

# PATENT SPECIFICATION

(11) 1 553 364

1 553 364

- (21) Application No. 18676/76 (22) Filed 6 May 1976  
(31) Convention Application No. 578061  
(32) Filed 16 May 1975 in  
(33) United States of America (US)  
(44) Complete Specification published 26 Sept. 1979  
(51) INT CL<sup>2</sup> C01B 31/10 31/14 C10B 57/02  
(52) Index at acceptance

C1A J241 J243 J244 J246 J370 J371 J372 J392 J393 J394 J3 J403  
J404 J406 J431 J461 J462 J500 J502 J520 J540 J603 J604  
J632 J634 J681 J685 J686  
C5E 203 204 207 211 BE



## (54) GRANULAR ACTIVATED CARBON MANUFACTURE FROM SUB-BITUMINOUS COAL TREATED WITH DILUTE INORGANIC ACID

(71) We, THE CARBORUNDUM COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 1625 Buffalo Avenue, Niagara Falls, 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:—

This invention relates to granular activated carbon manufacture, and more particularly to a new and improved process for making granular activated carbon from sub-bituminous coal leached with dilute inorganic acid, and to a new and improved granular activated carbon made by such process and having properties which make it suitable for use in waste water treatment and other applications.

In order to facilitate a clear understanding of this invention, various terms of art employed herein are defined as follows.

Abrasion number—is a measure of the resistance of the activated carbon granules to degrading on being mechanically abraded. It is measured by contacting a sample with steel balls in a pan on a machine and shaking the contents for a given time and determining the resultant particle size distribution and hence the mean particle diameter. The abrasion number is the ratio of the final average (mean) particle diameter to the original average (mean) particle diameter (determined by screen analysis) times 100.

Activated carbon—is carbon which is "activated" by heating to high temperature preferably with steam or carbon dioxide as the activating agent in producing an internal porous particle structure.

Adsorption isotherm—is a measurement of the adsorptive capacity of an absorbent (viz. granular activated carbon) as a function of the concentration, or pressure, of the adsorbate (viz. N<sub>2</sub>) at a given temperature. It is defined

as the constant temperature relationship between the amount adsorbed per unit weight of absorbent and the equilibrium concentration, or partial pressure.

Apparent density—is the weight per unit volume of homogeneous granular activated carbon. To assure uniform packing of the granules during measurement, a vibrating trough is used to fill the measuring device.

Ash—is a principle mineral constituent of coal, carbon and pitch. It is normally defined as a weight percent basis after a given amount of sample is reduced to ash.

Average (mean) particle diameter—is a weighted average diameter of a granular activated carbon sample. A screen analysis is run and the average particle diameter is calculated by multiplying the weight of each fraction by its average diameter, adding the products, and dividing by the total weight of the sample. The average diameter of each fraction is taken as the size midway between the sieve opening through which the fraction has passed and the sieve opening on which the fraction was retained.

Coking value—is usually expressed as percent residual carbon obtained when a dry sample of coal, tar or pitch is vaporized or pyrolyzed for a specific time at a specific temperature that limits the available oxygen supply (ASTM Method D-2416). The coking value, expressed as percent residual carbon, indicates the coke forming properties of the material.

Granular activated carbon—is "activated carbon" which has a particle size, i.e., "mesh", which is not less than about 40.

Iodine number—is the milligrams of iodine adsorbed by one gram of granular activated carbon at an equilibrium filtrate concentration of 0.02 N iodine. It is measured by contacting a single sample of carbon with an iodine solution and extrapolating to 0.02 N by an assumed isotherm slope. This number can be correlated with the ability of granular acti-

50

55

60

65

70

75

80

85

90

vated carbon to adsorb low molecular weight substances.

Mesh—(or mesh size) is the particle size of granules as determined by the U.S. Sieve Series (equivalent to the Tyler Series). Usually, this term refers to the sizes of the two screens, in either of the above Series, between which the bulk of a sample falls. For example, "8/30 mesh" (or "8 by 30 mesh" or "8×30 mesh") means that 90% by weight of the sample will pass through a No. 8 screen but will be retained on a No. 30 screen. Alternatively, this term refers to a maximum particle size, such as in defining the fineness of powder material. For example, "65% by weight—325 mesh powder" means that 65% by weight of a given sample passes through a No. 325 mesh screen.

Pitch—is a black or dark viscous substance obtained as a residue in the distillation of organic materials and especially tars.

Powder—means a particle size, i.e., ("mesh" which is smaller than about 40. The larger the mesh number, the smaller the size.

Sub-bituminous coal—is an intermediate stage coal which ranks above lignite and brown coals, but below bituminous coal. In the as received condition it has, by weight, (1) a proximate analysis of: from about 10% to about 25% moisture, from about 35% to about 45% volatile material, from about 2% to about 5% ash, and from about 25% to about 45% fixed carbon, and (2) an ultimate analysis of: from about 65% to about 75% carbon, from about 4% to about 8% hydrogen, from about 0.5% to about 2.0% nitrogen, and from about 0.5% to about 1.0% sulfur.

Surface area—is the amount of surface area per unit weight of granular activated carbon; it is determined from the nitrogen adsorption isotherm by the Brunauer, Emmett and Teller (BET) method, and it is expressed in m<sup>2</sup>/gram.

Granular activated carbon is particularly useful in waste water treatment not only because it is highly effective in purifying the effluent from municipal and industrial sewage but also because it can be regenerated for repeated use. However, in order to accomplish these objectives it must possess certain properties, namely, a minimum surface area of about 900 m<sup>2</sup>/gram for adequate adsorption capacity, a minimum iodine number of about 900 for adequate adsorption of low molecular weight substances, a maximum ash content (by weight) of not more than about 12 percent, and preferably not more than about 8% for purity, a minimum abrasion number of about 70 and preferably not less than about 80, for adequate hardness in maintaining granular integrity in use and in regeneration, and a minimum apparent density of not less than about 0.46 gram/cc, preferably about 0.48 gram/cc, for obtaining the dense, closely

packed beds and columns needed in waste water treatment.

These properties can be obtained by making granular activated carbon from bituminous coal, but until the present invention it is not known that anyone else has accomplished this by dilute inorganic acid treatment of sub-bituminous coal, which is considerably cheap, as the starting material.

Moreover, when so using bituminous coal, it has been found necessary not only to mix in pitch but also to char the granulated mixture prior to the devolatilizing and activating steps. Otherwise, because of the high coking tendency of the preferred bituminous coals, the granules fuse together during devolatilization and are thereby rendered unsuitable both for proper activation and for obtaining the aforesaid desired properties. Likewise, in the present work herein, it has been found that this charring step is necessary, whether or not the granules have been treated with a dilute aqueous solution of inorganic acid prior to the pitch addition and charring, and that such acid treatment has little, if any, beneficial effect upon either the overall yield of the resulting granular activated carbon or the aforesaid properties desired.

