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## TREATMENT OF COAL

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This invention relates to the treatment of coal to beneficiate it and provide products useful not only as fuel but also in the preparation of a variety of materials of widely different commercial use.

A major object of the invention is to beneficiate coal to separate carbonaceous matter from mineral matter, and particularly to separate useful coal substance from accompanying mineral matter and fusain, and further to recover and separate the fusain and mineral matter.

Another object is to form a substantially complete solution of coal except for its mineral matter and fusain content, which solution is applicable to various useful ends, such as the provision of commercially desirable products of widely variant character and applicability.

Yet another object is to provide coal substance in a form which is convertible easily and cheaply to carbon products such as carbon black and activated carbon of especially high quality.

Still another object is to convert coal into plastics.

A further object is to convert coal to a purified form capable of hydrogenation with avoidance of difficulties and disadvantages that may be encountered due to the presence of natural constituents in coal as it occurs in nature.

A still further object of the invention is to separate and recover fusain from coal.

Still another object is to separate the carbonaceous matter and mineral matter present in natural coal.

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

In studies made in connection with the constitution of coal, solvents have been used for extracting coal, but as far as I am aware, such solvent treatment of coal has been used only for analytical purposes and has been of a very limited applicability. Thus, in all instances of such prior work known to me the solvents have been of restricted effect because none of them has been capable of extracting substantially the entire coal substance. Consequently, such procedures have been merely of academic interest and have not been applied to successful commercial ends.

The chemical constitution of coal is not known although it is recognized that coal 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, as will appear hereinafter, in describing this invention it may be said to com-

prise 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 which is amenable to the treatment of the present invention, and for brevity of reference it will be termed herein as "coal substance" to distinguish it from the contents of fusain and inorganic matter.

The present invention 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 suitable solvent. In this manner substantially all of the coal substance may be separated from the mineral matter and fusain, and the coal substance as thus extracted from the coal is in a pure form capable of manifold valuable commercial uses.

A major feature of the invention resides in the use of initially oxidized coal because, as I have discovered, such oxidation conditions the coal for extraction of the whole, or substantially the whole of its coal substance content. In other words, oxidation to an appropriate degree appears 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 the 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 these 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 now believe that the oxidation acts to convert the coal substance, at least in some part, to hydroxy-carboxylic acids, and this indicates the extent to which the coal is to be oxidized. Peculiarly enough, the solubility of fusain remains unchanged in the solvents used, which explains why it is classed herein as different from the "coal substance."

I have discovered that 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, a fact which is of importance for reasons which will appear hereinafter.

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. My work indicates that crushing of the coal to pass a 20-mesh standard sieve is adequate for most purposes, and that finer sub-division is in general unnecessary, although it may be done if desired for any reason.

In the practice of the invention the coal is subjected to gentle oxidation to the degree indicated hereinabove, and thereafter it is extracted with a suitable solvent of the class indicated, for instance, furfural. The extraction 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. When completed the solution of coal substance is separated from the residual mineral matter and undissolved fusain. This insoluble residue may be worked up, if desired, to separate and recover the fusain and mineral matter, and this may be accomplished in various ways because of the difference in specific gravity and chemical properties of the two constituents. For instance, they may be separated by flotation methods. Both the fusain and the inorganic, or mineral, matter may be considered as valuable by-products since fusain may be used for various purposes, and since the mineral matter contains pyrites, apatite, and other minerals having commercial uses.

As exemplifying the practice of the invention, reference may be made to one test in which 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. At the end of the time the reaction was 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 extracted by agitating 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 its content of dissolved coal was 7 per cent by weight, which corresponds to 140 grams or 93 per cent by weight of the original coal. This indicates clearly the high degree of extraction attainable in the practice of the invention. The solid coal substance obtained by evaporation of the furfural was hydrophobic. The amount of residue insoluble in the furfural was 10.5 grams, or 7.7 per cent by weight of the original coal, and it consisted of mineral matter, fusain, and perhaps a little undissolved coal substance.

The solution of coal obtained in the practice of the invention may be used in various ways, and its applicability is enhanced by the fact that it presents the coal substance in an ash-free form. Thus, it may be used wherever a liquid fuel is desired, either with burners designed for that purpose or as a Diesel engine fuel, or it might be used as a medium for the production of colloidal fuel such as that made by suspending pulverized coal in a liquid vehicle. Or, the dissolved coal may be recovered, as by evaporation of the solvent, and put to various uses as will appear hereinafter.

