



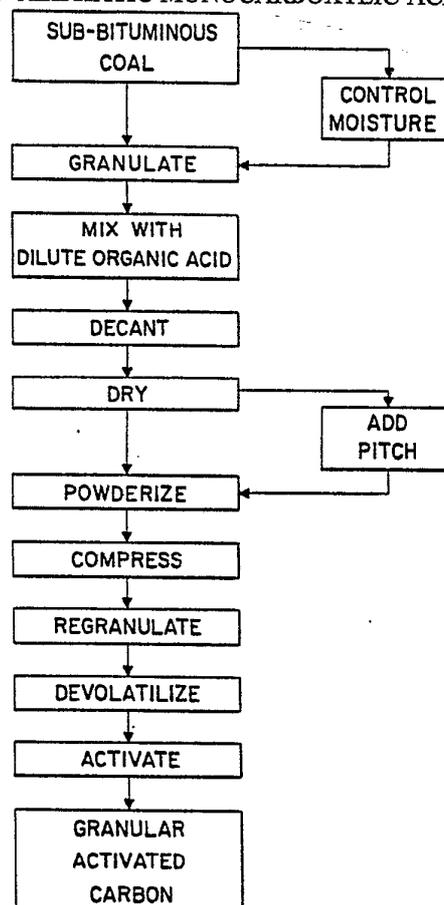
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(54) Title: HARD GRANULAR ACTIVATED CARBON MANUFACTURED FROM SUB-BITUMINOUS COAL TREATED WITH DILUTE SOLUTION OF SATURATED ALIPHATIC MONOCARBOXYLIC ACID

(57) Abstract

Hard granular activated carbon, suitable for liquid phase applications such as water and waste water treatment, is manufactured from sub-bituminous coal by crushing and screening the as received coal containing about 10 to about 25% moisture by weight to produce granules, treating the granules with a dilute aqueous solution of a saturated aliphatic monocarboxylic acid such as formic or acetic acid, at a concentration of about 2% to about 30% by weight, the concentration being increased as the acid strength decreases, for a time and at a temperature and solution to coal ratio sufficient for further processing, decanting the acid, and drying the granules at least partially to a moisture, including acid, content below about 25% by weight. The dried granules are mixed with from 0 to about 15% by weight of coal tar pitch, and are milled to form fine powder of not less than about 60% by weight -325 mesh, preferably more than about 65% by weight -325 mesh. The powder is compressed into shapes, such as pellets or thin corrugated sheets under high pressure, and then granulated to form 6/20 mesh granules. The reformed granules are devolatilized, without prior charring, by directly heating to and at a temperature higher than the charring temperature in a substantially oxygen-free atmosphere, and then activated by heating to and at a temperature higher than the devolatilizing temperature in an atmosphere containing a gaseous activating agent.



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HARD GRANULAR ACTIVATED CARBON MANUFACTURED
FROM SUB-BITUMINOUS COAL TREATED WITH
DILUTE SOLUTION OF SATURATED
ALIPHATIC MONOCARBOXYLIC ACID

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BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to granular activated carbon manufacture, and more particularly to a new and improved process for making hard granular activated carbon from sub-
10 bituminous coal treated with dilute solution of saturated aliphatic monocarboxylic acid, and to a new and improved hard granular activated carbon made by such process and having properties which make it suitable for use in liquid phase applications such as water and waste water treatment.

15 Glossary of Terms

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
20 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 abra-
25 sion number is the ratio of the final average (mean) particle



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diameter to the original average (mean) particle diameter (determined by screen analysis) times 100.

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

Activation or activating - means heating coal at high temperatures on the order of about 600°C. to about 1100°C. in the presence of a gaseous activating agent, as is well known in the art. The heating rate during activation from the minimum activation temperature to the maximum activation temperature may vary widely, e.g., from about 100 to about 1000°C. per hour, but usually is nearer 100°C. per hour.

Adsorption isotherm - is a measurement of the adsorptive capacity of an adsorbent (viz. granular activated carbon) as a function of the concentration, or pressure, of the adsorbate (viz. N₂) at a given temperature. It is defined as the constant temperature relationship between the amount adsorbed per unit weight of adsorbent 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 principal 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



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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. It usually is expressed in mm.

