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**3,726,808**
**PROCESS FOR THE PRODUCTION OF**
**ACTIVE CARBONS**
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U.S. Cl. 252—425                    14 Claims

## ABSTRACT OF THE DISCLOSURE

Desulfurized active carbon is produced by steam treating a sulfur-containing pre-pyrolyzed or unpyrolyzed composition containing an aromatic acid salt at a temperature in the range of 450° C. to 650° C. whereby the sulfur is converted to $H_2S$ and S (vapor) and a recyclable base is formed. When pyrolysis is conducted separately and prior to the steam treatment it is preferably conducted at a temperature between 450° C. and 1,000° C. Aromatic carboxylic acids are preferred and especially coke acid derived from the oxidation of petroleum coke.

## BACKGROUND OF THE INVENTION

This application is a continuation-in-part of co-pending application Ser. No. 705,901, filed Feb. 16, 1968, now abandoned.

This invention relates to a process for the production of active carbons, and more particularly to sulfur free active carbons.

Carbons obtained from thermally decomposed salts of aromatic acids are described in U.S. application, Ser. No. 706,146, filed on Feb. 16, 1968, now abandoned, and entitled, "Activated Carbon and Process for the Production of Activated Carbon," the inventors of which are A. N. Wennerberg and R. M. Alm (hereinafter designated "Wennerberg-Alm application"). The Wennerberg-Alm application relates to a process for the production of economical and efficient carbons. The present application provides an improved process for the production of such active carbons.

## SUMMARY OF THE INVENTION

It has now been discovered that an improved active carbon, significant economic improvement, and greater operating efficiency can be achieved by the process of this invention. Many of the more complex aromatic acid feeds (as is disclosed in Wennerberg-Alm application) contain a significant amount of sulfur which may be detrimental to the end use of the active carbon. It has also been found that the difficulty in re-cycling the electrolyte may be greatly minimized by use of the present invention.

Briefly, the process of the present invention comprises treating a sulfur containing aromatic acid feed with sufficient electrolyte to at least form the salt of the feed acid; drying said salt; thermally decomposing said dried salt in the course of which step by-product salts are formed; and treating said thermally decomposed salt with steam to convert the sulfur compounds to $H_2S+S$ (vapor), and generate from the by-product salts re-cyclable base for further treating of feed to produce the salt. As illustrative of the chemistry involved in the foregoing steam-treating would be the following generalized equation:

$$K_2S_x + H_2O \text{ (v.)} \rightarrow KOH + H_2S \text{ (v.)} + S_{x-1} \text{ (v.)}$$
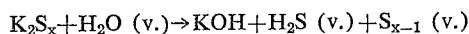
The process of this invention has a further advantage of providing reclaimable sulfur. The aromatic carboxylic acids are the preferred feed.

The steam-treating step, whether performed on pre-pyrolyzed or unpyrolyzed acid salts, may be accomplished in the temperature range of 450° C.–650° C., preferably 500° C.–550° C., at atmospheric pressure or slightly higher. At temperatures above 650° C., the product will deteriorate. Steam and/or inert gas flow will depend upon the feed rate of salts to the reactor for pyrolysis and the sulfur level in the feed. It may be desirable to provide the steam-treating step concurrently with the thermal decomposition step.

More specifically, this invention comprises feeding dry alkaline salts of coke acids to a pyrolysis furnace, or any similarly functional vessel to effect conversion of the salts to active carbon, plus by-product salts, either by sequential flow of inert gas during pyrolysis followed by steam hydrolysis to generate fresh base and remove sulfur and $H_2S$, or by concurrent pyrolysis and steam hydrolysis at the desired temperature within the aforementioned steam-treating range. The base referred to is the hydroxide of the alkali or alkaline earth salt of the coke acids used as feed for the process. The by-product sulfur vapor+$H_2S$ are carried out of the reactor to a condensing section for recovery of $H_2S$ and S. Sulfur-free active carbon, plus basic salts are removed at the bottom for subsequent washing to remove basic salts for re-cycle.