I have discovered that if the solution be heated progressively, for instance during evaporation or distillation of the solvent, the coal substance tends to be precipitated as an ash-free brownish powder of very fine particle size. This interferes with the formation of concentrated solutions such as are necessary for fuel purposes, and it may be undesirable in the distillation of solvent for the recovery of the coal substance. 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 extraction should be conducted at a temperature below that at which the solute will be precipitated. I have discovered further, however, that by subjecting the solution to mild hydrogenation, at low temperature and in the presence of a suitable catalyst, some change occurs which renders the solution stable toward heat and permits extensive concentration without precipitation of the coal substance. Very mild hydrogenation suffices for this purpose. For example, there may be suspended in the solution a suitable catalyst, such as a precious metal catalyst supported on barium sulfate, and hydrogen bubbled into the solution at normal room temperature and pressure. This is a striking phenomenon because, as far as I am aware, it has not been possible heretofore to hydrogenate coal at ordinary temperatures and pressures, and it indicates the unusual character

of this oxidized coal substance and its amenability to conversion into useful products of different character.

Such hydrogenation with furfural as the solvent may cause the solvent to be converted to a greater or lesser degree to furyl alcohol or to tetra-hydrofurfuryl alcohol. This is why it is advantageous that the solubility of the coal substance is not adversely affected by such furane derivatives for the solubility of coal substance in them permits the production of highly concentrated solutions. Also, the ability to use such furane derivatives and to have them present in the solvent is advantageous also for reasons of hydrogen economy.

Ash-free coal substance may be recovered by separation from the solvent, as a brownish powder in very finely divided form, and it possesses unusual and highly desirable properties. By treating it at high temperatures, say 700° C. and higher, with an activating agent such as those used for activating carbon, e. g., steam, there are obtained activated carbon preparations superior to those presently available because of their freedom from ash, and possessing high activity. On the other hand, the recovered coal substance may be heated in air at relatively low temperatures, say below 500° C., to obtain a product of deep black color and of physical characteristics such that it appears to be either identical with or closely related to commercial carbon black. Whatever be its constitution and physical nature, however tests have demonstrated that this latter material can be put to the same uses as commercial carbon black.

The dissolved coal substance, whether in solution or in solid form recovered from solution, also possesses the capability of responding to chemical treatment so that it is convertible to organic compounds. As an example, plastics have been made from it by condensation reactions with suitable substances such as casein, phenols, cresols, naphthols, the mono-, di-, or tri-methylamines and ethanolamines, resorcinol, formaldehyde, and many other compounds such as aniline, pyridine, quinoline, urea, proteins, and other organic nitrogen bases. All of these materials take part in condensation reactions involved in producing synthetic resins or plastics.

Various alternatives are permissible in the practice of the invention as will be recognized by those skilled in the art. For instance, instead of subjecting the coal to an initial oxidation there might be used, with the solvents contemplated, coals and related materials which have been naturally oxidized, such as brown coals and peats, provided the natural oxidation has been sufficient to condition the coals for treatment with a solvent in accordance with my invention. In some instances it may be desirable to treat these naturally oxidized products with hydrochloric acid, to decompose metallic carboxylates. And although the example given involved the treatment of a bituminous coal of medium content of volatile matter, other types of coal and of higher or lower content of volatile matter may be used.

Where the solid coal substance is recovered it may be obtained by distillation of the solvent, as described, preferably with recovery of the solvent, or in other ways, as by adding liquids in which the coal substance is insoluble, or by steam distillation. Similarly, the oxidized coal may be separated from liquid media by means other than filtration, as by centrifuging, dialysis, decantation, and the like.

Also, while the use of the solution or of coal substance recovered from it as a fuel has been described, together with the conversion of the coal substance into valuable commercial products such as activated carbon, carbon black and plastics, it will be understood that the invention is not limited thereto, it being possible to convert or use the coal substance or its solution in any way or for any purpose to which the material is adapted. For example, being readily amenable to hydrogenation it might be hydrogenated extensively to produce liquid products, such as lubricating oils, by procedures partaking of the nature of those now used for converting coal by hydrogenation into such products.

Likewise, in converting the recovered coal substance into other materials by chemical reaction there might be used sulfur and sulfur compounds, including organic compounds of sulfur, to produce plastics, cementing substances, sulfur dyes, and the like.

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 treating coal which comprises treating coal in mildly oxidized condition in which the coal substance is converted, at least in part, to hydroxy-carboxylic acids, with an organic solvent containing heterocyclic oxygen and thereby dissolving oxidized coal substance, and separating the thus-formed coal solution from undissolved mineral matter.

2. That method of treating coal which comprises treating coal in mildly oxidized condition in which the coal substance is converted, at least in part, to hydroxy-carboxylic acids, with a furane derivative and thereby dissolving oxidized coal substance, and separating the thus-formed coal solution from undissolved fusain and mineral matter.

