

Novel inventions of academician Oleg Figovsky A. Leykin, INRC. “Polymate”, Israel

Professor Oleg Figovsky is a leading world scientist in the field of novel materials technologies, member of European Academy, foreign member of two Russian academies (RAACN & REA) and founder, Director R&D of Israeli Research Centre Polymate was established in 1997 and since has developed many advanced and novel environmentally friendly superior polymer and composite materials and technologies, specialized in environmental engineering and nano-technologies. Now prof. O. Figovsky is also Director R&D of two US companies: Nanotech Industries, Inc. □ Hybrid Coatings Technologies, Inc. (Daly City, CA).

The main areas of researches of company “Polymate” and its employees are corrosion resistant polymer, silicate and hybrid coverings for various substrates as well as new binders for the concretes operating in adverse environments. The special attention is given the use of renewable raw material and environmentally friendly technologies particularly nonisocyanate polyurethane systems. Search of the new organic-modified silicates is conducted in the field of inorganic coatings. Development of the advanced binders for concrete are conducted mainly with the use of liquid rubbers and new silicone additives. A new direction in the creation of coatings and binders is a hybrid nano-structured composition.

Main inventions made by employees of “Polymate” were devoted to polymeric materials for coatings based on hybrid nonisocyanate urethane-epoxides. A promising method was introduced in the form of a nonisocyanate urethane-epoxy polymer network with lower permeability and increased chemical resistance properties to non-polar substances. Moreover, hybrid nonisocyanate networks are made by a synthesis process that uses far more environmentally benign materials than isocyanates and phosgene.

US patent issued to O. Figovsky [1] relates to a hybrid nonisocyanate polyurethane network polymer formed by cross-linking at least one cyclocarbonate oligomer and at least one amine oligomer. The cyclocarbonate oligomer contains a plurality of terminal cyclocarbonate groups. At least one cyclocarbonate oligomer further comprises from about 4% to about 12% by weight of terminal epoxy groups. Because at least one cyclocarbonate oligomer contains both cyclocarbonate and epoxy reactive groups, the network formed therefrom is referred to as a hybrid nonisocyanate polyurethane network. The cyclocarbonate oligomer or oligomers have an average functionality towards primary amines of from about 2.0 to about 5.44. The amine oligomer comprises at least one primary amine-terminated oligomer terminated with primary amine groups and has an average functionality towards cyclocarbonate groups of from about 3.0 to about 3.8. The amine oligomer is present in an amount from about 0.93 to about 0.99 of the amount of the amine oligomer that would be required to achieve a stoichiometric ratio between the primary amine groups of the amine oligomer and the cyclocarbonate groups of the cyclocarbonate oligomer. The hybrid nonisocyanate polyurethane network polymer formed has a gel fraction of not less than about 0.96 by weight. These materials, in particular, are useful as nonporous monolithic coatings, coverings and linings, which can be used for the corrosion protection and wear protection of concrete, metallic and wood surfaces.

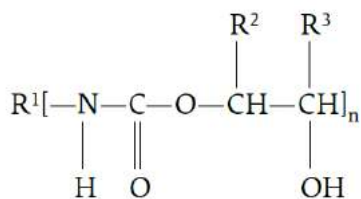
In US patent [2] chemically resistant materials with high mechanical properties was provided by using polycyclocarbonates of special structure. The polycyclocarbonates were prepared by the reaction of oligocyclocarbonates containing ended epoxy groups with primary aromatic diamines. Such oligomers may be used by two ways – by curing the oligomers with primary aliphatic amines and by preparing adducts which are used for curing epoxy resins or cyclocarbonate oligomers for preparing chemically resistant coatings, constructive glues, sealants, etc.

US patent [3] describes a foamable photo-polymerized acrylic composition for use in variety of indoor or outdoor sealing and coating applications, where it is required to seal, to fill or to repair cracks, joints, gaps etc. in concrete, masonry, stone, wood or other constructional materials. The composition comprises acrylic based reactionable oligomers and it can be foamed and then polymerized while producing foam with structure suitable for sealing. Said acrylic composition was received with use of a product of reaction of nonisocyanate urethane diol with metacrylic or acrylic anhydride.