The aromatic acid may be any compound having an acid radical directly attached to the benzene ring and capable of forming a soluble salt with electrolyte. Other functional groups may be present without deleterious effect. The acid radical may be COOH, $SO_3H$, $SO_2NH_2$, $PO_3H$, etc. Aromatic carboxylic acids are preferred, and may be simple mono-carboxylic acids, such as benzoic acid or polycarboxylic acids, such as terephthalic, isophthalic, trimesic, or trimellitic, polynuclear carboxylic acids, such as naphthoic acid, or polynuclear polycarboxylic acid, such as coke acid. It is also contemplated that the aromatic carboxylic acids may be derived from any suitable carbonaceous material which is subsequently oxidized to form the carboxylic acid. For example, petroleum coke may be oxidized to form the coke acid. While petroleum coke acid having any degree of oxidation is suitable in my process, the preferred petroleum coke acid is one having, on analysis, an elemental oxygen content of between about 20 to 30 percent. The feed material may be treated, when necessary, to remove contaminants or undesirable elements. For example, petroleum coke has a metal content, which, of course, is unsuitable for obtaining an ash-free carbon, but oxidation with nitric acid serves a dual function, i.e., forms the acid and removes metals.

The electrolyte apparently performs a blocking or defecting function. This is, upon drying and thermal decomposition, a highly cross-linked carbon structure is formed within which the included electrolyte, along with salts formed by decomposition, occupies and maintains the defect (pore) volume during the carbonization process. When the electrolyte is removed from the product carbon structure, a defect volume or pore space is retained in the interlocking, stabilized carbon structure. The electrolyte should also be of such nature and the quantity used should be sufficient to at least be capable of converting the acid to the salt form, however, the term electrolyte, as used herein, is intended to mean (1) a compound capable of forming salt with the acid used and capable of providing the blocking effect or (2) more than one compound, one of which is used to neutralize the acid and additional compound or compounds which may be added simultaneously with or subsequently to neutralization to provide higher surface areas, and/or to control pore size and distribution. Examples of substances used as co-electrolytes are potassium hydroxide with potassium chloride or potassium carbonate or sodium hydroxide with sodium chloride. It is possible that by use of an electrolyte containing ions of different sizes, different size pores will re-

sult. The ability to form the salt is necessary in order that the compound may be soluble. The solubilizing of the compound allows for proper alignment of the molecules. Broadly useful in my process is any electrolyte with an anion chosen from among: hydroxide, oxide, halide, carbonate, sulfate, phosphate and nitrate; and a cation chosen from a metal of Group I–A or II–A of the Periodic Table.

The preferred electrolyte is an alkali metal compound because of the solubility of the salts and the ease of removal after thermal decomposition. It has been found, for example, that when calcium salts are used, digestion is required for removal. The alkali metal hydroxide may be used as the electrolyte to form the salt of the acid, and excess hydroxide may be used to provide additional blocking and, hence, increase surface area. In addition to excess hydroxide, alkali metal halide, carbonate, sulfate, phosphate, nitrate, oxide and other metal ion sources, etc., may be used as the electrolyte. Mixtures of electrolyte and aromatic carboxylic acid or more specifically petroleum coke acid have been used wherein the amount of excess electrolyte has varied widely. For example, up to 5.8 excess equivalents of potassium hydroxide and 7.0 excess equivalents of sodium hydroxide have been used. The following salts have been used as co-electrolytes with potassium or sodium hydroxides in the indicated concentrations per equivalent of petroleum coke acid: 6.0 moles potassium carbonate, 8.3 moles sodium chloride, and 10.0 moles of potassium chloride. Although active carbons may be prepared from salts of metals included with Groups I–A and II–A of the Periodic Table, and from ammonium, etc., the potassium salts are by far the most preferred. In fact, it is difficult to obtain surface areas of active carbons in excess of 1,000 sq. meters per gm., without additional treatment if potassium is not used. Potassium is also preferred because of its availability, cheapness and it provides high water solubility (water is, of course, a preferred solvent). Active carbons prepared by use of metals other than potassium, in spite of this, have been found to be highly desirable and highly preferred over commercial products. Another interesting and unexpected result of our invention is that although it has been found that pore size is related to the size and quantity of the defecting material, it has also been found that metals other than potassium do not provide as great an incremental increase in surface area as a result of the addition of a given excess quantity of a defecting material, as is true of potassium. Active carbons made from cations other than potassium may be produced with surface areas approaching those obtained with potassium by increasing the solubility of the salt, e.g., by raising the temperature of the solution.