3. That method of treating coal which comprises treating coal in mildly oxidized condition in which the coal substance is converted, at least in part, to hydroxy-carboxylic acids, with furfural and thereby dissolving oxidized coal substance, and separating the thus-formed coal solution from undissolved fusain and mineral matter.

4. That method of treating coal which comprises treating coal in mildly oxidized condition in which the coal substance is converted, at least in part, to hydroxy-carboxylic acids, with an organic solvent comprising heterocyclic compounds including heterocyclic oxygen compounds and thereby dissolving oxidized coal substance, and separating the coal solution from undissolved fusain and mineral matter.

5. That method of treating coal which comprises treating coal in mildly oxidized condition in which the coal substance is converted, at least in part, to hydroxy-carboxylic acids, with an organic solvent comprising heterocyclic compounds including furane derivatives and thereby dissolving oxidized coal substance, and separating the thus-formed coal solution from undissolved fusain and mineral matter.

6. That method of treating coal which comprises subjecting coal to gentle oxidation to convert the coal substance, at least in part, to hydroxy-carboxylic acids, treating the oxidized coal

with an organic solvent containing heterocyclic oxygen and thereby dissolving coal substance, and separating such solution from residual mineral matter.

7. That method of treating coal which comprises subjecting coal to gentle oxidation to convert the coal substance, at least in part, to hydroxy-carboxylic acids, treating the oxidized coal with furfural and thereby dissolving coal substance away from fusain and mineral matter, and separating such solution from the residual fusain and mineral matter.

8. That method of treating coal which comprises treating coal in oxidized condition with an organic solvent containing heterocyclic oxygen and thereby dissolving oxidized coal substance, separating the thus-formed coal solution from undissolved fusain and mineral matter, and subjecting said solution to hydrogenation.

9. As a new article of manufacture, coal substance characterized by being substantially free from fusain and mineral matter, and by being of hydrophobic nature, and derived by extraction of coal in mildly oxidized condition in which the coal substance has been converted, at least in part, to hydroxy-carboxylic acids, with an organic solvent containing heterocyclic oxygen to form a solution of substantially the whole of the coal substance free from fusain and mineral matter, and recovering the solute from said solution.

10. As a new article of manufacture, coal substance characterized by being substantially free from fusain and mineral matter, and by being of hydrophobic nature, and derived by extraction of coal in mildly oxidized condition with a furane derivative to form a solution of substantially the whole of the coal substance free from fusain and mineral matter, and recovering the solute from said solution.

11. As a new article of manufacture, coal substance characterized by being substantially free from fusain and mineral matter, and by being of hydrophobic nature, and derived by extraction of coal in mildly oxidized condition in which the coal substance has been converted, at least in part, to hydroxy-carboxylic acids, with furfural to form a solution of substantially the whole of the coal substance free from fusain and mineral matter, and recovering the solute from said solution.

12. As a new article of manufacture, a hydro-

genated solution of coal substance which has been oxidized at least in part, to hydroxy-carboxylic acids, in an organic solvent containing heterocyclic oxygen and characterized by retention of the coal solute upon heating and upon concentration of the solution by removal of solvent.

13. As a new article of manufacture, a hydrogenated solution of coal substance which has been oxidized at least in part, to hydroxy-carboxylic acids, in furfural and characterized by retention of the coal solute upon heating and upon concentration of the solution by removal of solvent.

14. That method of extracting coal which comprises extracting coal in mildly oxidized condition with an organic solvent containing heterocyclic oxygen and thereby dissolving in said solvent substantially the whole of the coal substance while leaving mineral matter and fusain substantially undissolved, and separating the resultant solution from undissolved matter.

15. A process according to claim 14 in which said solvent is a furane derivative.

16. A process according to claim 14 in which said solvent is furfural.

17. As a new article of manufacture, a solution of coal substance oxidized, at least in part, to hydroxy-carboxylic acids, said substance being dissolved in an heterocyclic organic solvent containing heterocyclic oxygen.

18. As a new article of manufacture, a solution in accordance with claim 17, said solvent being a furane derivative.

19. As a new article of manufacture, a solution in accordance with claim 17, said solvent being furfural.

20. That method of extracting coal which comprises contacting coal in mildly oxidized condition in which the coal substance has been converted, at least in part, to hydroxy-carboxylic acids with an organic solvent containing heterocyclic oxygen at a temperature substantially below the boiling point of said solvent and thereby dissolving therein substantially the whole of the coal substance while leaving mineral matter and fusain substantially undissolved, and separating the resultant solution from undissolved matter.

21. A process according to claim 20, said solvent being furfural and said extraction being conducted at a temperature below about 120° C.

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