US patent [4] relates to a method and apparatus for the synthesis of oligomeric cyclocarbonates from epoxy compounds and carbon dioxide in the presence of a catalyst. Also patent describes star epoxy compounds and their preparation and use in making star cyclocarbonates, star hydroxy urethane oligomers, and star NIPU and HNIPU, acrylic epoxy compounds, acrylic cyclocarbonates, acrylic hydroxy urethane oligomers, and acrylic NIPU and HNIPU and their methods of preparation. Coating on the base of these highly functionalized star compounds posses lower permeability and increased chemical resistance properties to aqueous solutions of acids and alkalis.

US patent [5] discloses a nanostructured hybrid liquid oligomer composition including at least one epoxy-functional component (A), at least one cyclic carbonate component (B), at least one amine-functional component (C), and, optionally, at least one acrylate (methacrylate) functional component (D), wherein at least one epoxy, amine, or acrylate (methacrylate) component contains alkoxy silane units. The composition is highly curable at low temperatures (approximately 10 to 30° C.) with the formation of nanostructure under the influence of atmospheric moisture and the formation of active, specific hydroxyl groups by reaction of cyclic carbonates with amine functionalities. According to the invention, the cured compositions, particularly coatings, have excellent resistance to weathering, solvents and abrasion, good appearance, strength-stress properties and adhesion to a variety of substrates.

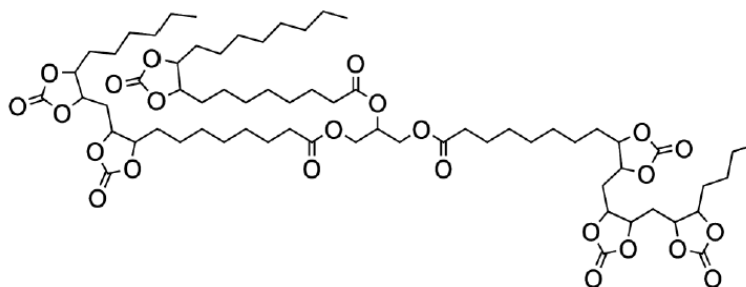
US patent [6] describes a novel epoxy-amine composition modified with hydroxyalkyl urethane, which is obtained as a result of a reaction between a primary amine and a monocyclocarbonate, wherein modifier is represented by the formula:



wherein **R₁** is a residue of the primary amine, **R₂** and **R₃** are the same or different and are selected from the group consisting of **H**, alkyl, hydroxyalkyl, and **n** satisfies the following condition: $n \geq 2$. Diluents, pigments and additives can be used. Doping with the hydroxyalkyl-urethane modifier imparts to the cured composition superior coating performance characteristics, such as pot-life/drying, strength-stress, bonding, appearance, resistance to abrasion and solvents, etc. Modifier does not form covalent chemical bonds with the major components of the reaction mixture and does not cause unwanted distortion when forming nanostructure of cured polymer. As a result, the cured materials, such as coatings, adhesives, foams have a well-balanced set of properties.

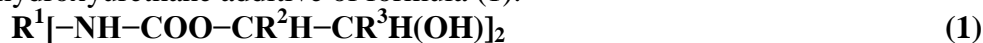
US patent [7] proposes a method of producing hybrid polyhydroxyurethane network on a base of carbonated-epoxidized unsaturated fatty acid triglycerides. The method comprises: (a) reacting epoxidized unsaturated fatty acid triglycerides with carbon dioxide in the presence of a catalyst to obtain carbonated-epoxidized unsaturated fatty acid triglycerides, wherein conversion of oxyrane groups to 2-oxo-1,3-dioxolane groups

(cyclic carbonate groups) for said carbonated-epoxidized unsaturated fatty acid triglycerides ranges from 35% to 85%; (b) mixing and reacting the carbonated-epoxidized unsaturated fatty acid triglycerides with a compound having amine functionality comprising at least one primary amine group realized at stoichiometric or within nearly balanced stoichiometry; (c) mixing and reacting the product of step (b) with a compound having amine functionality comprising at least two primary amine groups realized at excess of an amine-functional compound; (d) subsequently mixing the product of step (c) with a compound having amino-reactive groups.



