Chinese inventions on the field of nonisocyanate polyurethane

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Annotation: For last 10 years creating of new patents in the field of nonisocyanate polyurethane have passaged Chinese inventors. Chinese inventions in the field of NIPU consist about 15% all such inventions, but that are not pioneer ones, especially for foam application.
Key words: patents, nonisocyanate polyurethanes oligomeric cyclocarbonates.

In 2022, the total number of patents filed in China was 4.21 million, of which 3.28 million were held by inventors from mainland China Although it files more patents. China has struggled to convert its research and development spending into valuable and successful innovations. Chinese inventors filed more than 3 million patents last year, the first country in the world to reach that milestone, as the second-largest economy strives to transform into an innovation-driven super power. While innovation is the primary driving force for technology development, patents are often considered one of the key indicators of innovative activities. High-value patents related to strategic emerging industries totaled 952,000 in 2022, up 18.7 per cent year on year, accounting for 71.9 per cent of the total. A total of 355,000 enterprises in China hold invention patents, up 21.8 per cent from 2021. Among them, hi-tech enterprises and “little giants” – smaller businesses with special products and know-how in their sector – owned 1.512 million valid invention patents, accounting for 65.1 per cent of the total.

The first inventions on the field of nonisocyanate polyurethane (NIPU) was created in USSR and first industrial productions was establishing later in USA by Nanotech Technology Inc. (director R&D – EAS academician Oleg Figovsky) based on more his 15 US patents. (see: [1]). For last 10 years creating of new patents in this fields have passaged Chinese inventors – see below the part of them.

The invention CN107857879A [2] discloses a preparation method of diphenolic acid based nonisocyanate polyurethane. The method includes: adopting diphenolic acid as the raw material to synthesize diphenolic acid isopropyl alcohol ester diglycidyl ether, then carrying out reaction with carbon dioxide to obtain diphenolic acid based bicyclic carbonate, and finally carrying out reaction with polyamine to obtain the diphenolic acid based nonisocyanate polyurethane. The invention provides the novel diphenolic acid based nonisocyanate polyurethane and the preparation method thereof, enriches the variety of nonisocyanate polyurethane, and further gives application of the product in preparation of coatings.

The invention CN108659689A [3] discloses sorbitol-based nonisocyanate polyurethane coating and a preparation method thereof. The preparation method includes: adding sorbitol-based epoxy resin into a high-pressure reactor, adding catalysts, feeding carbon dioxide to keep pressure intensity in a range of 1.0-4.0MPa, performing reaction at a reaction temperature of 60-150 DEG C for 4-30h to obtain sorbitol-based cyclic carbonate solution; well stirring sorbitol-based cyclic carbonate, a diamine curing agent or a polyamine curing agent, a solvent and an antifoaming agent under room-temperature conditions to form the sorbitol-based nonisocyanate polyurethane coating, and performing spray coating and baking-curing to form a film. The prepared sorbitol-based cyclic carbonate is yellow transparent liquid, nontoxicand great in biodegradability. The prepared nonisocyanate polyurethane coating is high in hardness and excellent in impact resistance and chemical resistance and is expected to be excellent-performance environment-friendly coating for substituting traditional polyurethane.

The invention CN103951960A [4] provides modified polypropylene carbonate comprising the following components: 1-15wt% of nonisocyanate polyurethane and 85-99wt% of polypropylene carbonate, wherein nonisocyanate polyurethane has a structure as shown in the formula I. Nonisocyanate

polyurethane provided by the invention contains a great number of hydroxyl radicals and urethane bonds and is used as a proton donor, and polypropylene carbonate contains carbonyl and is used as a proton receptor, so that a relatively strong intermolecular hydrogen bonding effect is taken between molecules of nonisocyanate polyurethane and polypropylene carbonate, the compatibility of nonisocyanate polyurethane and polypropylene carbonate is improved, the relatively high tensile strength and young modulus of modified polypropylene carbonate are kept, and meanwhile, the elongation at break of modified polypropylene carbonate is increased. An experimental result shows that the elongation at break of modified polypropylene carbonate is 11.16-36.81%.

