning of the SC, it is convenient to use the K coefficient, which shows how much of the total thickness of the SC is used for the growth of microcracks. Taking into account these considerations, the formulas for TR SC can be written in the form:

$$N = N_{00} + M\,D\,K(\gamma, M) / V_R.\ ; \qquad K(\gamma, M) = L_R / (M\,D); \qquad (6)$$

The V_R velocity and the γ parameter can be determined experimentally (from appropriate tests) for different SC designs, as well as for different SC operating modes.

Figure 2 shows the dependences of the efficiency coefficient K on the parameter $\gamma = (VF / VR)$ and on the M - number of layers of SC

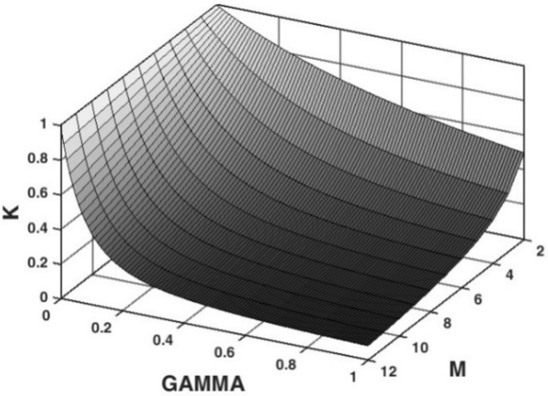

Fig. 2. The dependence of the efficiency coefficient K on the parameter γ for SC with a different number of layers (M).

When analyzing these dependencies, it was found that in order to increase the strength of SC (its cyclic TP), it is necessary to develop manufacturing technologies for SC that provide values of γ in the range $0 < \gamma < 0.1$. Thus, the main process of fatigue wear of SC will be the process of growth of microscopic cracks, and fretting wear between layers of SC will have a slight effect on SC.

4 Results and discussion

The general physical and mathematical model (5), (6) is applicable to all existing manufacturing technologies of SC. So, for the usual manufacturing technology of SC, the cyclic TR of SC, which we denote by N1, will be described by the formulas:

$$N_1 = M\,D\,K(\gamma_1\,, M) / V_R. \qquad (7)$$

Here, the parameter y_1 corresponds to the fretting wear rates obtained as a result of the use of conventional manufacturing technology and traditional ones. materials used for the UK. According to the results of the conducted tests of SC [8], it can be estimated that the parameter y_1 is in the range $0.35 \leq y1 \leq 0.45$. That is, such a technology is not very effective for TR SC.

The technology of modification of fluorine surfactants on the surfaces of all layers of SC does not change its strength properties, but can increase the TP and durability of SC several times [8]. To describe the functioning of such SCS, the previous scenario of the development of SD and fretting wear should be supplemented by the following two factors. Due to their properties [6,7], FOK nanocoating can lead to a decrease in fretting friction (fretting wear rate - V_{2F}) between the inner layers of the SC shell. In the mathematical model, this can be taken into account by replacing the parameter γ with $\gamma_2 = V_{2F} / V_R$. Obviously, $0 \leq \gamma_2 \leq \gamma$. The experiments and tests carried out confirm that when applying the FOC "WET" to the SC, the rate of fretting wear can decrease several times (depending on the design of the SC and the parameters of the loading of the SC) [8].

In addition, at the boundary of the SC with the liquid, the surfactant layer is a multilayer structure (with a number of layers from five to 20-30 layers) [3, 6]. As a result, we have a protective surfactant layer that prevents the Rebinder effect for two reasons. The multilayer surfactant coating protects the surface of the SC from the Rebinder effect until it loses its continuity. The size of the surfactant molecule is significantly larger than the size of water molecules (ten times or more), which also delays the onset of the Rebinder effect. These factors lead to an additional cyclic operating time of N_{00}, corresponding to the first stage of the development of microcracks at the SC–liquid boundary.

During the first stage, the process of fretting wear between the layers of the SC shell exists. This leads to a decrease in the thickness of each inner layer of the SC by an amount ($2\ \delta_{00}$); and the thickness of the first and last layers of the SC decreases by an amount of δ_{00}. Therefore, the expression for L_R takes the following form:

$$L_R = M\,(D - 2\,\delta_{00})\,K(\gamma_2, M) + 2\,\delta_{00}\ ; \quad \delta_{00} = N_{00}\,V_{2F} = \gamma_2\,N_{00}\,V_R\ ; \tag{8}$$

Taking into account formula (5), the cyclic TR of the SC, which is denoted by N_2, for this technology is described by the expression:

$$N_2 = N_{00} + [\,M\,(D - 2\,\delta_{00})\,K(\gamma_2, M) + 2\,\delta_{00}\,] / V_R; \tag{9}$$

Formula (10) can be converted to a form from which the advantages of modification technology over conventional technology are obvious:

$$N_2 = N_1\,K(\gamma_2, M) / K(\gamma_1, M) + N_{00}\,[1 + 2\,\gamma_2\,(1 - M\,K(\gamma_2, M))] \tag{10}$$

Since the available surfactant nanolayer can reduce the fretting friction between the layers of the SC, therefore the ratio $K(y_2, M) / K(y_1, M) \geq 1$. For example, according to the test results [5], the parameter y_2 can be estimated in the range $0.035 \leq y_2 \leq 0.05$. Thus, when using the SC modification technology, the cyclic TR of the SC can be increased significantly due to a decrease in fretting friction.