US patent [8] related to a radiation-curable composition comprising (meth)acrylic monomers and/or oligomers, photoinitiators, and a nonreactive non-isocyanate urethane composite additive, wherein the nonreactive composite additive comprises

a) a biobased hydroxyurethane additive of formula (1):



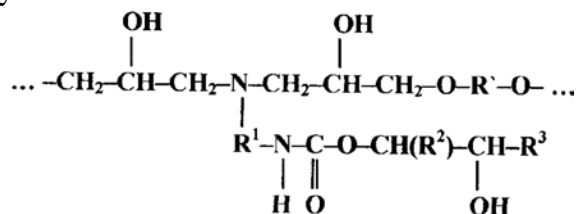
wherein \mathbf{R}^1 is a residue of the biobased primary diamine, and \mathbf{R}^2 and \mathbf{R}^3 are the same or different and are selected from the group consisting of \mathbf{H} , alkyl, and hydroxyalkyl; and

b) a silane-based hydroxyurethane additive of formula (2):



wherein \mathbf{R}^2 and \mathbf{R}^3 are the same as stated above, \mathbf{R}^4 is generally an aliphatic group having from 1 to 6 carbon atoms, \mathbf{R}^5 and \mathbf{R}^6 , independently, are hydrocarbon radicals containing from 1 to 20 carbon atoms and selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups or combinations thereof, and n is equal to 1, 2, or 3.

The newest invention [9] describes a linear hybrid epoxy-amine hydroxyurethane-grafted polymer with the following structure of the polymer backbone unit:



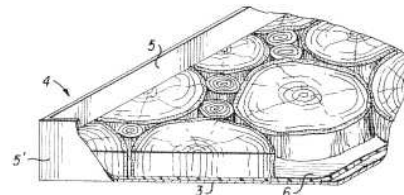
where R' is a residue of a diglycidyl ether (epoxy resin); R^1 is a residue of a di-primary amine; R^2 and R^3 are residues of monocyclic carbonate and are selected from the group consisting of H , alkyl $\text{C}_1\text{-C}_2$, and hydroxymethyl; and at least one of R^2 and R^3 is hydrogen. The described polymer may be used in manufacturing of synthetic leather materials.

Of special interest are inventions that relate to methods to manufacture a biodegradable compositions containing nano-particles of cellulose for forming a protective coating on natural materials. Composite cellulose containing materials which are waterproof and biodegradable are produced which consist essentially of cellulose and hydrophobic polymer-based composition in the amount about 4 to 40 wt % [10].

The polymer-based composition comprises first polymer, which is partially saponified polyvinyl acetate, second polymer, which functions as plasticizer for improving elasticity of the first polymer and cross-linking agent, which is capable to cross-link the first polymer. The polymer-based composition may additionally contain environmentally friendly hydrophobizators, fillers and pigments.

It is an object of the invention [11] to provide a composition for forming a protective coating layer on a biodegradable natural material that imparts to the material improved waterproofing and grease-resistant properties. It is another object to provide a composition to form a protective coating on natural biodegradable materials based on the use of nano-cellulose particles and that protects these materials from swelling, warping, and mechanical damage during contact with water, other aqueous liquids, or grease.

A method of manufacturing tiles from waste wood uses round crosscut wood slices, a binder, and filler was disclosed [12]. The slices, all generally of a thickness, are placed on the flat bottom of a die within side walls. Adhesive is applied to the slices and the die is filled with a mixture of the binder and the filler. The die contents are hot pressed to achieve the required tile thickness. The tile is ejected from the die and then maintained at room temperature for not more than 72 hours. The face side of the tile is ground and the dimensions of the tile are brought within the required tolerances.