The invention CN104231191A [5] relates to a preparation method of waterborne non-isocyanate polyurethane modified polyester and provides a preparation method of the waterborne non-isocyanate polyurethane modified polyester. The preparation method comprises the following steps: (1) preparation of unsaturated prepolymer containing a urethane bond; (2) preparation of polyester containing an unsaturated double bond; (3) graft polymerization of the prepared polyester containing the unsaturated double bond, and the prepolymer; and (4) dispersion of a graft polymer. The invention also provides an application of the prepared waterborne non-isocyanate polyurethane modified polyester in vehicle coatings.

The invention CN103232428A [6] discloses a preparation method of terpenyl cyclocarbonate and non-isocyanate polyurethane thereof, which comprises the following steps: synthesizing terpenyl cyclocarbonate from terpenyl maleic anhydride ethylene oxide ester epoxy resin and CO2 under the composite catalytic action of quaternary ammonium salt/ortho-glycol, and further reacting with a diamino compound to prepare the non-isocyanate polyurethane. According to the invention, the yield of the prepared terpenyl cyclocarbonate is high, the epoxy group conversion rate is 99.7%, and the cyclocarbonate selectivity is 94.0%. The

polyurethane material prepared by the method is free of virulent isocyanates, and has the advantages of biodegradability, excellent environmental compatibility and the like; and the preparation technique is safe and environment-friendly.

The invention CN105176349A [7] discloses a water-borne woodenware coating with a formaldehyde decomposing function. The water-borne woodenware coating comprises components in parts by weight as follows: 40-48 parts of nonisocyanate polyurethane, 0-28 parts of pigment filler, 0-0.2 parts of a defoaming agent, 0-0.4 parts of a wetting agent, 0-0.4 parts of a leveling agent, 0-4 parts of an adhesion promoter, 0-5 parts of a water-borne hand feeling agent, 1-5 parts of a film coalescing aid, 1-3 parts of a dispersing agent, 1-6 parts of a pH regulator, 0-2 parts of a thickening agent, 8-12 parts of an air catalyst, 0-0.3 parts of a sterilizing agent and 7-15 parts of deionized water. The water-borne woodenware coating is prepared from nonisocyanate polyurethane as a raw material, contains no formaldehyde, has the function of decomposing formaldehyde released from other materials indoors and reduces the environment pressure.

The invention CN101260232A [8] relates to hybrid non-isocyanate polyurethane which is prepared through adopting the following method: epoxidized soybean oil and weak base catalyst are added in a reaction kettle, and then carbon dioxide gas is pumped in; at the action of reaction temperature, reaction pressure and stirring, reaction is started, and cyclic carbonate is generated after the reaction; the cyclic carbonate is mixed with epoxy resin and organic base catalyst is added; then, the mixture is mixed with primary amine compound so as to be formed into sheets; finally, sulfuration is carried out under the condition of sulfuration with the product placed for 7 to 9 days at room temperature. The hybrid non-isocyanate polyurethane has the advantages that: the hybrid non-isocyanate polyurethane is synthesized through the mixing and the reaction of natural regenerable vegetable resource and epoxy resin, thereby reducing the dependence

on petrochemical resource, making full use of the regenerable vegetable resource and carbon resource and reducing environmental pollution.

This invention CN100593547C [9] relates to a method for producing non-isocyanate polyurethane using renewable natural resources, comprising: add epoxy soybean oil and catalyst into the reactor, wherein the amount of catalyst added is 3-5mol% of epoxy soybean oil, and then aerate in carbon dioxide gas, with reaction temperature 100-140Deg C, and reaction pressure 6-14 atmospheric pressure, start the reaction with magnetic stirring . for 25-40h. The produced cyclic carbonates are mixed with amine at 70-80Deg C, perform flaking at 100-110Deg C for 7-8h, perform sulfidization at 90-110Deg C for 24-72h, and are placed at room temperature for 7-9d. This invention synthesizes non-isocyanate polyurethane by replacing petrochemical products with epoxy soybean oil and CO2 via two-step reactions, forming a green, clean, high efficient and simple line for producing non-isocyanate polyurethane.