Furthermore, it has been found herein that granular activated carbon of the aforementioned properties can not be produced from sub-bituminous coal when such coal is not subjected to such acid treatment or charring, despite the fact that such coal usually is not well coking. Although it has been found herein that sub-bituminous coal can be charred, without such acid treatment, to produce granular activated carbon the yield is very low and the properties, at best are borderline or below the minimum acceptable for granular activated carbon suitable for use in waste water treatment and other applications. As a matter of fact, it has been found herein that the charring step, originally thought necessary for so processing sub-bituminous coal, can be eliminated, and that if appropriate dilute inorganic acid treatment is employed, this results in significant increases not only in yield, but also in the desired properties. In addition, it has been found herein that, while a combination of dilute inorganic acid treatment and carbonaceous binder addition make for optimum yield and properties, the carbonaceous binder can be eliminated entirely and still produce a significantly increased yield, as well as acceptable properties.

Accordingly, a general primary objective of the present invention is (1) to provide a new and improved process for making granular activated carbon from lower cost sub-bituminous coal instead of higher cost bituminous coal, and wherein the charring step necessary for processing bituminous coal is eliminated, while the overall yield of granular activated carbon is increased significantly by

70

75

80

85

90

95

100

105

110

115

120

125

130

appropriate treatment of sub-bituminous coal by treating with a dilute aqueous solution of inorganic acid, with or without the addition of carbonaceous binder; (2) as well as to provide a new and improved granular activated carbon made by such process and having the aforementioned desired properties of adsorption (as measured by surface area and iodine number) purity (as measured by ash content), hardness (as measured by abrasion number), and density (as measured by apparent density), which make it suitable for use in waste water treatment and other applications.

According to the present invention there is provided a process for making hard granular activated carbon comprising:

forming granules from sub-bituminous coal; treating the granules with a dilute aqueous solution of inorganic acid, washing off the acid, and drying the washed granules at least partially to a moisture content below 25% by weight;

Optionally mixing the dried granules with up to 15% by weight of a carbonaceous binder;

reducing the dried granules to form fine powder;

compressing the powder;

reducing the compressed powder to reform granules;

Devolatilizing the reformed granules, without charring, by heating to and at a temperature higher than the charring temperature in an oxygen-free atmosphere; and

activating the devolatilized granules by heating to and at a temperature higher than the devolatilizing temperature in an atmosphere containing a gaseous activating agent.

Preferably the sub-bituminous coal has a moisture content of 10 to 25% by weight and an ash content of not more than 5% by weight.

Preferably also the acid is  $H_2SO_4$ ,  $H_3PO_4$ ,  $HCl$  or mixtures thereof. The acid is preferably used at a concentration of 1 to 50% by weight, more preferably from 1 to 20% by weight and at an aqueous solution to coal ratio of at least 2/1 by weight, more preferably at least 4/1 by weight. In a still more preferred embodiment, the concentration of the acid is 6.5% by weight and the aqueous solution to coal ratio is 10/1 by weight. The most preferred acid is  $H_3PO_4$ .

The fine powder produced by reducing the dried granules is preferably more than 65% by weight—325 mesh.

The process of the invention may be effected with or without the addition of the carbonaceous binder. If such a binder is to be used then the dried granules are preferably mixed with 5 to 15%, preferably 7 to 12% by weight of the carbonaceous binder. The carbonaceous binder is preferably pitch, e.g., coal tar pitch.

The hard granular carbon produced by the

process of the invention will preferably have an abrasion number of not less than 70, more preferably not less than 80.

A specific, but non-limiting, example of carrying out the process of the invention is to form granules from sub-bituminous coal having a moisture content of 10 to 25% by weight; to use an acid having a concentration of 1 to 10% by weight and an aqueous solution to coal ratio of at least 4/1 by weight; to devolatilize the reformed granules by heating to a temperature of 450°C at a rate of 300 deg. C/hour in an atmosphere of  $N_2$  and the volatiles and by maintaining the devolatilizing temperature for a time of 1 hour; and to activate the devolatilized granules by heating to a temperature of 800 to 900°C in an atmosphere of  $N_2$  and steam and by maintaining the activating temperature for a time of 4 to 5 hours; in order to produce an overall yield of granular activated carbon of 25 to 33% by weight, dry basis. Granular activated carbon made by such process will generally have a surface area of 900 to 1100  $m^2$ /gram, an iodine number of 1000 to 1100, an ash content of 5 to 7% by weight, an abrasion number of 70 to 80, and an apparent density of 0.46 to 0.50 gram/cc.

The above process may be carried out with the addition of a carbonaceous binder, in which case the granules are preferably dried thoroughly and mixed with 7 to 12% by weight of coal tar pitch.

Additional objectives and advantages of the invention will become apparent upon consideration of the following detailed description and accompanying drawing wherein:

The accompanying drawing is a block diagram or flow sheet illustrating schematically the various steps of the process as well as the resulting product, both embodying the invention.

In this detailed description, reference will be made to ten Examples, of which Examples 1 and 6—8 relate to and provide background for the present invention, while Examples 2—5, 9 and 10 are illustrative of the invention per se. Moreover, the order or sequence of the Examples has been selected in order to show a progression in experimentation from Example 1, which represents an attempt to apply a known charring technique for making granular activated carbon from bituminous coal to sub-bituminous coal; through the inventive acid treatment techniques of Examples 2—5; to Examples 6 and 7 which compare the results obtained by attempting to superimpose an inventive acid treatment technique (Example 7) on a known charring technique (Example 6) for making granular activated carbon from bituminous coal; to Example 8, which shows that an inventive acid treatment technique does not work as well for lignite, and finally to inventive Examples 9 and 10 which show the importance of fineness of

grinding in powderizing (Example 9) and the workability of HCl (Example 10) along with  $R_2SO_4$  (Example 4) and  $H_3PO_4$  (Example 5).

### EXAMPLE 1

#### 5 Charring of Sub-Bituminous Coal in Making Granular Activated Carbon

In making granular activated carbon from bituminous coal it has been found necessary to char the coal granules prior to activation, as will be seen below in Examples 6 and 7. Thus, this technique was adopted in order to see what sort of product could be so obtained from sub-bituminous coal. The starting material for this and each of the ensuing Examples 2—5, 9 and 10 was a batch of Wyoming sub-bituminous coal having the following analyses, by weight in the as received condition:

| Proximate Analysis |        | Ultimate Analysis |        |
|--------------------|--------|-------------------|--------|
| Moisture           | 17 %   | Carbon            | 69.8 % |
| Volatile           |        |                   |        |
| Material           | 44 %   | Hydrogen          | 5.4 %  |
| Ash                | 2.05 % | Nitrogen          | 0.9 %  |
| Fixed              |        |                   |        |
| Carbon             | 35 %   | Sulfur            | 0.55 % |

These analyses are, in general, typical of a sub-bituminous coal. The as received coal was crushed to a very fine size such that more than 65% by weight of the material passed through 325 mesh screen, preferably 75 to 85% — 325 mesh. The powder was pressed at 40,000 to 80,000 psi pressure into cylindrical pellets approximately 1/2 in. high and 1/2 in. diameter. The apparent density of these pellets was in the range of 1.1 to 1.2 grams/cc. The pellets then were granulated to obtain granules of 6 by 20 mesh with an apparent density in the range of 0.64 to 0.68 gram/cc. In the course of experimentation, as will be seen from Examples 2 and 3, it was found that to obtain compact granules (suitable for obtaining hard granular activated carbon) without the use of a carbonaceous binder such as coal tar pitch, the moisture content of the sub-bituminous coal and the treated granules is important. Too low a moisture content, i.e., below about 10% by weight, or too high a moisture content, i.e., above about 25% by weight, led to poor compaction, and hence granules that were not hard and dense. Likewise, if the moisture content of the coal is too great, in the as received condition, for example as the result of a rainstorm, it must be dried, before granulating, to the desired moisture content range. Otherwise, crushing and screening are unduly difficult. In this Example, the 17% by weight content of the coal was well within the prescribed limits, and hence no drying was necessary, in the first instance.