An adhesive composition with improved corrosion resistance to copper, silver and other metals was proposed in patent [13]. The composition comprising mixture of a copolymer of butylacrylate and acrylonitrile (said co-polymer being a cross-linkable clathrate matrix resin) and a second resin, said second resin being an oligodieneurethane resin with the end oxymethyloxazolidone groups. The composition also comprise of inorganic filler chosen from the group consisting of oxides, nitrides, carbonates (in particular it is TiO_2) and of a cross-linking agent capable of cross-linking said co-polymer, said agent is a solution of a polyisocyanate, in particular it is a solution of triphenylmethane triisocyanate in dichloroethane, methylene chloride or ethyl acetate. The adhesive composition is used in electronic industry for securing various electrical radio and electronic components on a printed circuit board, a base plate, etc. as it is required during the manufacturing process. It is hardened at room temperature and has, besides corrosion resistance, improved adhering strength and thermal shock resistance.

Another direction of the Polymate's investigations are liquid rubber-based and polymer concrete compositions.

RU patent [14] discloses polymer concrete mix for chemically stable, highly strong building materials. Mixture comprises low molecular cisoligodiene, low molecular diene oligomer of mixed microstructure, sulfur, thiuram, pyrite cinders, zinc oxide, calcium oxide, quartz sand, crushed granite stone. New material has greater bending and tensile strength.

US patent [15] issued to O. Figovsky relates to a synthetic rubber-based composition comprising: a low molecular weight rubber selected from polybutadiene comprising from about 75% to about 92% cis-1,4 units, a copolymer comprising butadiene units and from about 27 wt % to about 45 wt % pentadiene units, and mixtures thereof, a high molecular weight rubber comprising isobutylene units and not more than about 6 wt % isoprene units, the high molecular weight rubber being present in an amount of about 0.5 parts to about 4 parts by weight based on the weight of low molecular weight rubber, sulfur, a vulcanization accelerator, and an active filler where the sulfur, the accelerator, and the active filler are each present in the form of a powder within a particular particle size range(s). Additionally, these compositions may be used to form

coatings and rubber concretes. The invention also relates to the methods of producing such compositions, coatings and rubber concretes.

RU patent [16] describes organic concrete blend for manufacturing chemically stable high-strength parts and structures of building materials with improved consumer's properties. Blend contains, lowmolecular polybutadiene, sulfur vulcanizing group (sulfur, thiuram, captax, zinc oxide, calcium oxide, diphenylguanidine, synthetic fatty acids), fly ash from heat-and-power stations, silica sand, and crushed granite. Due to such quantitative and qualitative selection of components, a possibility is enabled to prepare composite having advantages concerning workability as compared to known blends containing low-molecular diene oligomers, for instance hardening temperature is lowered from 125 to 90° C. Other characteristics of blend are on a level of those of known analogs.

US patent issued to O. Figovsky [17] discloses a synthetic-rubber-based composition that consists of a low-molecular-weight rubber selected from polybutadiene comprising about 75% to about 92% cis-1,4 units, sulfur, a vulcanization accelerator, and an active filler wherein the sulfur, accelerator, and active filler are each present in the form of powder having a particular particle size range. Additionally, the compositions comprise epoxy terminated low number-average molecular weight rubber comprising butadiene-acrylonitrile copolymer with not less than 3 epoxy terminal groups per molecule. These materials may be used to form protective coatings such as anticorrosive coatings or chemically resistant rubber concrete. The proposed liquid composition can be combined with various organic and inorganic fillers and has improved properties and decreased cost as compared to known compositions. The invention also relates to a method of preparing the proposed composition.

US Patent [18] relates to a polymer concrete composition, preferably for decorative and shock resistant building structures and goods includes a binder based of polyfunctional unsaturated compounds, namely acrylated/ methacrylated vegetable oil, preferably acrylated/methacrylated soybean oil in an amount of not less than 60 part by weight and at least one acrylated/methacrylated monomer and/or oligomer in an amount of not more than 40 part by weight, and an aggregate blend. The polymer concrete composition based on acrylated/methacrylated vegetable oil has high wear and shock resistance with low shrinkage and can be used for prefabricated building decorative structures and particularly in civil engineering.

One else direction of Polymate LTD.-INRC activity is organic-mineral coatings.