The invention CN111410755A [10] relates to the field of carbon dioxide conversion and utilization and the field of self-repairing materials, in particular to repeatedly shaping self-repairing hydrogel and a preparationmethod. The hydrogel is polyacrylic acid/non-isocyanate polyurethane hydrogel. The non-isocyanate polyurethane is prepared by taking polyethylene glycol diglycidyl ether or polypropylene glycol diglycidyl ether as a raw material and preparing five-membered cyclic carbonate from the raw material and carbon dioxide under the action of a catalyst. The preparation method comprises the following steps: reacting five-membered cyclic carbonate with binary primary amine to obtain non-isocyanate polyurethane, dispersing the non-isocyanate polyurethane in a solvent, adding glycidyl methacrylate to react to prepare the non-isocyanate polyurethane with different double bond contents, and polymerizing an acrylic monomer and the non-isocyanate polyurethane in an oxidation-reduction system to prepare the hydrogel. The non-isocyanate polyurethane taking carbon dioxide as a raw material

is introduced into the polyacrylic acid hydrogel, so that the hydrogel is endowed with good self-repairing capability while the mechanical property of the hydrogel is improved, and the hydrogel shows excellent performance of repeated shaping.

The invention CN109796485A [11] discloses an organosilicon-modified bifunctional urethane acrylate monomer and a preparation method and application thereof. The monomer has a large organosilicon hydrophobic chain segment, the flexibility, the smoothness, the hydrophobicity and the fingerprint resistance and the drying speed of a paint film can be improved, internal stress generated during cross-linking and solidification of the paint film is reduced, and therefore, the flexibility and adhesion of the paint film are improved. The nonisocyanate polyurethane structure and amido bonds contained in the monomer can improve the flexibility, the wear resistance and the handfeeling fullness of the paint film can be improved. The monomer contains two polymerizable acrylic ester structures, therefore, the monomer canbe used for polyurethane-crylic acid emulsion polymerization, modification of acrylic resin for stoving varnish and UV light curing, the cross-linking density of the resin can be improved, and the hardness and the salt fog resistance of the paint film can be improved. The synthesis method is simple, the reaction conditions are mild, neither organic solvents nor toxic and high-corrosion substancesare adopted, and the organosilicon-modified bifunctional urethane acrylate monomer is safer and more environmentally friendly.

The invention CN107746458A [12] discloses room temperature curing cyclocarbonate prepolymers and a preparation method and an application thereof. According to the preparation method, two-membered cyclocarbonate is synthesized with epoxy resin and a catalyst as raw materials in a CO2 atmosphere, furthermore, cyclocarbonate prepolymers with different molecular weight are synthesized from the two-membered cyclocarbonate and diamine, and then a high-performance non-isocyanate polyurethane coating layer is synthesized from the cyclocarbonate prepolymers and a polyethyleneimine curing agent at room

temperature. The prepared cyclocarbonate prepolymers are yellow transparent liquids, are nontoxic and have relatively good biodegradability. The prepared non-isocyanate polyurethane coating layer has high hardness and excellent impact resistance and chemical resistance, and is expected to become a green environmentally friendly excellent-performance coating instead of traditional polyurethane.

The invention CN109762008A [13] discloses an organosilicon modified single functionality urethane acrylate monomer and a preparation method and application thereof. The organosilicon modified single functionality urethane acrylate monomer has two large organosilicon hydrophobic chain segments, flexibility, smoothness, water resistance and cold and hot resistance of a paint film can be improved, meanwhile internal stress generated during cross-linking curing of the paint film can be lowered, thus the flexibility of the paint film is improved, and adhesive force of the paint film is increased; the double organosilicon hydrophobic chain segments can increase the drying speed of the pain film; the organosilicon modified single functionality urethane acrylate monomer contains a nonisocyanate polyurethane structure and amido bonds, the flexibility, abrasion resistance and hand feeling fullness of the paint film can be improved; the organosilicon modified single functionality urethane acrylate monomer containsa polymerizable acrylate structure and can serve as a functional monomer to be applied to polyurethane-acrylic acid composite emulsion polymerization, modification of acrylic resin for stoving varnish and UV light curing; and a synthesizing method is simple and mild in reaction condition, organic solvents and poisonous and highly-corrosive substances are not used, and thus the more environmentally friendly and safer effects are achieved.

The invention EP2889359A1 (authors from Tiwan) [14] disclosure provides a fire-resistant composite material comprising at least one inorganic component and at least one nonisocyanate polyurethane having a formula of:

(Drawings (espacenet.com)) wherein R and R' are each independently chosen from hydrocarbylene groups and hydrocarbylene groups having at least one heteroatom chosen from oxygen, nitrogen, and sulfur; and n=1-30. Also provided are processes for preparing the disclosed fire-resistant composite material.

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