Patented Mar. 2, 1943 2,312,707

# UNITED STATES PATENT OFFICE

2,312,707

## CARBON

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No Drawing. Application January 17, 1941, Serial No. 374,896

3 Claims. (Cl. 23—209.1)

This invention relates to carbons of coal-derived origin, especially to activated carbons and carbon blacks, and this application is a continuation-in-part of my copending application Serial No. 214,567, filed June 18, 1938, now Patent No. 2,242,822, granted May 20, 1941.

The primary object of this invention is to provide carbon products such as carbon black and activated carbon of especially high quality.

Other objects of the invention will appear from the following description.

The chemical constitution of coal is not known although it is recognized that it is made up of a variety of different materials. For instance, it comprises mineral matter and carbonaceous matter. The carbonaceous matter is of complex character but for the purposes of this invention it may be said to comprise two general classes of material which are differentiated by their behavior in the practice of the invention. One of these is the portion of coal that is termed fusain by workers in this field. The other is made up of the remainder of the organic, or non-mineral, portion of the coal, and it is this portion of which use is made in the practice of the present invention, and for brevity of reference it will be termed herein as "coal substance" or as "non-fusain organic matter of coal" to distinguish it from the contents of fusain and mineral, or inorganic, matter in coal.

The invention of my aforesaid application is predicated in part upon my discovery that, contrary to prior experiences with solvents, substantially the entire content of coal substance may be extracted from coal in the form of a solution in an organic liquid solvent by having the coal initially in an oxidized form and by the use of a solvent of a particular class. In this manner substantially all of the coal substance may be separated from coal in a form substantially free of mineral matter and fusain, and the coal substance as thus extracted from the coal is in a pure form capable of industrial use.

In the practice of that invention it is necessary that the coal be initially oxidized because oxidation to an appropriate degree acts in some manner to convert the coal substance to a form in which it is amenable to ready and complete extraction by the solvents applicable in the practice of the invention, without solubilizing the fusain content or inorganic matter. Gentle oxidation of a character which effects oxidation of the coal substance with minimized, or without, oxidation to carbon dioxide, suffices for the purposes of that invention, and for most purposes it is preferred to effect the oxidation in such manner that the coal does not lose weight appreciably. As exemplifying oxidizing agents which are applicable to this end, I have used, among others, such oxidizing agents as hydrogen peroxide, potassium permanganate, potassium dichromate, sodium hypochlorite, perchloric acid in the presence of a vanadium catalyst, and elemental halogen, such as chlorine, which may be used satisfactorily by, for instance, passing chlorine into a suspension of coal in aqueous solution of an alkali, e. g., sodium hydroxide. At present it is preferred to use nitric acid as the oxidizing agent because of the rapidity with which the desired degree of oxidation is attained. Other means of oxidation may also be applied in the practice of the invention. Thus, there may be used oxygen or mixtures of oxygen and other gases, for instance, air, preferably moist air, at temperatures low enough to avoid complete oxidation, or to minimize its extent. In such cases the oxidation is normally slow and the use of a catalyst is desirable to accelerate the oxidation while permitting the use of but moderately elevated temperatures.

For most purposes and with most oxidizing agents, heating gently or to moderately elevated temperatures, say to 100° or 150° C., or even somewhat higher, is desirable because it accelerates the oxidation. The temperature should be low enough, however, that no substantial proportion of the coal is completely oxidized.

While the precise reason why oxidation renders the coal substance content soluble is not positively known, I have found that the oxidation acts to convert the coal substance, at least in some part, to hydroxy-carboxylic acids, i. e., the so-called humic or ulmic acids, and this indicates the extent to which the coal is to be oxidized. As further indicating the degree of oxidation necessary for the purposes of the invention, the coal substance, when properly oxidized, is insoluble in mineral oil although it is wholly, or almost wholly soluble in a certain class of solvents that is identified hereinafter. Peculiarly enough, the solubility of fusain, which like the coal substance is of carbonaceous nature, remains unchanged in the solvents used, which explains why it is classed herein as different from the "coal substance." Naturally oxidized coals may, of course, be used.

As disclosed in my aforesaid application the coal substance content of such oxidized coal is readily and substantially completely soluble in organic solvents containing heterocyclic oxygen, more especially the liquid furane derivatives, of which furfural provides particularly desirable results. These solvents may be used alone or in admixtures with themselves or with other solvents. Thus, the solvent power of furfural for coal substance in the practice of the invention is not impaired by the presence of furyl alcohol or tetra-hydrofurfuryl alcohol, both of which are furane derivatives.

There appears to be nothing especially critical

in the particle size of the coal undergoing treatment. Generally speaking, the oxidation and the subsequent extraction are accomplished more rapidly when the coal is crushed than with bulk or coarse lump coal, and for reasons of economy it is therefore usually desirable for the coal to be sub-divided somewhat. Crushing of the coal to pass a 20-mesh standard sieve is adequate for most purposes, and finer sub-division is in general unnecessary although it may be done if desired for any reason.