Carbon tetrachloride activity number - is the steady state percentage increase in the weight of a bed of activated carbon after air which has been saturated with carbon tetrachloride at 0°C. is passed through the carbon at 25°C. It is expressed as a percentage number.

Charring - means heating coal at low temperatures on the order of about 175°C. to about 275°C. in the presence of oxygen.

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.

Devolatilizing - means heating coal at intermediate temperatures on the order of about 400°C. to about 600°C. in an oxygen-free atmosphere.

Direct activation or directly activating - means heating a coal, preferably in a granular form, directly (without prior charring and devolatilization) and rapidly (at a heating rate of about 500°C. per hour or more) to an activating temperature higher than the devolatilization temperature (of the order of 600° to 1100°C.) in an atmosphere containing a gaseous activating agent and maintaining the desired activating temperature for the desired period of time.



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Granular activated carbon - is "activated carbon" which has a particle size, i.e., "mesh", which is not less than about 60 and preferably not less than about 40.

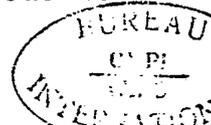
Iodine number - is the milligrams of iodine adsorbed by one gram of granular activated carbon at an equilibrium filtrate concentration of 0.02 N iodine. It is measured by contacting a single sample of carbon with an iodine solution and extrapolating to 0.02 N by an assumed isotherm slope. This number can be correlated with the ability of granular activated 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 or 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 x 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. Likewise, 6/0 mesh means that 90% by weight will pass through a No. 6 screen, with no lower limit on granular size. 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.

Molasses number - is calculated from the ratio of the optical densities of the filtrate of a molasses solution treated with a standard activated carbon and the activated carbon in question.

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

Powder - means powdered activated carbon which has a particle size, i.e., "mesh", which is smaller than about 40



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and preferably smaller than about 60. The larger the mesh number, the smaller the size.

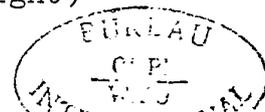
Sub-bituminous coal - is an intermediate stage coal which ranks above lignite and brown coals, but below bituminous coal. In the as received condition it has, by weight, (1) a proximate analysis of: from about 10% to about 25% moisture, from about 35% to about 45% volatile material, from about 2% to 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. See ASTM Standard D-388-66.

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^2 /gram.

Volumetric Iodine and Molasses Numbers - are determined by multiplying by the apparent density, in order to express these properties independently of such density.

20 Discussion of the Art

Granular activated carbon is particularly useful in liquid phase applications, such as water and waste water treatment, not only because it is highly effective in purifying the intake, as well as the effluent from municipal and industrial systems but also because it can be regenerated for repeated use. In order to accomplish these objectives, however, it must possess certain properties, namely, a minimum surface area of about $900 m^2$ /gram for adequate adsorption capacity, a minimum volumetric Iodine number of about 410, preferably about 480, for adequate adsorption, especially of low molecular weight substances, a minimum volumetric Molasses number of about 90, preferably about 100, for adequate decolorizing, a maximum ash content (by weight)



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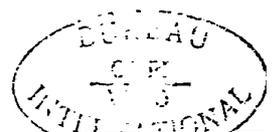
of not more than about 12%, and preferably not more than about 8%, for purity, a minimum abrasion number of about 70 and preferably not less than about 80, for adequate hardness in maintaining granular integrity in use and in regeneration, 5 and a minimum apparent density of not less than about 0.46 gram/cc, preferably not less than about 0.48 gram/cc, for obtaining the dense, closely packed beds and columns needed in water and waste water treatment.

Hard granular activated carbon can be obtained from 10 bituminous, sub-bituminous and brown coals, such as disclosed in U.S. Patents 4,144,193, 4,032,476, 4,131,566, 4,149,994, 4,149,995, and 4,157,314.

However, in each of these patents, inorganic mineral acids were employed, and until the present invention, it was 15 not known that anyone else had accomplished this objective by a saturated aliphatic monocarboxylic acid treatment of sub-bituminous coal.

In the '193, '566, '994 and '314 patents, a dilute aqueous solution of inorganic mineral acid was employed, re- 20 quiring removal of the acid prior to further processing, in order to avoid corrosion of the heat treating equipment. In the '476 and '995 patents, a small amount of concentrated mineral acid was mixed with the coal granules, thereby eliminating the acid removal step, but requiring special lining 25 of the heat treating equipment in order to avoid the corrosive action of the acid.

