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WAYS OF NANODIAMONDS' PURIFICATION

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Diamondblend, formed in the process of the detonation synthesis, contains nanodiamonds as well as a number of impurities. These impurities include various metals and their compounds, non-diamond carbon, therefore it is necessary to allocate nanodiamonds of detonation products. Isolation of nanodiamonds from diamond blend may include the following steps: chemical treatment of metal impurities and non-diamond carbon, fine purification and separation from an aqueous suspension of nanodiamonds.

There are many different ways to allocate nanodiamonds. Let's consider some of chemical treatment methods.

There is a method,which comprises addition of 5-20% nitric acid solution at a temperature of 50-100˚. Itallowsto transform metal impurities and their oxides into a soluble state and thus to achieve higher nanodiamonds' cleaning quality and subsequent processing of a deposit by oxidizing sulfur-nitrogen or nitro-oleummix in the flow reactor.The processing of blend by nitric acid solution allowsto increase the speed of the nanodiamonds' cleaning process by nitro-oleum or sulfuric-nitrogen mixtures in 1,5- 3 times.Another method of nanodiamonds purification applies diamond blend combustion reaction with a mixture of the volatile acetylacetonates of metals, which are used as combustion activators. Heating of reagents is performed in a crucible in air up to the moment when reagents' combustion starts at a temperature of 300˚C, and then the heat input is stopped. The combustion wave minutes is being distributedfor 3-5 in the volume of material, mostly non-diamond carbon is being burned. Combustion products are subjected to acid treatment followed by washing with water.The preliminary burning of the bulk of non-diamond carbon can significantly reduce acid consumption and accelerate the process of nanodiamonds' cleaning.Also there is purification process which includes treating of the diamond blend in air at a temperature of 300-550˚C with of boric anhydride in an amount not less than 9 % by weight of the diamond content in the mixture. The diamond blendis mixed with an aqueous solution of boric acid or boric anhydride, the product is dried at 210˚C for glassy boric anhydride. The dried product in the crucible is placed in an oven and being maintained for 4-5 hours at appropriate temperatures, being stirred occasionally. The residue is boiled in a diluted hydrochloric acid to remove metallic impurities, washed by distilled water and dried at 110°C.

There is also a method of purification, which comprises a two-step process. The first step is washing of diamond blend with distillated water and later drying. Then the processing of dried blend is subjected by oxidizing sulfuric-nitric mixture with a ratio of components:HNO_3 ~ 64-89%; H_2SO_4 - 11-36% at a weight ratio of the dry blend: a sulfuric-nitric mixture), 1: (20-25), wherein during the processing of the nitric acid is introduced portionwise periodically.The treatment is carried out at a temperature of 200 -250˚C. Further, the blend processing is carried out with oxidizing sulfuric-nitric mixture as well as with a catalyst from the group of: K_2SO_4, $K_2Cr_2O_7$, MnO_2.The use of catalysts can reduce the process time up to 2,5-4 hours.Pre-rinsing and drying of diamond-graphite blend allows to remove a significant portion of its impurities and to obtain pure bulk product, which is well prepared for further processing.The addition of a large amount of nitric acid (64-89%) in the oxidation mixture and parting it to the oxidation by small portions (each subsequent portion is delivered after the complete oxidation of the previous one) contributes to loosening and increasing the volume of dry and clean diamond blend weight and providing conditions in its structure for better separation of the ultrafine diamond particles.Sulfuric acid is introduced into the blend processing only once at the initial stage to accelerate oxidation. Such conditions of the oxidation process eliminate necessity for tracking the temperature of the reaction mixture when acid is being added.

Another two-step purification method is a diamond blend treatment by an aqueous solution of nitric acid in two stages: during the first stage the blend is processed at a temperature of 80-180^{o}C with a nitric acid with concentration 50-99% , and atthe second stage it is treated with nitric acid with a concentration 10-40% at a temperature of 220-280^{o}C.

It is a method, which comprises mechanical filtration of diamond blend by means of a sieve set under vibration and subsequent treatment with concentrated sulfuric acid by heating to 105-110˚C for 1-1,5 hours to remove metals and their compounds.Purification from non-diamond carbon is made by adding water to the blend solution of chromic anhydride in a mixture of concentrated sulfuric acid, forming a reaction mixture with the following component ratio : 28-30 % of sulfuric acid , 14-16% of chromic anhydride and 54-58 % of water . Washing ofultrafine diamond from products of acid treatment at a temerature 60-70˚C with water is carried out later. Application of this technology of nanodiamonds' purificationallows to abandon the use of several different types of acids (nitric, hydrochloric, etc.), limited to only one (sulfuric acid),as well as to reduce the amount of acid.

Another purification method is diamond blend treatment by oxidant mixture, which comprises 10-30 % of hydrogen peroxide, 0,05-5 % of a mineral acid salt or metal of variable valency and 65-90% of water. Diamondblend is suspended in an aqueous solution of a mineral or a hydrochloric acid, the suspension is placed into a high pressure reactor,then it is heated to a predetermined temperature and later mixed with a calculated amount of the hydrogen peroxide, which is taken in an aqueous solution. In thiscase non-diamond carbon is converted into carbon dioxide and purified diamond stored as a suspension in a concentrated solution of a weakly acid or salt.

For nanodiamond powder purification from its surface contaminants it is treated with aqueous solution containing 5-30% of hydrogen peroxide under a pressure of 2-10 MPa at a temperature of 150-250˚C. Due to it, the amount of desorbed gases is double reduced on the surface of nanodiamonds and impurities of silicon, calcium, sulfur, potassium and iron are removed. High-impedance nanodiamond powders with an electrical resistivity of 10^{11}-10^{12} Ohms comes as a result. The diamond powders of the same quality are obtainedby the ion-exchange purification. For this purpose, diluted aqueous suspension of ultrafine diamonds (0,01-2%) is passed through a cation-exchanging anionite column. So, lossesare reduced to 4,5% and the content of incombustible impurities is reduced to 0,5-1%. However, these ion exchangers do not operateunder acidic conditions. Usage of ion exchangers,which are able to work under strongly acidic conditions, dilution step could be avoided or offset, and diamonds could be cleaned directly after acid cleaning step. The adsorbed gases can be removed due to a heat treatment at high temperature in a gaseous medium,which are neutral in respect to carbon (in hydrogen, argon and carbon dioxide). But it is impossible to eliminate outgassing from ultrafine diamonds because of the fact that carboxyl groups dominate the surface detonation diamonds. A further ultrafine diamonds' purification from iron by means of 1-oxyethylidendiphosphone acidis described in the paper.

The following method of nanodiamond allocation from aqueous suspension is also known. In terms of this method an aqueous suspension of ultrafine diamonds is heated up to 20-90 ° C and separation is carried out by means of a flow rate of suspension inultrafilter channels of 2-6 m/s and with a pressure of (0,5-6) • 10^{5} Pa. There is also a process of nanodiamonds' separation, comprising diamond coagulation by treating stable aqueous suspensions of electric field with intensity at 2-50 kV/m in the interelectrode space, isolated from the electrodes of Teflon membrane with a pore size of 150-600 microns.Another method is the treatment of a stable aqueous suspension, which contains ultra-fine diamond particle concentration of 0.1% at a temperature of 81-190˚C under a pressure of 49-1200 kPa for 5-15 min. The complete coagulation of ultrafine diamond particles comes within the specified time.