600 grams of the granules obtained according to the procedure described above were

loaded into a cylindrical container prepared from 5 mesh screen. The container was mounted onto a cylindrical shaft and the assembly was loaded into a cylindrical furnace so that the container and the granules therein were rotated slowly and uniformly inside the furnace.

The granules then were subjected to a charring treatment wherein the granules were heated in an atmosphere of air and nitrogen (deficient oxygen) to 200°C at the rate of 100 deg. C/hour, and maintained at this temperature for 1 hour. During this process, the granules were slowly and uniformly rotated (1 to 8 rpm) so that they were exposed to the oxidizing action of  $O_2$  present. During the course of experimentation, it was found that higher temperatures and/or higher oxygen content in the atmosphere led to poor process control and eventually a poor product. The loss of weight in the charring step was in the range of 5 to 10% by weight based on the dry coal.

The granular material then was subjected to a devolatilization process. The granules were loaded into the furnace described above and heated to 450°C at the rate of 300 deg. C/hour in an atmosphere free from oxygen (in the present case an atmosphere composed of  $N_2$  and the volatiles given off by the granules), and maintained at the devolatilizing temperature for 1 hour and then cooled. During the course of experimentation it was learned that the charring and devolatilization steps could be carried out sequentially without cooling down, provided the atmosphere was altered such that it was nearly free of oxygen during heat up beyond 200°C. It also was learned that presence of oxygen at these higher temperatures led to higher losses, poorer yield of product and inferior granular product.

The yield of granules after devolatilization was about 60% by weight based on charred granules, and their apparent density was about 0.6 gram/cc.

Next, the devolatilized granules were loaded into a cylindrical furnace and were subjected to activation by heating the granules to 800 to 900°C in an atmosphere composed of a carrier gas of  $N_2$  and steam and by maintaining the granules at the activating temperature for 4 to 5 hours. The amount of steam fed in was pre-determined such that it amounted to 1 to 3 grams of steam/gram of charge/hour.

The yield of granular activated carbon from this step was in the range of 30 to 40% by weight based on devolatilized material. The granular product has a surface area of 900 to 1000  $m^2$ /gram, an ash content in the range of 7 to 10% by weight, an abrasion number of 60 to 70 and an apparent density in the range of 0.45 to 0.48 gram/cc.

The overall yield based on dry coal was 20 to 22% by weight and the granules had

65

70

75

80

85

90

95

100

105

110

115

120

125

adsorption properties, ash, density and hardness which were below or on the borderline in being acceptable as a granular activated carbon for use in waste water treatment and other applications. During the course of experimentation, it was learned that if the sub-bituminous coal was processed as above, but without the charring step, the resultant product was soft and had little activity, thus indicating the importance of charring the sub-bituminous coal (when processed by itself), even though such a coal is not very highly coking.

The following Examples 2-5 represent preferred embodiments of the present invention, which is represented schematically in the drawing. Thus, from a method standpoint, the inventive process includes the steps of granulating the sub-bituminous coal, which preferably either, in the as received condition, has a moisture content range of 10 to 25% by weight, or is dried, as shown at the upper right of the drawing, to give such a preferred moisture content prior to granulating; followed by the steps of treating the granules with a dilute aqueous solution of inorganic acid, by washing off the acid and by drying; powderizing; pelletizing; regranulating; devolatilizing; and activating; all in order to produce the desired inventive product of granular activated carbon which is acceptable for use in waste water treatment and other applications. Examples 2 and 3 represent two preferred embodiments of such treatment wherein the granules are treated with dilute aqueous solutions of  $H_2SO_4$  and  $H_3PO_4$  respectively, washed and partially dried to the above noted preferred moisture content range, and preferably to about 15% by weight, followed directly by powderizing, etc., without the addition of pitch, as shown in the drawing. Examples 4 and 5 represent two different and more preferred embodiments of such treatment wherein the granules are treated with dilute aqueous solutions of  $H_2SO_4$  and  $H_3PO_4$  respectively, followed by washing off the acid, by drying thoroughly and by mixing with pitch, prior to powderizing, etc., as shown at the middle right side of the drawing.

#### EXAMPLE 2

Dilute  $H_2SO_4$  treated Sub-Bituminous Coal Granules (without Pitch) in making Granular Activated Carbon

A batch of Wyoming sub-bituminous coal having the analyses described in Example 1 was crushed and screened to obtain  $8 \times 30$  mesh granules. 300 grams of the granules were loaded into a 4 liter kettle, and a dilute aqueous acid solution consisting of 150 cc. of 98% concentrated  $H_2SO_4$  and 2850 cc. of water was added to the granules (about 6.5% acid, by weight, or 5% by volume). The granules and the acid solution were heated to

80°C and maintained at this temperature for 5 hours, while the granules were continuously stirred. During the course of experimentation, it was learned that size of granules, temperature of acid treatment (which is usually below 100°C because of the use of the dilute aqueous acid solution), time of acid treatment, concentration of acid, and the ratio of dilute aqueous acid solution to coal all have important effects on further processibility of the coal to form granular activated carbon. Therefore, the specific numbers cited in this and the ensuing inventive Examples are merely illustrative and not restrictive. For example, both coarser and finer granules can be employed during acid treatment with corresponding results, with the time of acid treatment being longer for coarser particles and shorter for finer particles.

The contents of the slurry were allowed to cool, the solution decanted, and the granules were thoroughly rinsed such that wash water off the granules analyzed to a pH of 6 to 7. To complete the treatment, the treated granules were dried partially to an approximate moisture content of 15%, which is that preferred for good compaction in forming the pellets and hard, dense granules therefrom, without the use of a carbonaceous binder.

The treated granules containing roughly 15% by weight of moisture were milled into a very fine powder such that more than 65% by weight of the material passed through 325 mesh screen, preferably 75 to 85% - 325 mesh, as explained in Example 9 below. The powder was pressed into cylindrical pellets  $1/2$  in. diameter and  $1/2$  in. high using a pressure of 40,000 to 80,000 psi, the apparent density of the pellets being in the range 1.1 to 1.2 grams/cc. These pellets were regranulated to obtain  $6 \times 20$  mesh granules having an apparent density of 0.64 to 0.68 gram/cc. The reformed granules were loaded into a cylindrical furnace and devolatilized as described in Example 1, which consisted of heating the granules to 450°C at 300 deg. C/hour in an atmosphere free of oxygen and holding at temperature for 1 hour.