US Patent [19] describes a polymeric composition having self-extinguishing properties which is useful as both an adhesive and coating. The composition contains 9-45 weight percent of an organic polymeric component and 16-50 weight percent of quaternary ammonium silicate as a fire-retarding component. Fillers and hardening agents may also be a part of the self-extinguishing polymeric composition.

US Patent [20] discloses a composition for use as a conductive coating for applying to various substrates. The composition has a particulate conductive component and temperature resistant component. The temperature resistant component contains an organic-mineral compound. The molar ratio of the conductive component to the temperature resistant component is (15-45):1, and the temperature resistant component is an aqueous solution of quaternary ammonium silicate having a silicate modulus of at least 4 and containing organic radicals with at least four atoms of carbon.

RU patent [21] relates to the composition of a nanostructuring binder for composite construction materials based on liquid glass and nanostructuring additives used for making acid resistant concrete, putty and other compositions. The nanostructuring binder for composite construction materials contains liquid

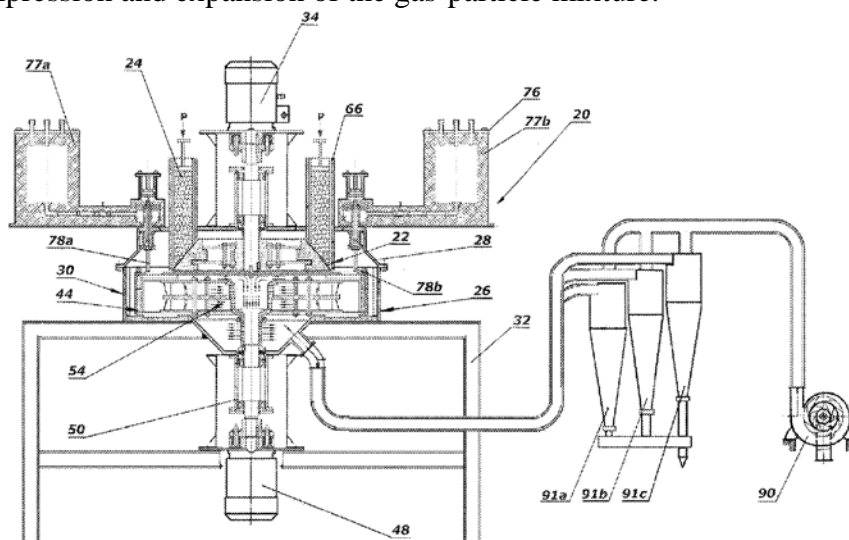
glass, tetrafurfuryl ester of orthosilicic acid and a hardener. A portion of the liquid glass is replaced with organic alkaline liquid glass containing an organic cation 1,8-Diazabicyclo[5.4.0]undec-7-ene or 1,5-Diazabicyclo[4.3.0]non-5-ene. Use of the nanostructuring binder enables to increase acid resistance, water resistance and strength of construction materials and widens their field of use.

Method of producing soluble silicates with organic cations at a given silicate modulus in the range of 1.5 to 20 was proposed [22]. The method consists of the reacting liquid suspension of a silica sol with the aqueous solution of a strong organic base. The silicate modulus is a molar ratio of $\text{SiO}_2:\text{M}_2\text{O}$, wherein M is an organic alkali cation. The aqueous solution of a strong organic base has a constant of base dissociation pK_b equal to or greater than 4. If necessary, the soluble silicates with organic cations are obtained in a powdered form by evaporating the solution of the soluble silicates under vacuum below 4.2 kPa and at a temperature in the range of 20 to 30°C and the product of evaporation are then dried by spraying.

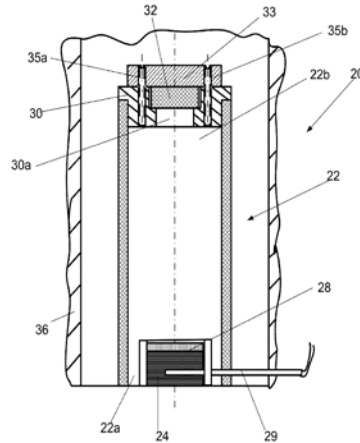
Some inventions relates to special fields of the nanotechnology.

