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Preparation of Complex Nitric Fertilizers During Recycling of Acidic Wastes of Detonation Nanodiamonds Purification Stage

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Abstract—Herein we report on the promising technology of recycling of the nanodiamond production wastes in order to obain complex nitric fertilizer as a by-product.

Keywords: nanodiamond, purification, waste, recycling, fertilizer

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Recently, the interest to development of new applications of nanodisperse matter has emerged. This can be due to the fact that the earlier expectations related to the application of fullerenes and nanotubes have not been completely realized. The detonation nanodiamonds (DND) are expected to combine the properties of macroscopic diamonds with those arising from their dispersed state. In particular, highly stable colloid DND-based systems have been developed, significantly enhancing the range of their medical and biological applications. The most promising areas of DND applications are as follows:

–sorption systems for purification and separation of proteins;

–efficient non-toxic enterosorbents;

–detoxication systems with high sorptive activity capable of efficient decompositions of mycotoxins including aflatoxin;

–detection systems for environmental monitoring of the phenol-contaminated systems;

–organic and biological catalysis;

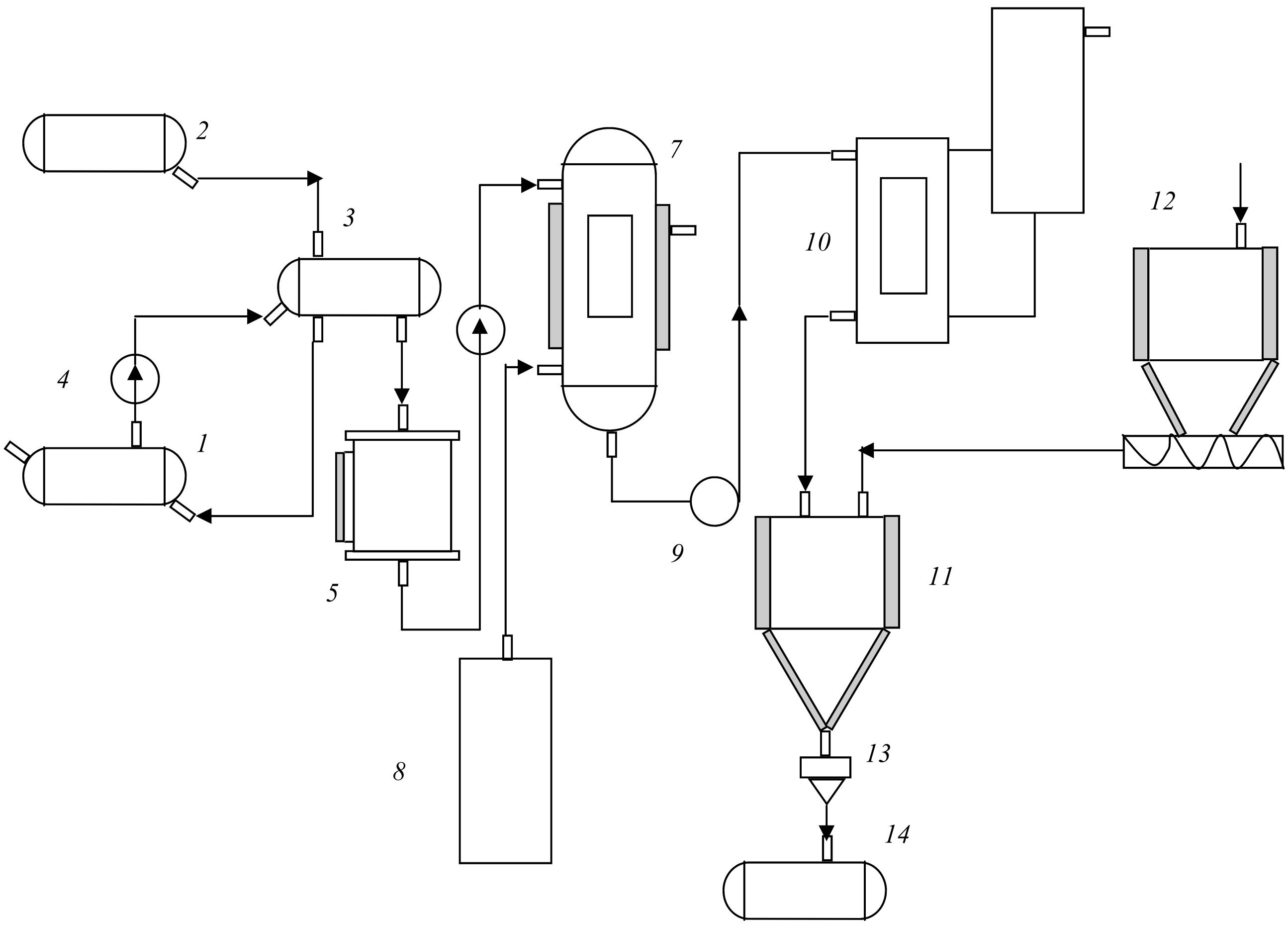
–targeted drug delivery systems;

–express testing of dangerous infections;

–antimicrobial compositions including coatings, package, and biomembranes for sterilization of gases and liquids.

Technologies based on DNDs are already known [1–8] in the fields of composite materials and electrochemistry. The biocompatible composites, systems for intelligent drug delivery, nanodispersed catalyst carriers, and some other applications of DNDs are about to be practically used. Therefore, the large-scale production of DND is of extreme importance. Noteworthily, biological and anthropological consequences of DND production and application have not been studied in detail so far. However, analysis of the environmental effects of DNDs production should be taken into account in planning the related activities.

