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2,596,793

PROCESS FOR THE EXTRACTION OF VALUABLE CONSTITUENTS FROM UNEXPOSED OIL-BEARING SHALES NOT SPENT BY OXIDATION

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This invention relates to the treatment of certain naturally occurring carbonaceous materials; namely, coals, lignites, peats and shales which have certain common characteristics and differ as to other characteristics. The present invention relates particularly to the predetermined partial solvent extraction of extractable matter from coals, and to the complete solvent extraction of substantially all extractable matter from coals, lignites, peats and shales.

Thus, one aspect of the invention relates to the treatment of bituminous coals which contain an undue proportion of highly volatile materials and possess a relatively high content of resinous, waxy, oily and similar materials which lower the calorific value and carbon content of the coals and render such coals practically non-cokable. Such coals are not economically useful either for the production of coke for use in blast furnaces and kindred metallurgical industries, or suitable as commercial fuels for home furnace use and the like.

Heretofore attempts have been made to treat the mentioned bituminous coals to render them cokable by adding quantities of pitch or other agents capable of imparting a degree of cokability to the mentioned bituminous coals. However, such processes are not only expensive but are not entirely satisfactory. Moreover, many usable constituents originally found in such coals are destroyed and lost in the coking process and also the coking of such coals, even under such attempted conditions, fails to yield the normal coking by-products conventionally recovered in conventional coking plants employing conventional coking coal. In view of the last indicated circumstance the by-products recovery systems of conventional coking plants are upset and the economics of the whole coking procedure are very seriously disturbed. In my Patents Nos. 2,453,543 and 2,453,544 issued on November 9, 1948, I have disclosed and claimed the partial extraction of poorly cokable bituminous coals by leaching with ethylene dichloride at atmospheric temperatures to obtain a cokable coal and recover the resinous and other ethylene dichloride soluble constituents extracted from the coal.

In another aspect, this invention also relates to the complete solvent extraction of the usual bituminous or anthracite coals to obtain therefrom substantially all of the extractable matter.

This invention also relates to the complete extraction treatment of lignites (brown coal) to obtain therefrom the resins, waxes, and oils which become valuable commercial products for chemi-

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cal, pharmaceutical, cosmetic and dye uses. Of special value are lignites which contain a relatively high percentage of montan wax in addition to various resins and oils normally found in bituminous coals.

It has previously been proposed to remove resins, waxes and oils from lignite by various processes involving the use of a number of solvents. Thus, it has been proposed to remove montan wax from lignite by the use of alcohol and benzene solvents (Bulletin I. C7417, July, 1947. U. S. Bureau of Mines Annual Report on Coal for 1946), but processes of this type involve considerable expense, including high temperatures, numerous solvents and long periods of treatment.

Thus, this invention is distinguished from processes heretofore known where it was sought to extract the lignite with various combinations of solvents for a long period of time with or without further extraction to remove as many of the soluble constituents as possible, elevated temperatures being used to effect maximum or other extensive extraction.

This invention also relates to the complete solvent extraction treatment of peat to obtain certain waxes, resins and oils which become valuable products. Of special value are peats containing a relatively high percentage of valuable waxes of the montan type in addition to various resins and oils.

It has previously been proposed to remove resins, waxes and oils from peat by various processes involving the use of a number of solvents. Thus, it has been proposed to remove peat wax from peat by the use of benzene solvents (Petroleum—for April, 1948, pages 77-82, inclusive; Ester Waxes from British Peat by C. M. Cawley). The ordinary solvent extraction of peat wax from peat by the use of benzol or alcohol has resulted in the extraction of black wax which has been used as a substitute for montan wax in polishes and the like. However, solvent extraction processes of this type generally involve considerable expense and have not proved either commercially practicable or economically sound.

This invention further relates to the complete solvent extraction treatment of shales which have been unexposed and have not been spent by oxidation in order to obtain valuable petroleums including benzene, high grade gasoline, kerosene, fuel oil and other hydrocarbons, some waxes and minor amounts of resins.

Having in mind the serious consequences attending efforts to produce coking coals and suit-

able domestic fuel from highly resinous, waxy and oily bituminous coals, I have made the unexpected discovery that such bituminous coals may be easily solvent-treated with methylene chloride in a closed circulatory system at the boiling point thereof and at predetermined pressures and for a comparatively brief predetermined interval of time, ranging from 1-2 hours so as to render them cokable to produce metallurgical cokes and at the same time render them useful for domestic fuels, while also making it possible to recover as extracts for various uses the mentioned resinous, waxy, oily and similar materials including fractions of unusually low boiling points. I have discovered that my process makes it possible to treat bituminous coal substantially in the condition in which it comes from the mine, that is, run of mine coal, it being necessary merely to break or remove unusually large lumps, such as those which will not pass about a seven inch screen. Thus, by the term "run of mine coal" or the term "coal as mined," I mean to include all coal sizes below the very large lumps such as just above indicated. I have further discovered that when such coal is treated as required by my process the conventional by-products systems of coking plants may be employed in a conventional manner and the conventional coking or so-called "coal-tar" by-products recovered, thereby maintaining the economics of the usual coking and by-products recovery systems.