The thermal decomposition of the salts is accomplished by pyrolyzing the salts in an inert atmosphere. Since no oxidants are present, this is a true thermal decomposition. Prior to pyrolysis, the solvent is removed in order to provide structural stability to the molecule incorporating the defecting agent. The drying step may be accomplished by slowly raising the temperature prior to pyrolysis. This will ensure structural integrity. However, any evaporative technique may be used. Thermal decomposition may be accomplished in a pyrolysis chamber where the alkaline decarboxylation pyrolysis is carried out. The reaction may use a fluidized technique, continuous conveyor surface or fixed bed method. The temperature, where pyrolysis is conducted separately and prior to steam treatment, should be sufficient to decompose the salt, but less than the graphitization temperature of the carbon; preferably between 450° C. and 1,000° C. Temperatures between 700° C. and 900° C. are particularly preferred. The crude pyrolyzate produced is then treated with steam according to the present invention to convert the sulfur compounds to $H_2S + S$ (vapor), and is then washed with water to remove by-product salts and excess alkali metal compounds. Removed products may be re-cycled for the formation of additional salts. The washed, neutral, carbon powder may then be dried and thereafter fabricated to the particular

particle size or form desired. For some uses a granular adsorbent is more desirable than the powdered material (e.g., for use in bed systems). The granular adsorbent may be prepared by deposition of the salt on a suitable substrate prior to pyrolysis; the material may then be pyrolyzed, washed to remove soluble salts, and dried. Suitable solids on which the salts may be deposited are petroleum coke, ground coal, silica, alumina, ground limestone, dolomite, lime and other substances that can be heated to the temperatures needed to pyrolyze the salts without being decomposed themselves.

It may be possible to minimize the evaporation of solvent required prior to pyrolysis. This would represent a saving of the heat necessary to dry the salt. The elimination of the drying step, therefore, is desirable.

To avoid the drying step, the acid may be neutralized in a saturated solution of the acid salt and the electrolyte. Upon further neutralization of acid, the salt will precipitate, and the precipitate may be filtered. The precipitate, depending upon the quantity of the electrolyte used, would also include electrolyte. It is possible that because of the highly saturated solution, gelling of the salts may occur. This can be avoided by suitable agitation.

A preferred method for preparing the petroleum coke acid comprises the controlled oxidation of petroleum coke by the use of aqueous nitric acid in the concentration range of 20% to 80% by weight in water.

More specifically, suspended, finely divided coke is oxidized at atmospheric or elevated pressures in either a batch type reactor or a continuous suspension flow system. The suspended coke acid is then separated by filtration and the filtrate, aqueous nitric acid solution, may then be recycled for reuse in the oxidation. The crude coke acid produced may then be washed with water to remove any traces of nitric acid.