During the course of experimentation it was learned that the charring step described in Example 1 is not necessary to make hard and adsorptive granular activated carbon. Two batches of identical material, treated in dilute aqueous acid solution as described above, were processed, one with a charring step and the other without. While the yields in specific process steps varied, the overall yield and activity of the granular activated carbon product were the same, indicating that the charring step can be eliminated for this material. This presumably was a result of the coal being subjected to the dilute aqueous acid solution treatment.

The devolatilized granules which had an apparent density of 0.60 gram/cc, were loaded

65

70

75

80

85

90

95

100

105

110

115

120

125

14

6

1,553,364

6

into a cylindrical furnace and subjected to activation by heating the granules to 800 to 900°C in an atmosphere composed of N<sub>2</sub> and steam, and by maintaining the granules at this temperature for 4 to 5 hours. The amount of steam fed into the furnace was precalibrated such that it amounted to 1 to 3 grams of steam/gram of charge/hour.

The resulting overall yield of granular activated carbon, based on the dry coal, was in the range of 25 to 28% by weight versus 20-22% for Example 1. The granules had a surface area of 900 to 1100 m<sup>2</sup>/gram, as compared to 900 to 1000 for Example 1, an iodine number of 1000, an ash content of 5 to 6% by weight, as compared to 7 to 10% for Example 1, an abrasion number of 70 as compared to 60-70 for Example 1, and an apparent density of 0.46 to 0.48 gram/cc, as compared to 0.455 to 0.48 for Example 1.

Thus, these granules were hard, very adsorptive, low in ash and in most respects comparable to the grades of granular activated carbon preferred for use in waste water treatment and other applications. Further, it is to be noted that not only can an acceptable granular activated carbon product be made from sub-bituminous coal without the use of any carbonaceous binder such as coal tar pitch, and without charring, but also that treatment with dilute aqueous acid solution significantly reduces the ash content while increasing yield and adsorption, all as compared to Example 1. It also is noteworthy that a hard granular activated carbon was prepared from sub-bituminous coal (with abrasion number of 70) for the first time without the use of a carbonaceous binder.

#### EXAMPLE 3

Dilute H<sub>3</sub>PO<sub>4</sub> treated Sub-Bituminous Coal Granules (without Pitch) in making Granular Activated Carbon

A batch of Wyoming sub-bituminous coal having the analyses described in Example 1 was crushed and screened to obtain 8×30 mesh granules, 300 grams of which were loaded into a 4 liter kettle. A dilute aqueous acid solution consisting of 150 cc. of 75% concentrated H<sub>3</sub>PO<sub>4</sub> and 2850 cc. of water was added to the granules (about 6.5% by weight). The granules and the acid solution were heated to 80°C and maintained at this temperature for 5 hours, while the granules were continuously stirred. The contents were allowed to cool, the solution decanted, and the granules were thoroughly rinsed such that wash water off the granules analyzed to a pH of 6 to 7. To complete the treatment, the washed granules were dried partially to an approximate moisture content of 15%, as in Example 2.

The treated granules containing roughly 15% by weight of moisture were milled into a very fine powder such that more than 65%

by weight of the material passed through 325 mesh screen (65% by weight -325 mesh), preferably 75 to 85% -325 mesh.

The powder was pressed into cylindrical pellets of 1/2 in. diameter and 1/2 in. long using a pressure of 40,000 to 80,000 psi. and the apparent density of the pellets was in the range 1.1 to 1.2 grams/cc. The pellets were regranulated to obtain 6×20 mesh granules which had an apparent density of 0.58 to 0.62 gram/cc.

The reformed granules were loaded into a cylindrical furnace and devolatilized as described in Example 1, but with no charring being necessary prior to such devolatilization. The devolatilized granules, which had an apparent density of 0.58 to 0.60 gram/cc, were activated in the manner also set forth in Example 1.

The overall yield of granular activated carbon, based on the dry coal was in the range of 26 to 30% by weight, versus 20 to 22% for Example 1 and 25 to 28% for Example 2. The granules had a surface area of 900 to 1100 m<sup>2</sup>/gram, versus 900 to 1000 for Example 1, an iodine number of 1000, an ash content of 5 to 6% by weight, as compared to 7 to 10% for Example 1, an abrasion number of 70, as compared to 60 to 70 for Example 1, and an apparent density of 0.48 to 0.50 gram/cc as compared to 0.45 to 0.48 for Example 1 and 0.46 to 0.48 for Example 2. The yield and apparent density properties were slightly higher than those observed in Example 2 (H<sub>2</sub>SO<sub>4</sub> treatment).

Thus, the resulting granules were hard, very adsorptive, low in ash, and in most respects comparable to the grades of granular activated carbon preferred for use in waste water treatment and other applications. It is to be noted once again that an acceptable product can be made from sub-bituminous coal without a carbonaceous binder and without charring, and that treatment with dilute aqueous acid solution significantly reduces ash content while increasing yield and adsorption, as compared to Example 1. As for using H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> as the acid in the aqueous solution, H<sub>3</sub>PO<sub>4</sub> is believed to be more effective in producing a granular activated carbon product with higher yield. As becomes evident, the exact amount of improvement in yield depends upon the specific leaching conditions and other process conditions employed.

#### EXAMPLE 4

Dilute H<sub>2</sub>SO<sub>4</sub> treated Sub-Bituminous Coal Granules (with Pitch) in making Granular Activated Carbon

The procedure of Example 2 was followed up to the drying step, but instead of drying partially to about 15% moisture the granules were dried thoroughly, and then, as shown on the right side of the drawing, the treatment was completed by mixing the granules

uniformly with a No. 125 coal tar pitch or any other pitch having the following properties:

|   |                      |                 |
|---|----------------------|-----------------|
|   | Softening Point      | 129.2°C         |
| 5 | Benzene Insolubles   | 33.2% by weight |
|   | Quinoline Insolubles | 13.1% by weight |
|   | Coking Value         |                 |
|   | (Conradson)          | 61.1% by weight |
|   | Ash                  | 0.17% by weight |

10 The thoroughly dried granules and pitch were mixed in the proportion of 90 grams coal and 10 grams pitch (i.e., 10 parts pitch per hundred parts coal, by weight), and this mixture milled into more than 65% by weight—325 mesh powder, preferably 75 to 85%—325 mesh, which powder was pressed into pellets of 1/2 in. diameter and 1/2 in. high using a pressure in the range of 40,000 to 80,000 psi. The bulk density of the pellets was in the range 1.1 to 1.2 grams/cc, and they were granulated to obtain granules of 6/20 mesh and having an apparent density of 0.68 gram/cc.

25 600 grams of the granules were loaded into a cylindrical container and were devolatilized according to the procedure described in Example 2, without the charring step. The devolatilized granules had an apparent density of 0.62 gram/cc and a yield of 60% by weight based on the dry coal-pitch mixture.

30 The devolatilized granules were loaded into a cylindrical furnace and subjected to activation as also set forth in Example 2.