Biologically active nanochip for treating seeds of agricultural plants in order to improve seed germination conditions and development of plants and for protecting plants from anticipated and averaged adverse conditions was proposed [23]. The biologically active nanochip contains a solid porous carrier, such as mineral, clay, turf, or polymer, the pores of which are intended for accommodating nanoparticles of biologically active substances that penetrate the pores when the substances are applied onto the nanochip surface, e.g., by spraying. Alternatively, the biologically active substances can be retained on the surface of the carrier by adhesion. The composition of the biologically active nanochips is selected with reference to anticipated and averaged adverse conditions. Also proposed is a method for application of the biologically active substances onto the surfaces of the biologically active nanochips.

US Patent [24] discloses a method and apparatus for manufacturing a submicron polymer powder from solid polymer bodies or coarse particles, preferably of polytetrafluoroethylene powder, wherein powder is ground into fibrous particles in the first stage and is disintegrated into submicron particles by aerodynamic treatment in the second stage, where a gas-particle mixture is subject to the effect of centrifugal forces and suction forces acting in the direction opposite to the centrifugal forces, a pulsating sign-alternating temperature field generated by a pulsed supply of liquid nitrogen, turbulent forces of vortexes, and aerodynamic forces that cause alternating compression and expansion of the gas-particle mixture.



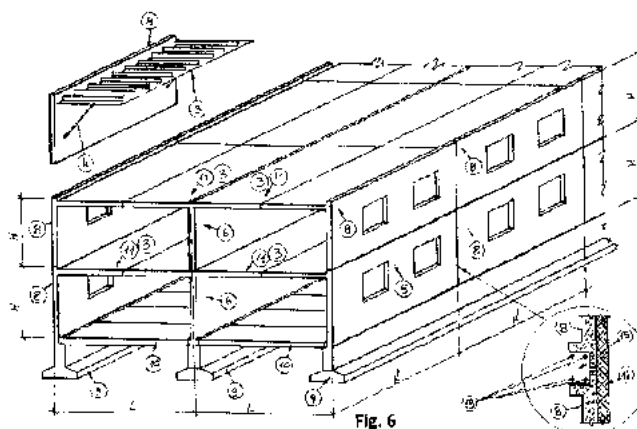
Method of manufacturing track membranes by penetration of working substances into and through the membrane matrix of polymer material was disclosed [25]. The matrix is placed into a holder that is inserted into one end of a tubular shell, the other end of which contains a cartridge with an explosive material and a working substance in the form of a supersaturated solution of a water-soluble salt. When the explosive material is detonated, the particles of the water-soluble salt interact with the matrix in the form of a high-speed jet with the velocity of particles in the range of 3800 to 4200 m/sec. As a result of penetrating the particles into and through the material of the matrix, a plurality of holes is formed in the matrix. The track membranes are produced by slicing the membrane matrix after removal of the residue of the particles by washing the pierced membrane with water.



A separate group of inventions relates to the field of civil engineering.

Proposed is a wall element which comprises a rigid metal space frame and exterior and interior facing slabs, secured on opposite sides of the above frame, the frame together with the above slabs form a space, having a zone intended for filling in with columns, beams, reinforced concrete, and a zone intended for filling in insulation material [26]. Method of erecting a building wall with the light hollow wall elements also described.

US Patent [27] discloses a construction element for erecting a structure that has a first panel extending vertically to form a wall and a second panel extending horizontally to form a horizontal partition when they are arranged in an erected structure, the panels together form a three-dimensional configuration and are connected with one another so that in the erected structure they extend perpendicularly to one another and are turnable to include an angle there between to reduce a horizontal extension of the construction element for transportation purposes.