I have also discovered that by a modification of my process I am able to completely extract coals to obtain substantially all the extractable matter therefrom by solvent treating with methylene chloride at the boiling point thereof in a closed circulatory system under a predetermined pressure for a comparatively brief period of about 5 hours, the particle size of the coal preferably being $\frac{1}{4}$ inch to No. 6 screen size in order to extract at the minimum pressure.

I have also discovered that by a modification of my process I am able to treat lignite with this solvent and by virtue of the complete extraction, substantially all of the soluble products are leached from the lignite, following which the solvent is recovered by distillation and the extracted resins, waxes and oils are then separated by fractional distillation into the desired number of their products, the resultant lignite being deprived of solvent by vacuum treatment and thereafter compressed into briquettes by conventional method for use as domestic and industrial fuel.

I have also made the discovery that by a further modification of my process, an unexpected high percentage of valuable resins, waxes and oils, particularly montan waxes and fractions of unusually low boiling points, may be recovered in a state of high purity by the complete solvent-treating of peat in accordance with this invention, and at the same time my discovery makes it possible to produce a peat product which is suitable for use as an industrial and domestic fuel.

I have further discovered that by still another modification of my process, it becomes possible to treat the mentioned shales to obtain a substantially complete yield of extractable petroleum, especially benzene, high grade gasoline, kerosene, fuels, other hydrocarbons, some waxes and minor amounts of resins and other oils. By virtue of the present process, the shale is subject to complete extraction, thereby resulting in

a neutral stone end-product which has a high affinity for tar and thereby provides an excellent raw material for the preparation of macadam roads.

The invention generally comprises the solvent extraction of coal, lignite, peat or shale with methylene chloride at substantially the solvent boiling point (40.5°C). in a closed system under a pressure varying from about 100 to 1500 lbs. for a period of time ranging from 1 to 2 hours for a predetermined partial extraction of bituminous coal to form a valuable coke, and for a period of about 5 hours time for a substantially complete extraction of all extractable matter from coal, lignite, peat or shale. In the case of complete extraction I have discovered that improved results are obtained and lower range pressures may be employed when the carbonaceous materials are of a particle size ranging from $\frac{1}{4}$ inch to No. 6 screen size. Following the solvent extraction under pressure in a circulatory system, the resulting carbonaceous material is rinsed with hot methylene chloride at a temperature between 35 to 40.5°C . and the rich solvent is then evacuated from the material by vacuum. The rich solvent containing the extractable (soluble) matter is then distilled to distill off the solvent from the extractable matter and the solvent is then available for re-use. The extracted material is then subjected to fractional distillation to separate the oil, wax, resin, etc. constituents thereof into the various desired grades and fractions.

It is, therefore, a general object of my invention to furnish to the industry a novel process for treating bituminous coals which are initially non-cokable because of high content of resins, waxes, oils and similar materials, so that they may be subsequently coked according to conventional coking practices. It is another object of my invention to provide a process for the treating of such bituminous coals, so that, when coked, they will yield the usual coking by-products which may be recovered in the usual by-products recovery system.

An additional object of my invention is to provide a process for treating bituminous coals whereby the constituents which deleteriously affect the coals for coking purposes may be extracted and recovered as useful by-products while at the same time rendering the treated coals economically useful and satisfactory for coking purposes, including the production of good metallurgical cokes, and for the usual recovery of coking by-products, as well as rendering the extracted coals useful as domestic fuels for home furnace use and the like.

Thus, it is an object of this invention to provide a process for the treatment of unsatisfactory bituminous coal such that all constituents thereof may be recovered in useful form, one of the products being a satisfactory cokable coal.

It is, therefore, not only an object of this invention to provide a new method for treating bituminous coal to produce an improved fuel and an improved coal for coking purposes, but it is also an object to provide a novel process for the production of a novel, commercially valuable coke from a low grade practically non-cokable bituminous coal. Another object is to produce a novel fuel from such a bituminous coal.

It is further an object of the invention to produce a metallurgical coke from such a coal, and an additional object is to obtain from bituminous coal a good coke while at the same time obtain-

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ing by-products which may be readily and economically processed in the usual coking by-products recovery plant.

A further object is to extract substantially all of the extractable matter from coals so as to obtain a high yield which will make it economically practicable to utilize coals as a source of resins, waxes and oils.

Another object is to extract substantially all of the numerous valuable resins, waxes and oils naturally occurring in lignite, particularly to obtain a high yield of montan wax, which process will be efficient and commercially practicable and will not require the use of excess temperatures or pressures and, additionally, will not require the use of numerous expensive solvents and which will not require an extended number of solvent reactions. Yet another object of the present invention is to provide a process for the treatment of lignites which are generally unsatisfactory for commercial use in their naturally occurring form so that the treated lignites and the recovered by-products will be available in commercially useful and valuable form.