As for the heat treatment itself, each of the aforesaid patents, except the '566 patent, discloses the elimination of the charring or low temperature heat oxidation step found 30 to be necessary in dealing with bituminous coal. In the '566 patent, both the acid treatment and charring steps were found to be necessary for attaining the desired results when treating low rank agglomerating but not good coking bituminous



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the '314 patent, it has been found that both the charring and devolatilization steps could be eliminated prior to the activation step in heat treating the sub-bituminous granules. Likewise, the disclosures of U.S. Patents 3,483,134, 5 3,876,505, and 4,014,817 are of interest, but each discloses the necessity for the charring or low temperature heat oxidation step, and none discloses a hard granular activated carbon product.

Various organic compositions have been added to coal to 10 facilitate its conversion into activated carbon. Pitch, which is a complex mixture of organic materials, has long been a well-known additive, e.g., see U.S. Patent 3,539,467. U.S. Patent 3,483,134 discloses the addition of a volatilizable organic material such as an aldehyde, amino compound, cereal 15 grain, or plant material to bituminous coal to facilitate activated carbon production, but, as noted above, does not produce a hard product. U.S. Patent 3,864,277 discloses the addition of lignosulfonate as a binder to transform soft, woody materials into activated carbon. In addition, Canadian 20 Patent 906,754 teaches the preparation of activated low grade coal (not carbon) by treatment with spent industrial acids including mineral and/or organic acids. However, only aromatic organic compounds are mentioned for admixture with mineral acids.

25 Therefore, while various organic additives and binders have long been utilized in the art, no one else has utilized saturated aliphatic monocarboxylic acids as treating agents for the production of hard granular activated carbon from sub-bituminous coal according to the process of this invention.

30

SUMMARY OF THE INVENTION

It is to be understood that coals are composed essentially of organic carbonaceous materials of varying volatiles together with portions of inorganic salts and other compounds. The object of processes for the formation of



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activated carbon is to produce carbon in an active form within a suitable physical environment - that is, with a suitable pore size, density and hardness. It is highly desirable that the ash content be as small a percentage of the total mass of product as is possible, this to improve the physical characteristics of said product. The ash, which arises primarily from the inorganic material present in the starting coal, may be minimized either by removal of the inorganic materials prior to activation or by increasing the overall proportion of carbonaceous materials retained in the product during the course of its production.

It is believed that the inorganic mineral acid treatment taught by certain of the patents referred to above serves to fix relatively volatile carbonaceous materials of the starting material coal in a relatively non-volatile form, thus minimizing loss of carbonaceous material via volatilization during the course of production. The salutary properties and yield resulting from the inorganic treatment are thought to be directly attributable, at least in part, to this fixation effect.

Viewing the inorganic acids used in the aforementioned treatment processes as being inorganic materials from which ash may form, makes it clear that removal thereof prior to further production is essential to a minimization of ash content in the product. The often elaborate washing procedure which is necessary to effect this removal adds measurably to the cost of production. In addition, subsequent drying of the washed coal is hindered by the residual inorganic acid.

The use of saturated aliphatic monocarboxylic organic acids, as taught by this invention, offers salutary benefits to the production of granular activated carbon from sub-bituminous coal. These organic acids are believed to be as effective in fixing volatile carbonaceous materials of sub-bituminous coal as are inorganic acids, but such organic acids do not require elaborate washing procedures prior to

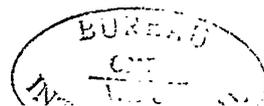


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further processing. Furthermore, due to the fact that these organic acids are carbonaceous materials in their own right, and are not inorganic, failure to remove the totality of the treating organic acid will not lead to a significant increase
5 in the ash content of the products. In addition, these organic acids are, in general, volatile and can be recovered upon heating of the treated coal. Thus, simple decantation of the organic acid from the coal or a simple rinsing procedure will generally suffice without further washing.