When carrying out the oxidation reaction at atmospheric pressure, the coke:nitric acid ratio may be in the range of from 1:2 to 1:10 by weight, preferably 1:5. The preferred concentration of the nitric acid is 30% to 50% by weight. The reaction temperature may vary from 50° C. to 125° C. It is preferred that the temperature initially be at the lower portion of this range and then be gradually increased to the upper portion of the range at the end of the reaction period. The reaction period may vary from 5 to 24 hours, depending upon the degree of agitation in the reactor, the degree of subdivision of the coke, the concentration of the aqueous nitric acid, and the rate of increase of temperature. For example, a 50 weight percent aqueous nitric acid solution, with a coke:acid ratio of 1:5 by weight which is vigorously agitated, may be heated from 60° C. to 120° C. for a 6 to 8 hour period to complete oxidation of the coke. A typical coke oxidation is shown in Example I:

### EXAMPLE I

Preparation of coke acid by oxidation of petroleum coke.—400 g. of petroleum coke was suspended in 2500 ml. (2856 g.) of 55% $HNO_3$ within a 3-necked 5 l. round-bottomed flask. The flask was equipped with a stirring rod and paddle inserted through the center neck. An efficient condenser and thermowell were connected to each of the two remaining side necks, respectively. The raw coke (about 20–40 mesh range) was stirred as a suspension while the reactor system temperature was raised from 25° C. to 112° C.–118° C. during the first 8 hours of reaction time. By-products gases from oxidation were vented out the condenser side during the course of reaction.

At the end of 8 hours reaction time, the spent aqueous $HNO_3$ solution was withdrawn from the suspension and replaced with a second charge of 2500 ml. (2856 g.) of 55% aqueous $HNO_3$. The reaction was continued for a second 8-hour period over a temperature range of 85° C. to 115° C. with most of the second reaction period at 100° C. to 118° C. At the completion of the second state

of oxidation, the reaction product suspension was cooled at 25° C. and the suspended coke acid product separated from unreacted aqueous $HNO_3$ by filtration.

The crude acid reaction product was washed with cold water; five consecutive washes of 2000 ml. volume per wash. The washed, finely divided product was dried in a vacuum oven to remove last traces of water. Yield of product was 480 g. having a neutralization equivalent of 240–260 mg. KOH/g.

| Elemental analysis: | Wt. percent |
|---|---|
| C | 63.2 |
| H | 2.6 |
| O | 27.2 |
| N | 4.5 |
| S | 2.5 |

The neutralization reaction may be carried out in any suitable solvent, for example, water, water-acetone, water-tetrahydrofuran, etc. The nature of the salt will dictate the particular solvent necessary. The quantity of the electrolyte should be at least sufficient to neutralize the acid. It is preferred that substantially all the carboxyl groups be neutralized. Therefore, a pH of at least 7 is desirable, advantageously between 8 and 14. The temperature of the neutralization reaction should be sufficient to effect substantially complete solution of the product salt.

During the pyrolysis of the coke acid salt, any free acid and the salt are decarboxylated. It is preferred that any water associated with the salt be minimized prior to and during the pyrolysis step. This is advantageously accomplished in an evaporation unit. The solid salt may then be inserted in a pyrolysis chamber, and inert gas flow started in the chamber before heating to expel air that would cause high temperature oxidation. The rate of temperature rise is preferably held constant. After the maximum desired temperature is reached, the pyrolysis chamber is allowed to cool, and inert gas flow continued until the chamber has cooled to room temperature.

The resultant pyrolyzate is then steam-treated between 450° C. and 650° C. alternately, instead of treating the pre-pyrolyzed acid salt, pyrolysis may be carried out concurrently on the undecomposed salt with the steam-treatment. Salt preparation and pyrolysis is exemplified below.

### EXAMPLE II

Salt preparation.—A solution was prepared containing 224 g. (1 equiv.) coke acids in 1000 g. of acetone-water solvent. To this solution is added an aqueous solution containing 90 g. (1.38 equiv.) of 86% potassium hydroxide in 150 g. of water. The salt solution was stirred for one hour after which the solvent phase was removed by evaporation. Total yield of product salt was 298 g.