In the practice of that invention the mildly oxidized coal is treated with a solvent of the class indicated, for instance, furfural. The treatment may be conducted in any desired manner and by any suitable apparatus, as by agitation of the oxidized coal and solvent in a container, or by counter-current leaching, and the like. The solution of coal substance is then separated from the residual mineral matter and undissolved fusain, and for the purposes of the present invention the coal substance is then recovered from the solution.

As exemplifying such practice, 150 grams of an air-dry Pennsylvania bituminous coal containing 23 per cent of volatile matter were treated in an open container with 1200 cc. of ordinary concentrated nitric acid (sp. gr. 1.42) at 100° C. for thirty minutes. The reaction was then stopped by removing the dish from the water bath which afforded the source of heat. Water was added to dilute the acid to an extent such as to permit filtration with ordinary filter paper, and the oxidized coal was separated from the diluted acid by filtration. The coal was unchanged in appearance. It was then agitated with successive portions of furfural until the solvent no longer became colored. At this point the volume of the solution was 1700 cc., its specific gravity was 1.155 at 25° C., and it carried as solute 7 per cent by weight of dissolved coal substance, which corresponded to 140 grams, or 93 per cent by weight of the original coal. This shows the high degree of extraction attainable in the practice of that invention. The solid coal substance recovered from the solution by evaporation of the furfural was hydrophobic. The amount of residue insoluble in the furfural was 10.5 grams, or 7.0 per cent by weight of the original coal, and it consisted of mineral matter, fusain, and perhaps a little undissolved coal substance.

The coal substance is recovered in pure form from the solution by removal of the solvent or by separation of the solute from the solvent. Thus, the solvent may be recovered by ordinary distillation at atmospheric or reduced pressure, or by steam distillation. Or there may be added a solvent which is miscible with the original solvent but in which the coal substance is insoluble such, for example, as water, alcohol, benzene, ethyl ether, isopropyl ether, and the like.

The solute may be separated from the solvent by such physical processes as dialysis, with or without application of electrical forces, by electroprecipitation, by supercentrifuging, and the like. This is accomplished most readily, however, by simple heating of the solution which causes the coal substance to be precipitated as an ash-free brownish powder of very fine particle size. Thus the solution may be boiled under a reflux condenser for, say, thirty minutes to effect such precipitation. In using furfural such precipitation becomes evident above about 120° C., and it is substantially complete at about 160° C., i. e., slightly below the boiling point of furfural. For this reason the original extraction of the coal should be conducted at a temperature below that at which the solute will be precipitated.

The present invention is predicated upon my discovery that pure coal substance recovered as just described is particularly adapted to the production of carbons of varying types such, for example, as carbon black and activated carbon. For instance, the pure coal substance may be heated at about 400° to 500° C. in air or an inert atmosphere such as nitrogen or carbon dioxide, to produce highly valuable carbons of pigment quality, i. e., carbon black. When heated up to about 400° C. little change appears to occur in the coal substance, except for some darkening in color, but at about 400° C. exothermic reaction sets in which is accompanied by gas evolution. After completion of this reaction, or the reactions as the case may be, the product is black, of little or no surface activity, and apparently has the properties of carbon blacks made by customary methods. Carbons made in this manner show considerable tinting strength when mixed with zinc oxide, and when mixed with varnishes produce dried films that are like those made using ordinary carbon blacks.

Or the pure coal substance may be converted into activated carbon by heating it at about 700° to 900° C. in steam or another of the activating atmospheres used in producing carbons of this type. The active carbons produced in this manner are ash free. In one typical case the yield was 32 per cent by weight of the starting material, the ash content was negligible, and the iodine value was 98.4.

These and similar carbons are, of course, valuable, and the invention is important not only for that reason but also because it provides new sources of such products and opens the way to increased production or to conservation of the usual sources of these materials. The various types of carbons may, of course, be made in ways other than those specifically described.

According to the provisions of the patent statutes, I have explained the principle and mode of practicing my invention and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. That method of making a carbon product which comprises treating coal in a mildly oxidized form, in which the non-fusain organic matter of the coal contains hydroxy-carboxylic acids, with an organic solvent containing heterocyclic oxygen and thereby dissolving substantially completely said non-fusain organic matter, separating the resultant solution from undissolved fusain and mineral matter, recovering said non-fusain organic matter from said solution and heating it to between about 400° and 900° C. and thereby converting it to said carbon product.

2. A method according to claim 1 of producing carbon black in which the recovered non-fusain organic matter is heated to about 400° C. to 500° C. in an inert atmosphere.

3. A method according to claim 1 of making activated carbon in which said recovered non-fusain organic matter is heated in an activating atmosphere at about 700° to 900° C.

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