10 Accordingly, a general primary objective of the present invention is (1) to provide a new and improved process for making hard granular activated carbon from low cost sub-bituminous coal wherein the charring step necessary for processing bituminous coal is eliminated, while the overall
15 yield of granular activated carbon is increased significantly by appropriate treatment of sub-bituminous coal with a dilute aqueous solution of saturated aliphatic monocarboxylic organic acid, with or without the addition of carbonaceous binder; (2) as well as to provide a new and improved hard granular
20 activated carbon made by such process and having the aforementioned desired properties of adsorption (as measured by volumetric Iodine number), decolorization (as measured by volumetric Molasses number), purity (as measured by ash content), hardness (as measured by abrasion number) and density
25 (as measured by apparent density), which make it suitable for use in liquid phase applications, such as water and waste water treatment.

To this end, the invention includes (1) a process for making hard granular activated carbon, comprising: forming
30 granules from sub-bituminous coal; reducing the granules to form fine powder; compressing the powder to form shapes; reducing the shapes to reform granules, and thereafter subjecting the reformed granules to heat treatment, without charring, until activated, wherein the improvement comprises:
35 treating the initially formed granules with a dilute aqueous solution of saturated aliphatic monocarboxylic acid, at a



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concentration from about 2% to about 30%, for a time and at a temperature and solution to coal ratio sufficient for further processing, decanting excess acid, and drying the granules at least partially to a moisture, including acid, content below about 25% and mixing the granules with 0 to about 15% of a carbonaceous binder; and (2) hard granular activated carbon made by such process and having the physical characteristic of high granular integrity permitting repeated handling, use, regeneration and reuse. All percentages used herein are by weight, unless otherwise specified, and the shapes formed by compressing may be of various configurations larger than the granules such as pellets, briquettes, thin sheets of corrugated cross-section, etc. Likewise, the heat treatment may involve separate sequential devolatilization and activation steps, or direct activation eliminating the separate devolatilization step.

A specific primary objective is to provide (1) such process wherein the preferred saturated aliphatic monocarboxylic acid is formic acid, at a preferred concentration of from about 3% to about 6% by weight, and (2) hard granular activated carbon made by such process and having an abrasion number of not less than about 70.

Another specific primary objective is to provide (1) such process wherein the treated granules are mixed within from 0 to about 15% by weight of a carbonaceous binder, and (2) hard granular activated carbon made by such process and having an abrasion number of not less than about 80.

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

BRIEF DESCRIPTION OF THE DRAWING

The single figure is a block diagram or flow sheet illustrating schematically the various steps of the process,

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as well as the resulting product, both embodying the invention.

EXAMPLE 1

(No Acid + Pitch)

5 The starting material for this and each of the following examples was a batch of Wyoming sub-bituminous (Elkol) coal, that being used in this Example having the following analysis percent by weight, in the as received and dry conditions respectively:

10

PROXIMATE ANALYSIS

| <u>CONSTITUENTS</u> | <u>AS RECEIVED</u> | <u>DRY</u> |
|---------------------|--------------------|------------|
| Moisture | 15.1 | - |
| Volatile Material | 37.1 | 43.70 |
| Ash | 2.92 | 3.44 |
| 15 Fixed Carbon | 44.88 | 52.86 |

2000 grams of coal granules having a mesh size of 8/30 and 220 grams of coal tar pitch (10%) were blended by stirring together in a Hobart mixer for approximately 10 minutes. The mixture was pulverized in a hammer mill to produce a
 20 fine powder of 81% -325 mesh. This powder was compressed into cylindrical pellets of 0.5 inch diameter by 0.5 inch height at 80,000 psi to an apparent density of 1.2 grams/cc, with the pellets being crushed in a jaw mill and screened to reform and collect granules of 6/20 mesh size. These re-
 25 formed granules then were devolatilized as follows.

600 grams were placed in a stainless steel screen basket which was rotated within a tube furnace at about 2 rpm. The furnace was constructed such that the gaseous environment of the basket and granules could be controlled. The granules
 30 were heated to about 600°C. while in an inert gas atmosphere of nitrogen or argon. This temperature and atmosphere were

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maintained for 1 hour, after which time the material was allowed to cool to room temperature. 336 grams of carbonized (devolatilized) material with an apparent density of .629 gram/cc were obtained, giving a yield on devolatilization of 56%.