Salt pyrolysis.—50 g. of the product salt was charged to a rotating Vycor kiln under argon blanket, and the solid salt composition was pyrolyzed in the rotating kilm at 780° C. under argon. The rate of heating and/or duration of exposure to the temperature range 25° C. to 780° C. was the same, as previously used, namely, 60 minutes.

### DESCRIPTION OF PREFERRED EMBODIMENTS

### EXAMPLE III

Hydrolytic desulfurization of pyrolysate.—An 18.0 g. sample of pyrolyzed K+ salt of a coke acid was treated in a rotating Vycor kiln with a continuous argon/steam; 1/1 vapor stream at 500° C. for 1½ hours. During the course of the treatment $H_2S$+sulfur vapor was expelled from the kiln exit. At the end of 1½ hours of treatment, no odor of $H_2S$ could be detected in the off gas. At this point, the steam was turned off and the sample cooled slowly with drying under argon sweep. The treated pyrolysate, 18.0 g. was then washed to remove all soluble, basic by-product including soluble by-product metal polysulfides. No sulfur was detected in the aqueous wash and the basic wash solution contained $K_2CO_3$ by-product+unreacted excess KOH. Desulfurization of the water soluble

basic phase was accomplished with a slight loss in active carbon yield. Measurement of surface areas of the carbons derived from the pyrolysate before and after the steam treatment was:

| | B.E.T. area, m.$^2$/g. |
|---|---|
| Before | 1679 |
| After | 1759 |

### EXAMPLE IV

Hydrolytic desulfurization of pyrolysate.—A 44.0 g. sample of pyrolyzed K+ salt of a coke acid was treated in a rotating Vycor kiln with a continuous $CO_2$/steam; 2/1 vapor stream at 500° C. for 1 hour. During the course of the treatment, $H_2S$+S vapor was expelled from the kiln exit along with steam and excess $CO_2$. At the end of 1 hour, reaction with steam+$CO_2$ vapor stream, the $CO_2$+steam was replaced with argon and the sample was dried and cooled to room temperature, 25° C. The treated pyrolysate, 44.0 g., was washed with water to remove all basic, water-soluble by-product from the active carbon. Analysis of the basic, water wash yielded $K_2CO_3$+unreacted excess KOH with no evidence of basic polysulfides usually present in the water wash from untreated pyrolysate. Measurement of surface areas of the carbons derived from the pyrolysate before and after the $CO_2$+steam treatment was:

| | B.E.T. area, m.$^2$/g. |
|---|---|
| Before | 1502 |
| After | 1719 |

### EXAMPLE V

A 24.0 g. sample of pyrolyzed K+ salt of a coke acid was treated in a rotating Vycor kiln with a continuous stream of steam/argon; 2/1, for 1½ hours at 780° C. During the course of the treatment $H_2S$+S vapor was expelled from the kiln exit along with steam and argon. At the end of 1½ hours, of treatment, the steam was shut off and the sample allowed to cool under argon sweep to room temperature. The treated pyrolysate, 14.4 g. was washed to remove all basic, water-soluble components from the product active carbon. Analysis of the water wash showed no evidence of sulfur, only by-product $K_2CO_3$+unreacted excess KOH. Untreated pyrolysate yielded 41.4% active carbon based on weight of pyrolysate. Treated pyrolysate yielded 2.8% active carbon based on weight of pyrolysate. Measurement of surface areas of the carbons derived from the pyrolysate before and after the steam treatment was:

| | B.E.T. area, m.$^2$/g. |
|---|---|
| Before | 1018 |
| After | 200 |

The previous examples illustrate that steam and steam+$CO_2$ may be effectively used for hydrolytic desulfurization of water soluble, basic components in basic coke acid salt pyrolysate with no active carbon loss if the treatment is carried out at 500° C. At 780° C., severe loss of both carbon and active carbon surface area occur along with hydrolytic desulfurization.

