

1 563 621

- (21) Application No. 38400/76 (22) Filed 16 Sep. 1976 (19)
- (31) Convention Application No. 616299 (32) Filed 24 Sep. 1975 in
- (33) United States of America (US)
- (44) Complete Specification Published 26 Mar. 1980
- (51) INT. CL.³ C01B 31/06
- (52) Index at Acceptance
C1A J2 J636 J691



(54) PROCESS FOR RECOVERING SYNTHETIC DIAMONDS FROM PRESSED RUNS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The synthesis of diamond crystals by high temperature, high pressure processes is well known. Preferred methods for making diamonds are disclosed in Hall et al., U.S. Patent No. 2,947,610, Strong, U.S. Patent No. 2,947,609. Apparatus for carrying out such processes is described in Hall, U.S. Patent No. 2,941,248.

Briefly, diamond growth in the aforementioned processes occurs by the diffusion of carbon through a thin metallic film of any of a series of specific catalysts, preferably an alloy of at least two metals with one of the metals selected from the class consisting of group VIII metals of the periodic table, chromium, tantalum and manganese. The reaction results in a composition, referred to as a "run", which contains a mixture of diamond; graphite (from the carbon source); and the catalyst.

The recovery of the diamond from the run has presented certain problems relating to cost and undesirable by-products. The recovery of diamonds from the runs has generally been accomplished by the treatment of the runs with acids. However, in these acid recovery processes, treatment of ventilation air and waste acids is necessary prior to discharge from the recovery facility into waste disposal facilities.

Therefore, the acid recovery process requires substantial capital expenditure to limit pollution discharge, and results in wasted material.

Additionally, drawbacks have been observed in all of these processes. A complete removal of graphite often requires repeating the process several times in the acid methods, thereby resulting in time consumption and material loss in addition to the pollution problems mentioned above.

Finally, complete removal of the graphite or non-diamond carbonaceous material is difficult when small amounts of graphite are left after removal of substantially all the other synthesis material from the diamond crystals. The final removal of the graphite by oxidation of the graphite, utilizing alkaline earth metal carbonates has been suggested, see Showa Denko KK, Japanese Patent No. SHOW 47-44159, issued November 8, 1972. However, some diamond loss due to oxidation is inevitable.

The synthesis of diamond crystals may also be achieved by a dynamic process as opposed to the so-called static processes just described. An example of such a dynamic process is described in Balchan, U.S. Patent No. 3,608,014 wherein an explosive charge is utilized to create the pressure and temperature necessary for the conversion of graphite into diamond.

The recovery of the diamond crystals from a dynamic process presents similar problems to those encountered with static processes and as described in Example I of the Balchan patent an oxidation process is used to separate the graphite and diamonds which leads to undesirable pollution problems.

According to the invention a process for recovery of synthetic diamond from a composition containing diamond crystals and a non-diamond carbonaceous material comprises the step of treating said composition with liquid bromine to exfoliate said material from said crystals.

The composition may be a diamond synthesis run further containing a metallic catalyst

and treated with said bromine until said non-diamond carbonaceous material is dissolved in which case the process may further comprise the steps of

(a) separating the bromine carbonaceous material mixture from the remaining run material; and

5 (b) treating the remaining run material to remove the catalyst. 5

The treatment may be by electrolysis to plate out the catalyst metal.

Graphite-halogen lamellar compounds have been the subject of investigation for many years. However, bromine as a medium for separating and recovering diamond crystals from synthesis compositions has not been suggested prior to the present invention. The ability to recycle or recapture major components of the recovery and synthesis materials provides a desirable process both from an economic and an environmental standpoint.

10 Graphite-halogen lamellar compounds are described in the literature but not for the use of the present invention. Ubbelohde et al, *Graphite and Its Crystal Compounds*, §§ 5.3, 5.4, 5.6.1; 6.3.2. Oxford (1960) describes a variety of observations of graphite halogen compounds including bromine. Sanders G.A. et al. have also reported on experimental observations of bromine graphite reactions in *The Formation of Graphite/Bromine, I. Hysteresis of Bromine Insertion Between The Carbon Hexagon Layers* and *II. The Influence of External Pressure on Bromine Uptake*, Proc. Roy. Soc. A271 499-511; 512-519 (1963). The investigations of several researchers are summarised in Reynolds, W.N., *Physical Properties of Graphite*, 126-128, Elsevier, N.Y. (1968). And the penetration of bromine in pyrocarbon is reported in Marchand, A. et al., *Direct Observation of Bromine Penetration Into a Pyrocarbon Sample*, Carbon 11, 666-668 (1973).