300 grams of this material were activated as follows: The granules were placed in a controlled atmosphere rotary kiln and were heated to a temperature of 870°C. under a nitrogen flow, at which time steam carried by the flowing nitrogen was passed through the system at a rate corresponding to about 800 grams of water per hour. This was continued for a period of 30 minutes, after which time the material was allowed to cool to room temperature under flowing nitrogen. 153 grams of granular activated carbon were obtained, with an activation yield of 51.0%, and an overall yield of 28.6% (51.0 x 56/100). The product had the following properties: apparent density .501 gram/cc; Iodine number 722 (722 x .501 = 361 volumetric); Molasses number 249 (249 x .501 = 125 volumetric); abrasion number 83; ash content 6.28%, and mean particle diameter 1.58 mm.

As will be evident, this material was not suitable for liquid phase applications, because of its low Iodine number.

EXAMPLE 2

(5% Formic Acid + Pitch)

The sub-bituminous coal employed in this Example had the following analysis:

PROXIMATE ANALYSIS

| <u>CONSTITUENTS</u> | <u>AS RECEIVED</u> | <u>DRY</u> |
|----------------------|--------------------|------------|
| Moisture | 17.40 | - |
| 30 Volatile Material | 38.20 | 46.25 |
| Ash | 2.44 | 2.95 |
| Fixed Carbon | 41.95 | 50.79 |



13.

The procedure of Example 1 was repeated, except as follows. 800 grams of 6/20 mesh granules were stirred for 1 hour at 95°C. with an aqueous solution of 150 cc of 90% formic acid in 3020 cc of water (about 5.1% acid and about 4/1 solution to coal ratio). The acid was decanted from the coal, which was quickly rinsed with water and decanted again. The treated coal was dried at 120°C. for 1/2 hour to a moisture content of about 2 or 3%, with 1592 grams of the dried coal being mixed with 102 grams of coal tar pitch (6% pitch), and this mixture was ground in a hammer mill to yield a fine powder of 77% -325 mesh. The powder then was compressed into the aforesaid cylindrical pellets in a hydraulic press operating at 80,000 psi, which pellets were then crushed into granules, those of 6/20 mesh being collected.

600 grams of the reformed granules were devolatilized as in Example 1, and following cooling to room temperature, 296 grams of the devolatilized material having an apparent density of 0.635 gram/cc were produced at a yield of 49.3%.

Next, 300 grams of this material were activated as in Example 1, but the temperature was increased to 1000°C., with the steam rate corresponding to 750 cc of water per hour and the temperature maintained over a period of 1/2 hour.

147 grams (activation yield 49.7%, overall yield 24.5%) of granular activated carbon having the following properties were produced: apparent density 0.495 gram/cc; abrasion number 84; mean particle diameter 1.46 mm; Iodine number 918 (volumetric 454); Molasses number 231 (volumetric) 107; and ash content 6.9%. Thus, the product was well suited in all respects for use in liquid phase applications.

During the course of experimentation, the following were learned. The size of the granules being acid treated, temperature of treatment (which usually is below 100°C because of the use of the dilute aqueous acid solution), time of treatment, concentration of acid and the ratio of dilute

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aqueous acid solution to coal all have important effects on further processability of the coal to form granular activated carbon. Therefore, the specific members cited in this and in the ensuing inventive Examples are merely illustrative and not restrictive. For example, both coarser and finer granules can be employed during treatment with corresponding results, with the time of treatment being longer for coarser particles and shorter for finer particles. Likewise, the lower the temperature the longer the time, and vice versa. In Addition, the lower the concentration of acid, the longer the time, and vice versa, while the solution to coal ratio probably should not be less than about 1/1. Generally speaking then, these parameters should be sufficient for further processing of the coal to form granular activated carbon.

Moreover, this acid treatment is believed to have a beneficial effect on the coal resulting in increased activity, as will be evident from the substantial increase in the Iodine number from 722 in Example 1 to well over 900 in this and in each of the remaining inventive Examples. Expressed in percentages, the Iodine number was increased by at least 25% (this Example) and as much as 45% (Example 4).