35 The overall yield of granular activated carbon in this more preferred embodiment of the inventive process, based on the dry coal pitch mixture was in the range of 25 to 30% by weight compared to 20 to 22% for Example 1. The granules had a surface area of 1050 m<sup>2</sup>/gram, as compared to 900 to 1000 for Example 1, an iodine number of 1000 to 1100, as compared to 1000 for Examples 2 and 3, an ash content of 6% by weight, as compared to 7 to 10% for Example 1, an abrasion number of 80, as compared to 60 to 70 for Example 1, and 70 for Examples 2 and 3, and an apparent density of 0.48 to 0.50 gram/cc, as compared to 0.45 to 0.48 for Example 1 and 0.46 to 0.48 for Example 2.

50 Thus, the resulting granules were hard, very adsorptive, low in ash, and in all respects comparable to the grades of granular activated carbon preferred for use in waste water treatment and other applications. It is particularly noteworthy that, compared to the no acid and the charring approach of Example 1, the overall yield was considerably improved when the coal was subjected to treatment with an aqueous acid solution, followed by mixing with pitch, with no charring, while at the same time yielding a product that was superior in adsorption properties, density and abrasion resistance.

As for the H<sub>2</sub>SO<sub>4</sub> treatment no pitch procedure of Example 2, there was a slight increase in adsorption (iodine number) and a significant increase in abrasion resistance and apparent density. With respect to the H<sub>3</sub>PO<sub>4</sub> treatment no pitch procedure of Example 3, there was a slight increase in adsorption (iodine number) and a significant increase in abrasion resistance.

#### EXAMPLE 5

Dilute H<sub>3</sub>PO<sub>4</sub> treated Sub-Bituminous Coal (with Pitch) making Granular Activated Carbon

The same procedure, as set forth in Example 4 was followed, except that 75% concentrated H<sub>3</sub>PO<sub>4</sub> was substituted for the H<sub>2</sub>SO<sub>4</sub> (making the acid about 6.5% by weight of the granules). The apparent density of the reformed compacted granules was 0.65 gram/cc instead of 0.68, while the devolatilized granules had an apparent density of 0.59 to 0.61 gram/cc instead of 0.62, and a yield of 60 to 65% by weight, based on the dry coal pitch mixture instead of 60%.

The overall yield of granular activated carbon in this most preferred embodiment of the inventive process, based on the dry coal pitch mixture was in the range of 30 to 33% by weight, as compared to 20 to 22% for Example 1, 25 to 28% for Example 2, 26 to 30% for Example 3, and 25 to 30% for Example 4. The granules had a surface area of 1050 m<sup>2</sup>/gram, as compared to 900 to 1000 for Example 1, an iodine number of 1000 to 1100, as compared to 1000 for Examples 2 and 3, an ash content of 6% by weight, as compared to 7 to 10% for Example 1, an abrasion number of 80, as compared to 60 to 70 for Example 1, and 70 for Examples 2 and 3, and an apparent density of 0.48 to 0.50 gram/cc, as compared to 0.45 to 0.48 for Example 1 and 0.46 to 0.48 for Example 2.

Thus, the resulting granules were hard, very adsorptive, low in ash and in all respects comparable to the grades of carbon preferred for use in waste water treatment and other applications. It is particularly noteworthy that the overall yield was considerably improved, not only over Example 1, but also over each of Examples 2, 3 and 4, with a substantial increase in adsorption, purity, abrasion resistance, and density over Example 1. Likewise, there was a significant increase in abrasion resistance over Examples 2 and 3, and a significant increase in density over Example 2.

This improved yield of hard, dense, adsorptive granular activated carbon, obtained by treating sub-bituminous coal with a dilute aqueous solution of H<sub>3</sub>PO<sub>4</sub>, is indeed an unexpected result over the art. Further, such improved yield is believed to be comparable to that obtainable from the higher valued bitu-

minous coal, the traditionally preferred raw material. More importantly, such unexpected result is achieved by eliminating the charring step believed to be necessary in the use of bituminous coal.

The next two Examples represent an endeavour to see what happens when bituminous coal is treated in accordance with the inventive process, first without dilute acid treatment (Example 6) and second with dilute acid treatment (Example 7).

#### EXAMPLE 6

##### Use of Bituminous Coal and Pitch to Make Granular Activated Carbon

The starting material was a batch of eastern bituminous coal having the following analyses by weight:

#### Proximate Analysis

|                     | As Received | Dry    |
|---------------------|-------------|--------|
| % Moisture          | 2.04        | —      |
| % Ash               | 1.20        | 1.26   |
| % Volatile Material | 33.10       | 33.80  |
| % Fixed Carbon      | 63.60       | 64.90  |
| BTU/lb              | 14,571      | 14,874 |

#### Ultimate Analysis

|                  | As Received | Dry   |
|------------------|-------------|-------|
| % Moisture       | 2.04        | —     |
| % Carbon         | 82.30       | 84.00 |
| % H              | 5.20        | 5.29  |
| % N <sub>2</sub> | 1.30        | 1.33  |
| % S              | 0.34        | 0.35  |
| % Ash            | 1.23        | 1.26  |

These analyses are, in general, typical of eastern bituminous coals. These coals also are highly coking and low in ash content. The dried coal was crushed to obtain 8×30 mesh granules which were mixed with No. 125 coal tar pitch of the type described in Examples 4 and 5, and in the ratio of 90 grams of coal granules and 10 grams of pitch (10 parts per hundred by weight).

The mixture was milled into very fine powder so that 65% of the powder passed through 325 mesh screen. The milled powder was compressed into pellets 1/2 in. diameter and 1/2 in. high using a pressure of 40,000 to 80,000 psi. The pellets had a bulk density of 1.18 grams/cc and were granulated to obtain 6×20 mesh granules having an apparent density of 0.65 gram/cc.

600 grams of the granules were loaded into a cylindrical furnace and were subjected to the charring process substantially as described in Example 1. However, in this case, the charring consisted of heating the granules from room temperature to 250°C at 100 deg. C/hour and maintaining at temperature for 2 hours. An atmosphere of 0.5 standard cubic

feet per hour at 1 atmosphere and room temperature (SCFH) of N<sub>2</sub> and 0.5 SCFH of air was fed into the furnace while the cylindrical container was rotating at 1 to 4 rpm.

In the course of experimentation it was found that heating rate, atmosphere (particularly the amount of oxygen present), temperature and time at temperature were critical variables that had an important influence on how the granules were suited for further processing in making hard granular activated carbon. For example, too small a time (less than 1/2 hour) at temperature or too low a temperature (lower than 200°C), in general, led to difficulties in further processing of the granules. Thus, without proper charring, during the devolatilization step, the granules fused together and were unsuitable for proper activation and for obtaining the desired properties of granular activated carbon.

When properly charred, as described above, the yield of the granules was 69% by weight, based on the dry coal pitch mixture and they had an apparent density of 0.62 gram/cc.

The charred granules then were devolatilized and activated in the same manner as described in Example 1.

At the end of the process, hard granular activated carbon was obtained, with an overall yield of 34.0% by weight based on the dry coal pitch mixture. The granules had an apparent density of 0.50 gram/cc, an iodine number of 1080, a surface area of 1040, an ash content of 2.2% by weight, and an abrasion number of 80.