15 Bromine and other halogens have been used with graphite for purification, Woodruff et al., U.S. Patent No. 1,380,458, Brooks, U.S. Patents Nos. 2,734,799 and 2,734,800 and to produce hyperconductive graphite structures, Olstowski, U.S. Patent No. 3,409,563, and lubricants Knappwoest, U.S. Patent No. 3,377,280.

20 While this invention is susceptible of embodiment in many different forms, there is contemplated and will hereinafter be described in detail a preferred embodiment of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the invention to the embodiment illustrated.

25 The production of synthetic diamonds is now commercially feasible when a source of carbon, i.e., graphite, is subjected to pressure and temperature in the diamond stable region of the carbon phase diagram provided that a metallic catalyst is present. As discussed in the above-identified Strong patent, incorporated herein by reference, the catalyst may consist of a metal selected from the class consisting of group VIII metals of the periodic table, chromium, tantalum and manganese. Preferably, however, the catalyst includes an alloy of two metals one of which is selected from the above class. The other elements of the alloy may be catalyst or non-catalyst metals.

30 After the diamond synthesis material has been treated by the high pressure, high temperature process, a portion of the carbon is converted into diamond crystals. These crystals are interspersed in the synthesis material and must be separated therefrom. This material referred to as a pressed run is generally a cylindrical shaped mass from which the diamonds must be recovered. Generally, the diamonds are located at the interface between the alloy catalyst and the carbonaceous material.

35 Recovery of the diamonds from the pressed run in accordance with the present invention involves a combination of steps to provide cleansed crystals. The run is first immersed in a bath of liquid bromine to dissolve the graphite. Graphite has a layer structure and consists of hexagonal networks in the layers. The distance between two adjacent atoms is 1.415 Å. The separation of the layers is 3.35 Å. This great distance between the layers suggests that the forces acting between the layers, Van der Waals bonds, are weak. This property makes it possible for many molecules and ions to penetrate between the layers forming intercalated, interstitial, or lamellar compounds. When bromine is introduced to graphite, a bromine lamellar compound C₈Br, is formed. Graphite can absorb up to 83% by weight of bromine. Measurements of the macroscopic volume expansion and the changes in X-ray diffraction indicate that bromine occupies only alternate layers, expanding the separation between them from 3.35 Å to 7.05 Å. This corresponds to a macroscopic increase in thickness of the graphite crystallites of 55% in the direction of the c axis. When the brominated graphite is subjected to a further attack of bromine, the exfoliated graphite is broken into small pieces.

40 After the graphite has been dissolved, the bromine-graphite mixture is separated from the run material, and the remaining metal can be removed by dissolving in mineral acid or by electroplating leaving the diamond crystals.

45 Thus, the use of liquid bromine provides a convenient method of reducing the mass of the run for subsequent metal removal. Moreover, the mixture of bromine and C₈Br (exfoliated 65

graphite) may be distilled and the condensed bromine recycled for subsequent treatment of runs. Preliminary recovery tests indicate that about 98% of the liquid bromine may be recycled.

5 The electrolysis of the catalyst may be achieved by the use of a proper electrolyte depending on the type of catalyst metals, discussed above. Examples of the process are given as follows: 5

Example I

10 A batch of pressed runs weighing 298 grams containing diamond crystals, graphite and NiFe catalyst were pretreated with 474 grams of liquid bromine at room temperature, initially. The pretreatment was carried out adiabatically for one hour. The pretreated batch was heated gently to expel the bromine. Subsequently, the remaining batch of materials (diamond crystal and catalyst) were subjected to electrolysis at a voltage of about 7 volts D.C., a current of about 15 amperes, and a temperature of about 77°C (170°F). The electrolysis was completed in 20 hours. The electrolyte had the following constituents: 15

NiCl₂ 6H₂O - 900 g./3000 c.c. of solution

20 HCl (36%) - 20 g./3000 c.c. of solution 20

NH₄Cl - 40 g./3000 c.c. of solution

Example II

25 This procedure was run in a full scale prototype recovery process in which a batch of 240 runs was pretreated with 20 gallons of liquid bromine for two hours. The liquid was then drawn off and distilled and condensed to recover the liquid bromine. About 15 pounds, i.e., approximately 1/2 gallon of bromine was not recovered. After bromination, 80 runs of the original 240 runs were placed on a horizontal circular graphite plate which was immersed in an electrolysis tank containing 55 gallons of the nickel chloride electrolyte as follows. The remainder of the electrolyte solution is water. 30