EXAMPLE 3

(3.5% Formic Acid + Pitch)

The sub-bituminous coal used herein had the following analysis:

PROXIMATE ANALYSIS

| | <u>CONSTITUENTS</u> | <u>AS RECEIVED</u> | <u>DRY</u> |
|----|---------------------|--------------------|------------|
| | Moisture | 18.67 | - |
| | Volatile Material | 35.84 | 44.07 |
| 30 | Ash | 2.43 | 2.99 |
| | Fixed Carbon | 43.06 | 52.94 |



aqueous acid solution to coal all have important effects on further processability of the coal to form granular activated carbon. Therefore, the specific members cited in this and in the ensuing inventive Examples are merely illustrative and
 5 not restrictive. For example, both coarser and finer granules can be employed during treatment with corresponding results, with the time of treatment being longer for coarser particles and shorter for finer particles. Likewise, the lower the temperature the longer the time, and vice versa.
 10 In Addition, the lower the concentration of acid, the longer the time, and vice versa, while the solution to coal ratio probably should not be less than about 1/1. Generally speaking then, these parameters should be sufficient for further processing of the coal to form granular activated carbon.

15 Moreover, this acid treatment is believed to have a beneficial effect on the coal resulting in increased activity, as will be evident from the substantial increase in the Iodine number from 722 in Example 1 to well over 900 in this and in each of the remaining inventive Examples. Expressed
 20 in percentages, the Iodine number was increased by at least 25% (this Example) and as much as 45% (Example 4).

EXAMPLE 3

(3.5% Formic Acid + Pitch)

25 The sub-bituminous coal used herein had the following analysis:

PROXIMATE ANALYSIS

| | <u>CONSTITUENTS</u> | <u>AS RECEIVED</u> | <u>DRY</u> |
|----|---------------------|--------------------|------------|
| | Moisture | 18.67 | - |
| | Volatile Material | 35.84 | 44.07 |
| 30 | Ash | 2.43 | 2.99 |
| | Fixed Carbon | 43.06 | 52.94 |



800 grams of coal sized 6/0 mesh were stirred for 1 hour at 90-100°C. together with an aqueous solution of 152 cc of 88% formic acid in 3000 cc of water (approximately 5% acid by weight and about 4/1 solution to coal ratio). The acid solution was then decanted, and the treated coal dried at about 120°C. until surface dry, i.e., about 10% to about 15% moisture. 1672 grams of the treated coal were milled in a hammer mill to yield a fine powder of 69% -325 mesh. This powder was pressed into cylindrical pellets utilizing a hydraulic press operating at 100,000 psi, which pellets were then crushed into granules, of which 6/20 mesh were collected.

662 grams of the 6/20 mesh granules were placed into a stainless steel mesh basket located within a tube furnace as described in Example 1. The granules were rotated and heated to 450°C. while in an inert atmosphere of nitrogen or argon. This temperature and atmosphere were maintained for 1 hour, at which time the material was cooled to room temperature. 399 grams of devolatized material with an apparent density of .674 gram/cc were obtained, this corresponding to a devolatilization yield of 60.3%. 300 grams of this material were activated as follows:

The granules were placed in a controlled atmosphere rotary kiln as described above. They were then heated to 1020°C. under a nitrogen flow, at which time steam carried by flowing nitrogen was passed through the system at a rate corresponding to 750 cc of water per hour. This was continued for 52 minutes. The material was allowed to cool to room temperature under a nitrogen atmosphere to produce 116 grams of granular activated carbon corresponding to an activation yield of 38.7% and an overall yield of 23.3%. The activated carbon had the following properties: apparent density .503 gram/cc; abrasion number 84; mean particle diameter 1.49 mm; Iodine number 1050 (volumetric 528); Molasses number 253 (volumetric 127); and ash content 9.4%.



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EXAMPLE 5
(Acetic Acid + Pitch)

The sub-bituminous coal in this Example had the following approximate analysis:

5

PROXIMATE ANALYSIS

| <u>CONSTITUENTS</u> | <u>AS RECEIVED</u> | <u>DRY</u> |
|---------------------|--------------------|------------|
| Moisture | 17.40 | - |
| Volatile Material | 38.20 | 46.25 |
| Ash | 2.44 | 2.95 |
| 10 Fixed Carbon | 41.95 | 50.79 |

A procedure similar to Examples 2 and 3 was followed, with the following exceptions, particularly the substitution of acetic acid for formic acid. 800 grams of granules of 6/0 mesh were stirred for 1 hour at 80-90°C. with an aqueous
 15 solution of 455 cc of glacial acetic acid in 2770 cc of water (about 14% acid and about 4/1 solution to coal ratio). The acid solution was decanted and the treated coal dried to a moisture level of about 16%. 1737 grams of the treated
 20 coal were mixed together with 111 grams of coal tar pitch (6% pitch), which mixture was ground in a hammer mill to a yield fine powder. Following pelletizing and reforming of granules, 600 grams were placed in a rotating tube furnace and heated to 450°C. while in an inert atmosphere of nitrogen, which was maintained for 1 hour, at which time
 25 the material was cooled to room temperature. 300 grams of devolatilized 6/20 granules were produced, having an apparent density of .651 gram/cc, with a devolatilization yield of 50%.