I claim:

1. A process for the concurrent production of desulfurized active carbon and the generation of a recyclable base comprising the steps of: (a) pyrolyzing a mixture of a salt of an aromatic acid and an electrolyte at a temperature between about 450° C. and about 1000° C. but less than the graphitization temperature of the carbon, and (b) contacting the product of step (a) with steam at a temperature between about 450° C. and about 650° C., and (c) separating said desulfurized active carbon from the product of step (b) wherein said salt contains a cation selected from the group consisting of the elements of Group I–A and Group II–A of the Periodic Table and wherein said electrolyte consists of a cation selected from the group consisting of the elements of Group I–A and Group II–A of the Periodic Table and an anion selected

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from the group consisting of hydroxide, oxide, halide, carbonate, sulfate, phosphate and nitrate.

2. A process according to claim 1 wherein said salt contains a cation selected from the group consisting of the elements of Group I–A of the Periodic Table and said electrolyte contains a cation selected from the elements of Group I–A of the Periodic Table and an anion selected from the group consisting of hydroxide, oxide, halide and carbonate.

3. A process according to claim 2 wherein said salt is a postassium salt and said electrolyte is potassium hydroxide.

4. The process of claim 1 wherein said salt of an aromatic acid is a salt of petroleum coke acid.

5. The process of claim 2 wherein said salt of an aromatic acid is a salt of petroleum coke acid.

6. The process of claim 3 wherein said salt of an aromatic acid is a salt of petroleum coke acid.

7. The process of claim 4 wherein said salt of petroleum coke acid is produced by adding at least one equivalent of base for each equivalent of petroleum coke acid, wherein said petroleum coke acid is made by oxidizing petroleum coke in aqueous 20–80 weight percent nitric acid at a temperature between 50° C. to 125° C., and wherein the weight ratio of petroleum coke to aqueous nitric acid is between 1:2 to 1:10.

8. The process of claim 5 wherein said salt of petroleum coke acid is produced by adding at least one equivalent of base for each equivalent of petroleum coke acid, wherein said petroleum coke acid is made by oxidizing petroleum coke in aqueous 20–80 weight percent nitric acid at a temperature between 50° C. to 125° C., and wherein the weight ratio of petroleum coke to aqueous nitric acid is between 1:2 to 1:10.

9. The process of claim 6 wherein said salt of petroleum coke acid is produced by adding at least one equivalent of base for each equivalent of petroleum coke, wherein said petroleum coke acid is made by oxidizing petroleum coke is aqueous 20–80 weight percent nitric acid at a temperature between 50° C. to 125° C., and wherein the weight ratio of petroleum coke to aqueous nitric acid is between 1:2 to 1:10.

10. The process of claim 9 wherein said pyrolysis is accomplished at a temperature between 700° C. and 900°

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C. and said contacting is accomplished at a temperature between 500° C. and 550° C.

11. A process for the concurrent production of desulfurized active carbon and the generation of recyclable base comprising the steps of: (a) pyrolyzing a mixture of a salt of an aromatic acid and an eelctrolyte in the presence of steam at a temperature in the range from about 450° C. to about 650° C. and (b) separating said desulfurized active carbon from the product wherein said salt contains a cation selected from the group consisting of the elements of Group I–A and Group II–A of the Periodic Table and wherein said electrolyte consists of a cation from the group consisting of the elements of Group I–A and Group II–A of the Periodic Table and an anion selected from the group consisting of hydroxide, oxide, halide, carbonate, sulfate, phosphate and nitrate.

12. A process according to claim 11 wherein said salt contains a cation selected from the group consisting of the elements of Group I–A of the Periodic Table and said electrolyte contains a cation selected from the elements of Group I–A of the Periodic Table and an anion selected from the group consisting of hydroxide, oxide, halide and carbonate.

13. A process according to claim 12 wherein said salt is a potassium salt and said electrolyte is potassium hydroxide.

14. The process of claim 13 wherein said salt of an aromatic acid is a salt of petroleum coke acid.

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