NiCl₂6H₂O - 300g./l. of water

35 HCl (100%) - 3 g./l. of water 35

NH₄Cl - 15 g./l. of water

40 H₃BO₃ - 15 g./l. of water 40

A mild steel plate 1/16 inch thick was used for the cathode and positioned about 5 inches above the anode (graphite plate). A potential of 6-8 volts, D.C. and 200 amperes was applied to produce electrolysis of the iron and nickel to the steel plate. The process was maintained at 125°F, and the process was completed in 60-80 hours. 45

Some of the synthetic diamonds are still covered with graphite from the synthesis process and this must be removed. This is accomplished by bathing the crystal in liquid bromine. The bromine due to its specific gravity of 2.928 causes the exfoliated carbon, specific gravity 2.23 or less, to float on the bromine. Most importantly, however, the bromine has an exfoliating property. As discussed above, this is achieved by the absorption of bromine by the graphite to form C₈Br and further attack of the C₈Br to release the carbon. This also results in the delamination of the carbon layer structure. Therefore, this final immersion of the crystals in bromine results in complete removal of the diamond synthesis materials. 50

The exfoliated carbon and bromine may then be decanted from the bath and the decant is evaporated and condensed to recover the bromine for repeated use with minimal loss of material and solution. 55

The graphite exfoliated diamond is then treated with NaOH to neutralize any trace of bromine on the crystals.

60 *Example III* 60

Fifty grams of graphite containing synthetic diamonds were placed in a 100 m.l. beaker. Bromine at room temperature was added to the beaker and allowed to stand for 1 hours. Subsequently, more bromine was added to float out the non-diamond carbon. The beaker was then emptied of bromine and treated with 10% NaOH solution to neutralise trace bromine on the crystals. 65

Although the process has been described with reference to bi-metallic catalyst pressed runs, it will be appreciated that the process is also effective for single metal catalyst pressed runs and diamond synthesis runs, which may not include a catalyst.

WHAT WE CLAIM IS:-

- 5 1. A process for recovery of synthetic diamond from a composition containing diamond crystals and a non-diamond carbonaceous material, said process comprising the step of treating said composition with liquid bromine to exfoliate said material from said crystals.
2. The process of Claim 1 wherein said composition is a diamond synthesis run, further containing a metallic catalyst, and is treated with said liquid bromine until said non-diamond carbonaceous material is dissolved; said process further comprising the steps of:
 - 10 (a) separating the bromine carbonaceous material mixture from the remaining run material; and
 - (b) treating the remaining run material to remove the catalyst.
- 15 3. The process of Claim 2 wherein said catalyst is an alloy of at least two metals, one of the metals being selected from the class consisting of group VIII metals of the period table, chromium, tantalum and manganese.
4. The process of Claim 3 wherein said catalyst is an alloy of nickel and iron.
- 20 5. The process of Claims 2-4, wherein said treating step is electrolysis to plate out the catalyst.
6. The process of Claims 2 or 5, wherein said catalyst is a metal selected from the class consisting of group VIII metals of the periodic table, chromium, tantalum and manganese.
7. The process of Claim 6 wherein said catalyst is nickel.
- 25 8. The process of Claim 1 wherein said composition is a diamond synthesis run, further containing a metallic catalyst and is treated with said liquid bromine until the non-diamond carbonaceous material is dissolved; said process further comprising the steps of:
 - (a) drawing off the bromine-carbonaceous mixture from the remaining run material;
 - (b) placing the remaining run material on an anode plate in a nickel-chloride electrolyte bath, and
 - 30 (c) and electrolyzing the remaining run material to plate out the metallic catalyst.
9. The process of any of the preceding claims including the steps of:
 - (a) distilling the bromine carbonaceous material mixture to condense the liquid bromine; and
 - (b) recycling the condensed bromine for subsequent use.
- 35 10. The process of any of the preceding claims including the steps of:
 - (a) immersing recovered diamond crystals in said liquid bromine to exfoliate remaining graphite adhering to said crystals;
 - (b) decanting the exfoliated carbonaceous material and bromine; and
 - (c) neutralizing the trace bromine on the crystals.
- 40 11. The process of Claim 1 further comprising the steps of:
 - (a) decanting the exfoliated carbonaceous material and bromine; and
 - (b) removing the graphite exfoliated crystals.
12. The process of Claims 10 and 11 wherein the removed crystals are treated with a solution of NaOH to neutralize trace bromine thereon.
- 45 13. The process of Claim 11 further including:
 - (a) evaporating the decanted graphite and bromine; and
 - (b) condensing the bromine vapors and recycling the condensed bromine for further use.
- 50 14. A process as claimed in Claim 1 substantially as described in any one of the Examples.

For the Applicants
 MATTHEWS, HADDAN & CO.,
 Chartered Patent Agents,
 Haddan House,
 33 Elmfield Road,
 Bromley,
 Kent,
 BR1 1SU.