300 grams of the devolatilized granules were activated
 30 in a controlled atmosphere rotary kiln, as described above, the granules being heated to 870°C. under a nitrogen flow, at which time steam carried by the flowing nitrogen was passed



18.

through the system at a rate corresponding to 700 cc of water per hour, and this was continued for 170 minutes. After cooling to room temperature under nitrogen, 131 grams of granular activated carbon of +30 mesh were produced, with an activation yield of 44%, and an overall yield of 22%. The product had the following properties: apparent density .522 gram/cc; abrasion number 82; mean particle diameter 1.46 mm; Iodine number 922 (volumetric 481); Molasses number 247 (volumetric 128.9); and ash content 8.09%.

From the foregoing specific Examples, it is evident that hard granular activated carbon suitable for use in liquid phase applications, such as water and waste water treatment can be obtained by treatment with a dilute aqueous solution of saturated aliphatic monocarboxylic acid, such as formic acid and acetic acid, with formic acid being preferred. In addition, other saturated aliphatic monocarboxylic acids can be utilized in the practice of the invention, such as propanoic, butanoic, pentanoic and hexanoic acids, with the acid concentration required being increased with the decrease in strength of the acid.



WHAT IS CLAIMED IS:

1. A process for making hard granular activated carbon comprising: forming granules from sub-bituminous coal, reducing the granules to form fine powder, compressing the powder to form shapes, reducing the shapes to reform
5 granules, and thereafter subjecting the reformed granules to heat treatment, without charring, until activated, wherein the improvement comprises: treating the initially formed granules with a dilute aqueous solution of saturated aliphatic monocarboxylic acid, at a concentration from about 2% to
10 about 30%, for a time and at a temperature and solution to coal ratio sufficient for further processing, decanting excess acid, and drying the granules at least partially to a moisture, including acid, content below about 25%, and mixing the treated granules with 0 to about 15% of a carbonaceous
15 binder.

2. Hard granular activated carbon made by the process of claim 1.

3. The process of claim 1 wherein the acid is formic acid.

4. The process of claim 3 wherein the concentration of the formic acid is from about 3% to about 6%.

5. Hard granular activated carbon made by the process of claim 4 and having an abrasion number of not less than about 70.

6. Hard granular activated carbon made by the process of claim 1 and having an abrasion number of not less than about 80.