The second factor in increasing the TR of the SC is the formation of a protective layer at the boundary between the SC and the liquid, which can lead to large values of the N_{00} value. In the tests carried out, this value was comparable to the SC TR performed using conventional technology.

Sometimes a simplified UK modification technology is used. It consists in the fact that surfactants are treated only on one surface of the SC, which borders on the liquid. The cyclic TP for this technology, designated by us as N_3, is described by formulas similar to (9) - (10):

$$N_3 = N_{00} + [\,M\,(D - 2\,\delta_{00})\,K(\gamma_1, M) + 2\,\delta_{00}\,] / V_R\ ; \quad \delta_{00} = N_{00}\,V_{1F} = \gamma_1\,N_{00}\,V_R\ . \tag{11}$$

$$N_3 = N_1 + N_{00}\,[1 + 2\,\gamma_1\,(1 - M\,K(\gamma_1, M))]; \tag{12}$$

The difference between this option and conventional technology is that a protective layer is added at the liquid boundary, which leads to an additional cyclic operating time of N_{00}, the same value as in the full modification technology. With the cheapness and simplicity of the simplified technology, it can give an increase in TP comparable to N_1.

Let's estimate the contribution of the protective layer (additional operating time N_{00}) to the overall balance of TR SC. From (10), (12) it follows that N_{00} is included in the balance of TR SC with an influence coefficient $F(\gamma, M)$:

$$F(\gamma, M) = 1 + 2\,\gamma_1\,(1 - M\,K(\gamma, M)). \tag{13}$$

Figure 3 shows the dependence of this coefficient F(γ, M) on the parameter γ for SC with a different number of layers (M).

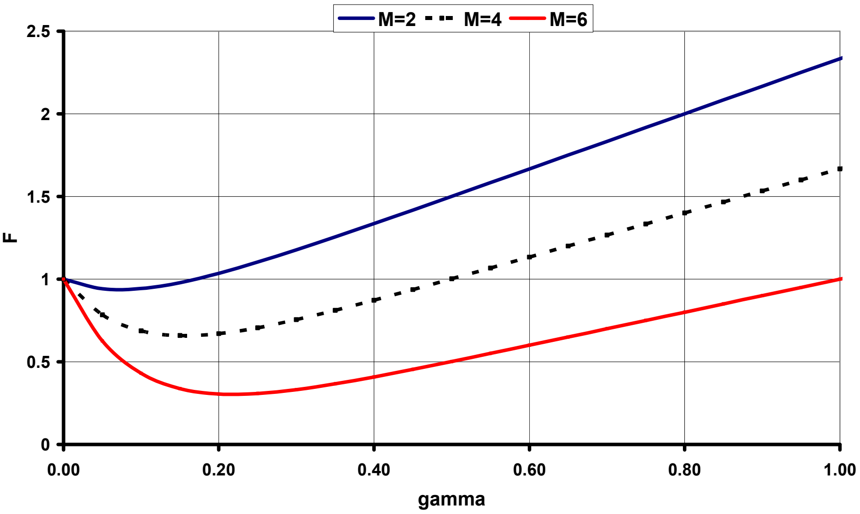

Fig. 3. Dependence of the function F(γ, M) on the parameter γ . The graphs correspond to the SC with a different number of layers: M = 2, 4, 6.

The contribution of the protective layer is greatest at small values of the parameter *γ*. At very large parameters γ, the contribution of N_{00} becomes large again, but at the same time the contribution of UR to TR SC is greatly reduced. Chemisorption, unlike physical adsorption, is selective; it proceeds with great intensity in places of violation of the regularity of the crystal lattice. In many cases, physical and chemical adsorption occur simultaneously, but one of them is predominant. Thus, the adsorption of fatty acids on metal surfaces at normal temperature is mainly physical, and at elevated temperatures - chemical. The forces of interaction between fluoropolymer molecules and a metal substrate are different in nature and depend on both the nature of the substances and the metal. Molecules with an active carboxyl group have the strongest bond. The existence of the adsorbed layer is determined by temperature.

5 Conclusion

When developing and studying a physical and mathematical model, as well as its use for existing technologies for obtaining SC, the following conclusions can be drawn:

1. It is desirable to have SC manufacturing technologies that provide small values of the parameter γ in the range 0 < γ < 0.1. For this, it is necessary to develop SC manufacturing technologies in which fretting wear can be reduced several times. One of these technologies is the modification of the surfaces of the SC layers by surfactants based on fluorine organic compositions, for example, "MOKOM".
2. The rate of growth of microscopic cracks in the SC is mainly due to the Rebinder effect, depending on the type of liquid and the material of the SC. In this regard, one of the promising directions for increasing the TR of the SC is the creation of an effective "protective" layer between the liquid and the surface of the SC material in contact with it. This effect is realized in a simplified and complete modification technology for the manufacture of SK. To maximize the TR of the SC, when designing and choosing a multilayer SC, the thickness of the material and the choice of the number of layers of the SC should be optimized.

3. The adsorbed fluoropolymer layer is monomolecular. Artificially, a polymolecular film can be formed in which each layer will consist of identically oriented molecules. The active ends of the first row are attached to the metal, the tails of the molecules of the second row are attached to their tails, and the ends of the third row are attached to their active ends, etc. In this way, films in tens and hundreds of molecular layers are obtained.

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