Thus, the resulting granules were hard, very adsorptive, low in ash, and in all respects very much comparable to the grades of carbon preferred for use in waste water treatment and other applications. However, it is particularly noteworthy that hard granular activated carbon would not be made from this bituminous coal without subjecting the granules to the charring step described above, prior to devolatilization and activation. During the course of experimentation, granules were devolatilized without the charring step and a fused mass (instead of granules) unsuitable for activation was obtained, thus indicating the necessity and importance of the charring step.

#### EXAMPLE 7

##### Dilute H<sub>3</sub>PO<sub>4</sub> Treated Bituminous Coal and Pitch to make Granular Activated Carbon

The same procedure, as set forth in Example 6, was followed through the initial granulating step. At this point, 300 grams of the coal granules were loaded into a 5 liter kettle. A dilute aqueous acid solution consisting of 150 grams of 75% concentrated H<sub>3</sub>PO<sub>4</sub> and 2850 grams of water was added to the granules (about 6.5% by weight). The mixture was heated to 80°C and maintained at this temperature for 5 hours, while the

granules were continuously stirred. The contents were allowed to cool, acid solution decanted and the coal was thoroughly washed such that the wash water off the granules analyzed to a pH of 6 to 7.

The treated coal was dried thoroughly, and then was mixed uniformly with the coal tar pitch of Example 4 in the same proportions of 90 grams coal and 10 grams pitch. The mixture was milled into 65% by weight -325 mesh powder, and was pressed into pellets of 1/2 in. diameter and 1/2 in. high using a pressure in the range of 40,000 to 80,000 psi. The bulk density of the pellets was in the range 1.1 to 1.2 grams/cc, and they were regranulated to obtain 6×20 mesh granules having an apparent density at this stage of 0.64 gram/cc.

The reformed granules were loaded into a cylindrical furnace and were subjected to the charring step described in Example 6, producing a 71% by weight yield and an apparent density of 0.63 gram/cc. In the course of experimentation, it was learned that, even for acid treated bituminous coal, the charring step was necessary as a pre-treating step, in order to obtain proper granular activated carbon.

The charred granules then were devolatilized and activated in the manner described in Example 1.

At the end of the activation step, hard granular activated carbon was obtained, with an overall yield of 35% by weight based on the dry coal pitch mixture. The granules had an apparent density of 0.50 gram/cc, a surface area of 1000 m<sup>2</sup>/gram, an iodine number of 1050; an ash content of 2.4% by weight, and an abrasion number of 82.

Thus, the granules were hard, very adsorptive, low in ash and in all respects very much comparable to the grades of carbon preferred for use in waste water treatment and other applications. At the same time, it is particularly noteworthy that hard granular activated carbon could not be made from this bituminous coal without subjecting the granules to the charring step described above, even though the coal had been dilute acid treated. In this regard, the result is very much unlike that for sub-bituminous coal, wherein acid treatment enables one to eliminate the charring step, while still producing an acceptable product.

Another important and notable feature was that the acid treatment of bituminous coal with dilute H<sub>3</sub>PO<sub>4</sub> did not appear to significantly alter the yield (from 34 to 35%). In contrast, this result was very much unlike that for the sub-bituminous coal of Example 5 wherein dilute H<sub>3</sub>PO<sub>4</sub> acid treatment of the coal led to substantially improved yield from the 20 to 22% for Example 1 to the 30 to 33% of Example 5, which closely approximates the 34 and 35% yields of these last

two examples. These two results were indeed unique and unexpected in dealing with sub-bituminous coal.

The next Example represents an attempt to apply the dilute acid treatment technique of the invention to lignite, which ranks lower than sub-bituminous coal.

#### EXAMPLE 8

Dilute H<sub>3</sub>PO<sub>4</sub> Treated Lignite Coal (with Pitch) in making Granular Activated Carbon

The starting material in this Example was a batch of lignite coal having the following analyses by weight:

#### Proximate Analysis

|                     | As Received | Dry  |
|---------------------|-------------|------|
| % Moisture          | 30.3        | —    |
| % Ash               | 9.9         | 14.2 |
| % Volatile Material | 50.0        | 71.7 |
| % Fixed Carbon      | 9.8         | 14.0 |

#### Ultimate Analysis

|                  | As Received | Dry  |
|------------------|-------------|------|
| % Moisture       | 30.30       | —    |
| % Carbon         | 41.50       | 59.5 |
| % H              | 3.15        | 4.5  |
| % N <sub>2</sub> | 3.50        | 5.0  |
| % S              | 0.73        | 1.4  |
| % Ash            | 9.90        | 14.2 |

These analyses are, in general, typical of lignite type coals, and these coals, in general, have a high ash content compared to other coals. The as received coal was crushed to 8×30 mesh granules and 300 grams of these granules were loaded into a 4 liter kettle and 150 cc of concentrated H<sub>3</sub>PO<sub>4</sub> (75%) and 2850 cc of water were added (6.5% by weight of acid). The granules and the acid solution were heated to 80°C and maintained at this temperature for 5 hours, while the granules were continuously stirred. The contents were allowed to cool, the solution decanted, and the granules were thoroughly rinsed such that the wash water off the granules analyzed to a pH of 6 to 7. The granules were dried thoroughly and mixed into 10 parts per hundred of coal tar pitch of the type described in Examples 3 and 4.

This mixture was thoroughly milled such that more than 65% of the powder material passed through 325 mesh screen, preferably 75 to 85% -325 mesh. The powder was pressed into cylindrical pellets of 1/2 in. diameter and 1/2 in. high, using a pressure of 40,000 to 80,000 psi, the apparent density of the pellets being in the range of 1.1 to 1.2 grams/cc. The pellets were granulated to obtain 6×20 mesh granules having an apparent density of 0.64 to 0.66 gram/cc.

The granules were loaded into a cylindrical furnace and were devolatilized as described in Example 1. Two batches of granules with identical processing were devolatilized; one with a charring step, as described in Example 1 and the other without a charring step, as described in Examples 2 to 5. The two batches were similar in regard to the overall yields and activity, indicating that the charring step is not a necessary requisite for this type of coal.

The devolatilized granules were activated as in Examples 1 to 5. The granules had very low apparent density, of 0.30 gram/cc, a surface area of 850, an iodine number of 900, an ash content of 11.5% by weight, and an abrasion number of 30. Repeated experiments to optimize the properties, while showing some improvement, did not produce the preferred required density of 0.48 gram/cc or higher, and abrasion number of 70 or higher. Thus, an acceptable granular activated carbon which is hard and suitable for waste water applications could not be produced under the aforementioned conditions from lignite coal.

Thus, it is patently obvious from this and the foregoing examples that:

A. Treating a bituminous coal in dilute aqueous acid solution did not materially affect the processability of the coal into hard granular carbon or the present yield of the said carbon from coal, and the dilute acid treatment step did not eliminate the necessity of a charring step.

B. Treating a lignite coal in dilute aqueous acid solution did not result in an acceptable granular activated carbon where the carbon from lignite was too light and too soft.