The detonation synthesis of nanodiamonds results in a complex micxture of varios forms of carbon (detonation carbon, DC) as the primary product. DC can be simplistically regarded as a composite containing the amorphous and the crystalline components. The latter is known as the DND. In real technology practice, DC contains additionally metals, their oxides, and other admixtures resulting from the corrosion processes involving the detonation chamber and explosive compounds. Therefore, DND separation off the amorphous carbon matrix is a complicated series of chemical and physical operations. Nowadays a method using the nitric acid-based oxidative system is among the most widely used. This method has been developed at the "Tekhnolog" enterprise (St. Petersburg) [5]. The final stage of the employed scheme is isolation and purification of the DND phase off the acidic medium to get the aqueous suspension of



Principal flowsheet of preparation of liquid nitrogen fertilizer KAS-28. See key in the text.

the product. The simulation of the process has revealed that in practice production of 1 t of pure DND will produce about 1000 m^3 of acidic wastes. The wastes essentially contains about 5 wt % of nitric acid, 10 wt % of nitrogen(III) oxide, and traces (less than 0.1 wt %) of metal salts. The metals majorly result from the equipment wear and corrosion. As their concentration is negligibly low, the wastes can be regarded as aqueous solution containing significant amount of the inorganic acids and nitrogen compounds.

Industrial-scale production of DND will evidently require the procedures to recycle the large volume of aggressive liquids produced at the stage of oxidative purification. Consequently, the wastes utilization should be undoubtedly included in the technology flow chart of DND production.

Herein we propose a solution to improve the environmental and economy parameters of DND production. It accounts for the requirements to neutralize the acidic wastes and to recycle the nitrogen compounds present in them. Along with phosphorus, nitrogen is the major element leading to water reservoirs eutrophication. As nitrogen is a part of many fertilizers, it is natural to combine the nitrogen compounds removal from the wastewater with production of a nitrogen fertilizer. In view of the above, the proposed process is aimed to produce the KAS-28 liquid nitric fertilizer containing amide (urea) as well as ammonium and nitrate (ammonium saltpeter) nitrogen components. This nitric fertilizer is readily assimilated with the plants, being the most efficient upon the external fertilizing. KAS-28 solutions can be used to prepare binary and ternary fertilizing mixtures.

The major chemical process of the target product production is oxidation of nitrogen oxides into nitric acid with ozone followed by the nitric acid neutralization with ammonia to form ammonium nitrate. Carbamide is added to the mixture so that the final nitrogen content in the product is of 28%. The technology flow chart of the process is shown in the figure.

The starting 5 wt% nitric acid containing nitrogen(III) oxide is fed into the mixer *3* from the tank *1* with centrifugal pump *4*. Ozone is simultaneously fed into the mixer *3* from ozonator *2*, and nitrogen(III) oxide is oxidized into nitric acid in the mixer. The oxide-free nitric acid then comes into the container *5*, and subsequently pumped into the neutralizer *7*. Neutralization is performed with gaseous ammonia with is fed from tanks *8*. Neutralization yields the 25.8 wt % solution of ammonium nitrate. This solution is pumped *9* to the evaporator *10* equipped with natural circulation system and external heating element. In the evaporator, the solution is concentrated to the concentration of 56 wt %. The concentrate then comes into the mixer *11* equipped with a stirrer where it is mixer with urea fed from the container *12*. The target product KAS-28 comes into a vacuum funnel to separate off the mechanical admixtures and finally reaches the storage *14* and then the packing assembly. Using the developed process will allow 742 t of KAS-28 (the wholesale price estimated to be of 9000 rubles per 1 t) from 1000 t of the acidic waste.

To conclude, the combined production of DND and KAS-28 is an example of practically waste-free technology significantly improving the ecology and economy parameters of DND production.

REFERENCES

1. Shenderova, O.A., Zhirnov V.V., and Brenner D.W., *Crit. Rew. Solid State Mater. Sci*., 2002, vol. 27, nos. 3–4, pp. 227–356.
2. Dolmatov, V.Y., *Russ. Chem. Rew*., 2001, vol. 70, no. 7, pp. 607–626.
3. Shenderova, O.A. and McGuire, G., *Nanomaterials Handbook,* Gogotsi, Y., Ed., CRC Press: Boca Raton, FL, 2006, pp. 203–237.
4. Dolmatov, V.Yu., *Detonatsionnye nanoalmazy* (Detonation Nanodiamonds), St. Petersburg: Professional, 2011.
5. Putyatin, A.A., Nikol'skaya, A.V, and Kalashnikov, Ya.N., *Sverkhtverd. Mater*., 1982, no. 2, pp. 2–28.
6. Gubarevich, T.M., Sataev, R.R., and Dolmatov, V.Yu., Abstracts of Papers, *V Vsesoyuznoe soveshchanie po detonatsii* (V All-Union Meeting on Detonation), Krasnoyarsk, Aufust 5–12, 1991, vol. 1, pp. 135–139.
7. Gubarevich, T.M., Dolmatov, V.Yu., Pyaterikov, V.F., and Larionova, I.S., *Zh. Prikl. Khim*., 1992, vol. 65, no. 11, pp. 2512–2516.
8. Dolmatov, V.Yu., Sushev, V.G., Marchukov, V.A., Gubarevich, T.M., and Korzhenevskii, A.P., RF Patent no. 2109683, *Byull. Izobret.*, 1998, no. 12.