7. The process of claim 1 wherein the acid is acetic acid.



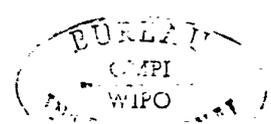
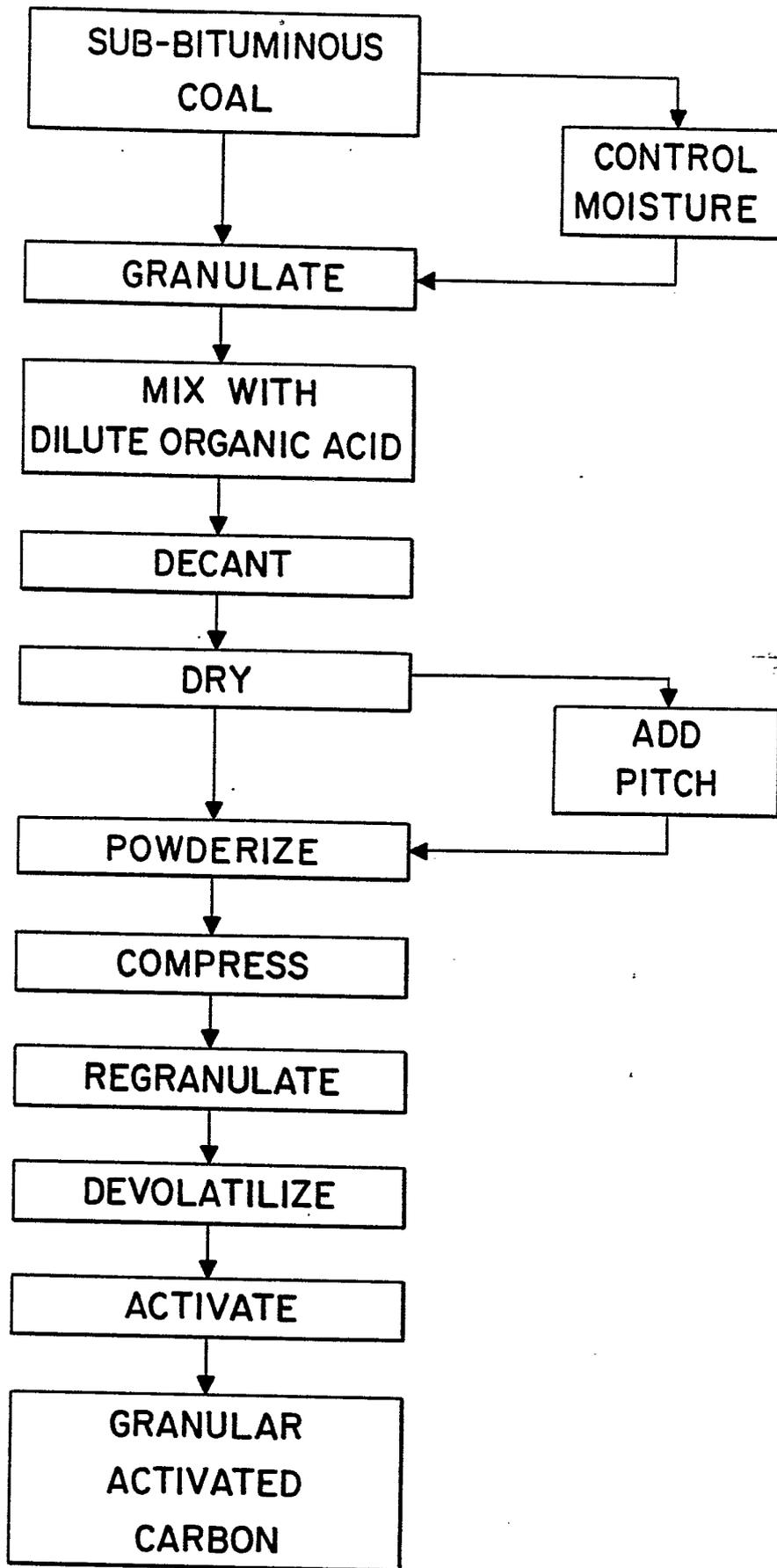
20.

8. The process of claim 7 wherein the concentration of the acetic acid is from about 10% to about 20% by weight.

9. The process of claim 8 wherein the treated granules are mixed with about 5% to about 15% by weight of a carbonaceous binder.

10. Hard granular activated carbon made by the process of claim 9 and having an abrasion number of not less than about 80.





INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/00933

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC
 INT. CL.3 C01B 31/08; C01B 31/12
 US CL. 252/444; 252/422

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

| Classification System | Classification Symbols |
|-----------------------|--|
| US | 252/421, 422, 444, 445 423/445, 449, 460, 461; 264/29.1 |

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

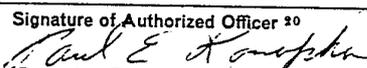
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

| Category [*] | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ |
|-----------------------|--|-------------------------------------|
| A | US, A, 4,144,193, Published, 13 March 1979, Murty | 1-10 |
| A | US, A, 3,974,227, Published, 10 August 1976, Berthoux et al | 1-10 |
| A | GB, A, 13,582, Published, 09 November 1885, Remmers et al | 1-10 |

^{*} Special categories of cited documents: ¹⁵

| | |
|---|--|
| <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> | <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> |
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IV. CERTIFICATION

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|--|---|
| Date of the Actual Completion of the International Search ² | Date of Mailing of this International Search Report ³ |
| 29 OCTOBER 1980 | 14 NOV 1980 |
| International Searching Authority ¹ | Signature of Authorized Officer ²⁰ |
| ISA/US |  PAUL E. KONOPKA |