C. In contrast, it clearly has been demonstrated in the preferred inventive embodiments that hard granular carbons suitable for waste water and other applications can be produced from sub-bituminous coal for the first time, provided the said coal is subjected to treatment in dilute aqueous acid solution (because very hard granular activated carbon can not be produced from the untreated sub-bituminous coal), and that such treatment does result in an unexpected and hence an inventive result of high percent yield of granular activated carbon from sub-bituminous coal, where the yield is fairly comparable to that from bituminous coal, particularly comparing Example 5 with Examples 6 and 7.

D. Another indeed unexpected result of the treatment of sub-bituminous coal in dilute aqueous acid solution is that the charring step found necessary for treated and untreated bituminous coal and for untreated sub-bituminous coal can be eliminated in making hard, dense, adsorptive granular activated carbons from treated sub-bituminous coal.

The next Example is similar to Example 5, but emphasizes the importance of fineness

of grind in powderizing the treated granules before pelletizing.

#### EXAMPLE 9

Fineness of Powder in Using Dilute  $H_3PO_4$  Treated sub-Bituminous Coal (with Pitch) in making Granular Activated Carbon

The same procedure, as set forth in Example 5, and as illustrated at the middle right in the drawing, was followed. The treated granules were washed with wash water, analyzed to a pH of 6 to 7 and dried thoroughly before mixing with 10 parts per hundred by weight of No. 125 coal tar pitch. Then the mixture was divided into 2 equal parts.

The first part was milled to a fine powder which was about 60 to 65% by weight - 325 mesh. The powder was compacted into pellets of approximately 1/2 in. high and 1/2 in. diameter under a pressure of 40,000 to 80,000 psi, and the apparent density of the pellets was in the range of 1.1 to 1.2 gram/cc. The pellets were granulated, to 6 by 20 mesh and the density of the granules was 0.64 to 0.66 gram/cc. The granules were devolatilized as in Example 5 and the density of granules was 0.57 to 0.59 gram/cc. These granules were activated as described in earlier Examples 1 and 5, and these activated granules had a density of 0.44 to 0.47 gram/cc, an iodine number of 1000 to 1100, a surface area of 900 to 1050  $m^2$ /gram, ash content of 5 to 6% by weight and an abrasion number of 55 to 65. Thus, these granules are considerably softer and hence are not too suitable for use in waste water applications, because of possible excessive loss of material in use and regeneration when the granules are not very hard.

The second part was milled to a very fine powder such that it had a particle size of 75 to 85% by weight - 325 mesh. The powder was compacted, as above, to a pellet density of 1.1 to 1.2 gram/cc; the pellets were granulated and had a density of 0.65 to 0.68 gram/cc. The granules were devolatilized as in Example 5 and the density of granules was 0.60 to 0.62 gram/cc. The granules were activated, as above, and the apparent density of the activated granules was 0.48 to 0.50 gram/cc. The granules had an iodine number of 1000 to 1100, surface area of 900 to 1050  $m^2$ /gram, ash content of 5 to 6% by weight and an abrasion number of 80.

Since the granules were subjected otherwise to identical processing conditions in part 1 and part 2, it is believed that the finer grinding of the treated sub-bituminous coal granules (75 to 85% - 325 mesh) resulted in compact granules and hence a hard granular product. In contrast, as described in Examples 6 and 7, grinding the bituminous coal to 65% - 325 mesh resulted in a hard granular product.

Thus, the fineness of the grind prior to compaction, required for sub-bituminous coal, as compared to bituminous coal, is an unexpected requirement which could not have been deduced from prior art, and hence forms a preferred embodiment of the present invention.

The next, and last Example represents the workability of HCl as the dilute aqueous acid in the inventive technique.

#### EXAMPLE 10

Dilute HCl Treated Sub-Bituminous Coal (with Pitch) in making Granular Activated Carbon

A batch of Wyoming sub-bituminous coal having the typical analyses described in Example 1 was crushed and screened to obtain 8×30 granules. 300 grams of the granules were loaded into a 4 liter kettle and a dilute aqueous acid solution consisting of 300 cc of 37.5% concentrated HCl and 2700 cc of water was added to the granules (about 5% by volume and 6.5% by weight). The granules and the acid solution were heated to 80°C and maintained at this temperature for 5 hours, while the granules were continuously stirred.

The contents of the kettle were allowed to cool, the solution decanted and the granules thoroughly rinsed such that the waste water off the granules analyzed to a pH of 6 to 7. The granules were dried either: (A) to 15% moisture, where further processed without a carbonaceous binder, as in Examples 2 and 3, to a granular activated carbon product, or (B) to complete dryness, where 10 parts per hundred of pitch were added and processed as in Examples 4 and 5.

The coal or coal pitch mixture was milled to a very fine size, such that more than 65% of the material passed through 325 mesh, preferably 75 to 85% of material passed through 325 mesh. The powder was pressed into cylindrical pellets of 1/2 in. diameter and 1/2 in. high using pressure of 40,000 to 80,000 psi; the apparent density of the pellets being in the range 1.1 to 1.2 gram/cc. These pellets were regranulated to 6×20 mesh having an apparent density of 0.60 to 0.65 gram/cc, and these granules were devolatilized, without charring, and activated, as in Examples 2 to 5.

(A) The resulting overall yield of granular activated carbon, based on dry coal (pitchless), was 25 to 28% by weight. The granules had a surface area of 900 to 1100 m<sup>2</sup>/gram, an iodine number of 1000 to 1100, an ash content of 5 to 7%, by weight, an abrasion number of 70 and an apparent density of 0.46 gram/cc. Compared to Example 1, the yield, adsorption and abrasion resistance were significantly increased, while the ash content was significantly decreased. Compared to Examples 2 and 3, the yield and other properties

were comparable to Example 2 (H<sub>2</sub>SO<sub>4</sub>), while the yield and apparent density were slightly less than for Example 3 (H<sub>3</sub>PO<sub>4</sub>).

(B) The resulting overall yield of granular activated carbon, based on the dry coal pitch mixture, was 25 to 30% by weight, and the granules had a surface area of 900 to 1100 m<sup>2</sup>/gram, an iodine number of 1000 to 1100, an ash content of 5 to 7% by weight, an abrasion number of 80, and an apparent density of 0.48 gram/cc. Compared to Example 1, the yield, abrasion number and apparent density were significantly increased. As compared to Examples 2 and 3 and (A) above (pitchless), the abrasion resistance was significantly increased, and the yield and apparent density were slightly increased over Example 2 and (A) above. As compared to Examples 4 and 5, the yield was slightly less than for Example 4 (H<sub>2</sub>SO<sub>4</sub> with pitch), and significantly less than for Example 5 (H<sub>3</sub>PO<sub>4</sub> with pitch).

However, in each of (A) and (B) above, as compared to Example 1, treating the sub-bituminous coal with a dilute aqueous solution of HCl resulted in higher yield and improved adsorption, greater abrasion resistance and higher purity, making such inventive product suitable for use in waste water treatment and other applications, while at the same time eliminating the need for the charring step.

It now is seen how the invention accomplishes its various objectives. Likewise, it is to be understood that while the invention has been described and illustrated herein by reference to certain preferred embodiments, the same are to be considered as illustrative, rather than as limiting.