References

1. Figovsky O. Hybrid nonisocyanate polyurethane network polymers and composites formed therefrom. US Patent 6,120,905, 2000.
2. Figovsky O., Shapovalov L., Blank N., Buslov F. Cyclocarbonate groups containing hydroxyamine oligomers from epoxy cyclocarbonates. US 6,407,198, 2002.
3. Figovsky O., Shapovalov L., Potashnikov R., Tzaid Y., Bordado J., Letnik D., De Schrijver A. Foamable photo-polymerized composition. US 6,960,619, 2005.
4. Figovsky O., Shapovalov L. Preparation of oligomeric cyclocarbonates and their use in nonisocyanate or hybrid nonisocyanate polyurethanes. US 7,232,877, 2007.
5. Birukov O., Beilin D., Figovsky O., Leykin A., Shapovalov L. Nanostructured hybrid oligomer composition. US 7,820,779, 2010.
6. Birukov O., Figovsky O., Leykin A., Shapovalov L. Epoxy-amine composition modified with hydroxyalkyl urethane. US 7,989,553, 2011.
7. Birukov O., Figovsky O., Leykin A., Potashnikov R., Shapovalov L. Method of producing hybrid polyhydroxyurethane network on a base of carbonated-epoxidized unsaturated fatty acid triglycerides US 9,102, 829, 2015.
8. Figovsky O., Potashnikov R., Leykin A., Shapovalov L., Birukov O. Radiation-curable biobased flooring compositions with nonreactive additives. US 9,487,662, 2016.
9. Birukov O., Figovsky O., Leykin A., Shapovalov L. Hybrid epoxy-amine hydroxyurethane-grafted polymer. US Application No. 14/296,478; filed: June 05, 2014.
10. Ioelovich M., Figovsky O. Hydrophobic biodegradable cellulose containing composite materials. US 6,294,265, 2001.
11. Ioelovich M., Figovsky O., Leykin A. Biodegradable nano-composition for application of protective coatings onto natural materials. US 8,268,391, 2012.
12. Figovsky O., Teper V. Composite wooden articles and a method of their manufacturing. US 6,186,200, 2001.

13. Sklyarsky L, Figovsky O. Adhesive composition. US 5,880,203, 1999.
14. Potapov Yu.B., Borisov Yu.B., Figovsky O.L. Polymer concrete mix. RU 2,135,425, 1999.
15. Figovsky O. Liquid ebonite mixtures and coatings and concretes formed therefrom. US 6,303,683, 2002.
16. Potapov Yu.B., Shutilin Yu.F., Figovsky O.L. et al. Polymer concrete mix. RU 2,185,346, 2002.
17. Figovsky O. Liquid solventless synthetic rubber-based composition. US 7,989,541, 2011.
18. Figovsky O., Potashnikov R., Trossman A., Yanov I. Polymer concrete composition. US 9,487,662, 2014.
19. Karchevsky V., Figovsky O., Romm F., Shapovalov L. Polymeric composition having self-extinguishing properties. US 6,329,059, 2001.
20. Karchevsky V., Figovsky O., Romm F., Aksenov O., Fiskin Z., But A. Conductive composition having self-extinguishing properties. US 6,337,036, 2002.
21. Beilin D.A., Borisov Y.M., Figovsky O.L., Surovtsev I.S. Nanostructuring binder for composite construction materials. RU 2,408,552, 2011.
22. Kudryavtsev P., Figovsky O. Method of producing soluble silicates with organic cations. US Application No. 14/860,708; filed: September 22, 2015.
23. Ruban I.N., Voropaeva N.L., Figovsky O.L., Sharipov M.D., Dadajanov T.K. Biologically active multifunctional nanochips and method of application thereof for production of high-quality seed US 8,209,902, 2012.
24. Gryaznov I., Gryaznov S., Gryaznova A., Figovsky O. Method and apparatus for manufacturing submicron polymer powder. US 8,485,456, 2013.
25. Figovsky O., Gotlib E., Pashin D., Leykin A. Method of manufacturing a track membrane. US 8,980,148, 2015.
26. Abramov D., Figovsky O. Light hollow wall element and method of erecting walls of buildings with the use of such elements. IL 121081, 2001.
27. Figovsky O., Futoriynsky A. Construction element for erecting structure and method of erecting structure with use thereof. US 8,615,967, 2013.