#### WHAT WE CLAIM IS:—

1. A process for making hard granular activated carbon comprising:

forming granules from sub-bituminous coal; treating the granules with a dilute aqueous solution of inorganic acid, washing off the acid, and drying the mashed granules at least partially to a moisture content below 25% by weight;

optionally mixing the dried granules with up to 15% by weight of a carbonaceous binder;

reducing the dried granules to form fine powder;

compressing the powder;

reducing the compressed powder to reform granules;

devolatilizing the reformed granules, without charring, by heating to and at a temperature higher than the charring temperature in an oxygen-free atmosphere; and

activating the devolatilized granules by heating to and at a temperature higher than the devolatilizing temperature in an atmosphere containing a gaseous activating agent.

19



\* C L M S \*

11

1,553,364

11

Thus, the fineness of the grind prior to compaction, required for sub-bituminous coal, as compared to bituminous coal, is an unexpected requirement which could not have been deduced from prior art, and hence forms a preferred embodiment of the present invention.

The next, and last Example represents the workability of HCl as the dilute aqueous acid in the inventive technique.

#### EXAMPLE 10

Dilute HCl Treated Sub-Bituminous Coal (with Pitch) in making Granular Activated Carbon

A batch of Wyoming sub-bituminous coal having the typical analyses described in Example 1 was crushed and screened to obtain 8×30 granules. 300 grams of the granules were loaded into a 4 liter kettle and a dilute aqueous acid solution consisting of 300 cc of 37.5% concentrated HCl and 2700 cc of water was added to the granules (about 5% by volume and 6.5% by weight). The granules and the acid solution were heated to 80°C and maintained at this temperature for 5 hours, while the granules were continuously stirred.

The contents of the kettle were allowed to cool, the solution decanted and the granules thoroughly rinsed such that the waste water off the granules analyzed to a pH of 6 to 7. The granules were dried either: (A) to 15% moisture, where further processed without a carbonaceous binder, as in Examples 2 and 3, to a granular activated carbon product, or (B) to complete dryness, where 10 parts per hundred of pitch were added and processed as in Examples 4 and 5.

The coal or coal pitch mixture was milled to a very fine size, such that more than 65% of the material passed through 325 mesh, preferably 75 to 85% of material passed through 325 mesh. The powder was pressed into cylindrical pellets of 1/2 in. diameter and 1/2 in. high using pressure of 40,000 to 80,000 psi; the apparent density of the pellets being in the range 1.1 to 1.2 gram/cc. These pellets were regranulated to 6×20 mesh having an apparent density of 0.60 to 0.65 gram/cc, and these granules were devolatilized, without charring, and activated, as in Examples 2 to 5.

(A) The resulting overall yield of granular activated carbon, based on dry coal (pitchless), was 25 to 28% by weight. The granules had a surface area of 900 to 1100 m<sup>2</sup>/gram, an iodine number of 1000 to 1100, an ash content of 5 to 7% by weight, an abrasion number of 70 and an apparent density of 0.46 gram/cc. Compared to Example 1, the yield, adsorption and abrasion resistance were significantly increased, while the ash content was significantly decreased. Compared to Examples 2 and 3, the yield and other properties

were comparable to Example 2 (H<sub>2</sub>SO<sub>4</sub>), while the yield and apparent density were slightly less than for Example 3 (H<sub>3</sub>PO<sub>4</sub>).

(B) The resulting overall yield of granular activated carbon, based on the dry coal pitch mixture, was 25 to 30% by weight, and the granules had a surface area of 900 to 1100 m<sup>2</sup>/gram, an iodine number of 1000 to 1100, an ash content of 5 to 7% by weight, an abrasion number of 80, and an apparent density of 0.48 gram/cc. Compared to Example 1, the yield, abrasion number and apparent density were significantly increased. As compared to Examples 2 and 3 and (A) above (pitchless), the abrasion resistance was significantly increased, and the yield and apparent density were slightly increased over Example 2 and (A) above. As compared to Examples 4 and 5, the yield was slightly less than for Example 4 (H<sub>2</sub>SO<sub>4</sub> with pitch), and significantly less than for Example 5 (H<sub>3</sub>PO<sub>4</sub> with pitch).

However, in each of (A) and (B) above, as compared to Example 1, treating the sub-bituminous coal with a dilute aqueous solution of HCl resulted in higher yield and improved adsorption, greater abrasion resistance and higher purity, making such inventive product suitable for use in waste water treatment and other applications, while at the same time eliminating the need for the charring step.

It now is seen how the invention accomplishes its various objectives. Likewise, it is to be understood that while the invention has been described and illustrated herein by reference to certain preferred embodiments, the same are to be considered as illustrative, rather than as limiting.

#### WHAT WE CLAIM IS:—

1. A process for making hard granular activated carbon comprising:
  - forming granules from sub-bituminous coal;
  - treating the granules with a dilute aqueous solution of inorganic acid, washing off the acid, and drying the mashed granules at least partially to a moisture content below 25% by weight;
  - optionally mixing the dried granules with up to 15% by weight of a carbonaceous binder;
  - reducing the dried granules to form fine powder;
  - compressing the powder;
  - reducing the compressed powder to reform granules;
  - devolatilizing the reformed granules, without charring, by heating to and at a temperature higher than the charring temperature in an oxygen-free atmosphere; and
  - activating the devolatilized granules by heating to and at a temperature higher than the devolatilizing temperature in an atmosphere containing a gaseous activating agent.

2. A process as claimed in claim 1 wherein the coal has a moisture content of 10 to 25% by weight and an ash content of not more than 5% by weight.
- 5 3. A process as claimed in claim 1 or 2, wherein the acid is selected from  $H_2SO_4$ ,  $H_3PO_4$ , HCl and mixtures thereof at a concentration of from 1 to 50% by weight and the aqueous solution to coal ratio of at least
- 10 2/1 by weight.
4. A process as claimed in claim 3 wherein the acid is  $H_3PO_4$ .
5. A process as claimed in claim 3 or 4, wherein the acid concentration is from 1 to
- 15 20% by weight and the aqueous solution to coal ratio is at least 4/1 by weight.
6. A process as claimed in claim 5 wherein the acid concentration is 6.5% by weight and the aqueous solution to coal ratio is 10/1
- 20 by weight.
7. A process as claimed in any one of claims 1 to 6 wherein no carbonaceous binder is used.
- 25 8. A process as claimed in any one of claims 1 to 6, wherein the dried granules are mixed with 5 to 15% by weight of a carbonaceous binder.
9. A process as claimed in claim 8, wherein the carbonaceous binder is pitch.
10. A process as claimed in any one of claims 1 to 9 wherein the fine powder is more than 65% by weight — 325 mesh.
11. Hard granular activated carbon when obtained by the process of any one of claims 1 to 10.
12. Hard granular activated carbon as claimed in claim 11 having an abrasion number of not less than 70.
13. Hard granular activated carbon as claimed in claim 12 having an abrasion number of not less than 80.
14. A process as claimed in claim 1 for producing hard granular activated carbon substantially as hereinbefore described in any one of Examples 2—5, 9 or 10.

## MARKS &amp; CLERK,

7th Floor,  
Scottish Life House,  
Bridge Street,  
Manchester, M3 3DP.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