Another object is to extract substantially all of the numerous valuable resins, waxes and oils naturally occurring in peat particularly to obtain a high yield of montan wax from peat deposits, which process will be efficient and commercially practicable and will not require the use of excess temperatures or pressures, and, additionally, will not require the use of numerous expensive solvents and which will not require an extended number of solvent reactions or an extended period of time. Yet another object is to provide a process for the treatment of peats which are generally unsatisfactory for commercial use in their natural occurring form so that the treated peat and the recovered by-products will be available in commercially useful and valuable form. Still another object is to provide a process for treating peat whereby the constituents which deleteriously affect the peat for fuel purposes may be removed as useful and valuable by-products, while at the same time rendering the treated peat useful for fuel purposes.

Another object is to extract substantially all of the valuable petroleums, especially benzene, high grade gasoline, kerosene, fuel oil and other hydrocarbons and some waxes and small amounts of resins from unexposed shales which have not been spent by oxidation, which process will be efficient and commercially practicable, will not require numerous expensive solvents or extended solvent reactions and which will require only moderately elevated temperatures and pressures and a relatively brief treating period. Still another object is to provide for the complete extraction of the mentioned shales so as to result in a neutral stone by-product which has a high-affinity for tar and thereby provides an aggregate for macadam roads or building structures.

These and other objects will be better understood by reference to the following description.

I. PROCESS OF TREATING BITUMINOUS COAL AND PRODUCTS OBTAINED THEREBY

A. Partial extraction of substantially non-cokable bituminous coal to obtain a cokable coal

In one embodiment of the invention, 250 lbs. run of mine Utah bituminous coal having a fairly high resin content was treated. A run of mine coal is intended to signify a coal which has lumps no larger than about 7 inches in transverse dimension and where the average lump size is

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about 3 or 4 inches. The coal was placed in a wire mesh basket in a cylindrical extraction vessel having a filter cloth in the bottom and equipped with a re-circulation outlet line running from the bottom thereof and connected through to a pressure pump to the top of the vessel for recirculation of the solvent. The methylene chloride solvent was maintained at a temperature ranging from 35 to 40.5° C. and was forced downwardly through the coal under a pressure of 1500 lbs. per sq. inch for a period of two hours. The treated coal was then washed with fresh hot solvent (35 to 40.5° C.) for several minutes. The residual solvent remaining in the treated coal was then removed by vacuum of about 28 inches mercury.

This leaching treatment resulted in a coal product from which was extracted that quantity of resins, waxes, oils and other methylene chloride soluble materials necessary to provide a cokable coal of such characteristics that the conventional by-products were obtained during the subsequent coking operation.

Analysis of the untreated coal showed 43½% untreated volatiles, 48½% fixed C, 7% ash, 1+-% S and 13,000 B. t. u. per lb.

Analysis of the leached coal showed 42½% fixed volatiles, 49½% fixed C, 6% ash, 1% S, and 14,000 B. t. u. per lb.

The coke yield was calculated at about 63½% with an analysis of 86% fixed C, 10% ash, 3¾% volatiles and -1% S.

The coke by-products were calculated to have 3400 B. t. u. per lb. of coal and 675 B. t. u. per cubic foot of gas. The gas totaled 1375 cubic feet per the 250 lbs. of coal treated equalling about 5½ cubic feet of gas per lb. of coal. Other coke by-products obtained in the basis of the 250 lbs. coal included ½ gal. lightoil, 3½ lbs. ammonium sulfate and 1½ lbs. tar.

The rich solvent was distilled in a solvent recovery still, resulting in the recovery of 8¼ lbs. residue comprising resins and oils. The resins were precipitated out from the oils by dissolving the residue in about an equal amount by weight of fresh solvent and then adding about 2 parts by weight of 95% ethyl alcohol as precipitant to bring down the resins.

The remaining solution of alcohol containing methylene chloride and dissolved oils was distilled to distill off the methylene chloride at 40.5° C. and the alcohol at 78.4° C. The oils were then fractionally distilled to obtain the component fractions. The precipitated resins were likewise fractionally distilled to separate the various wax and resin components.

B. Complete extratcion of bituminous coal

The general process set forth in Example IA was followed with certain modifications; namely, 250 lbs. of the same coal was reduced in size by grinding to particles from coarse sand size to ¼ inch size, although particles up to No. 6 mesh screen size are useable. An extraction temperature of 40.5° C., the boiling point of the methylene chloride solvent was maintained. The extraction time was continued for the full 5 hour period, the solvent being recirculated in the closed system by a force pump under a full pressure of 1200 lbs. per sq. inch. Thereafter the completely leached coal was rinsed under pressure with fresh hot solvent and then evacuated by vacuum at 28 inches mercury to remove the absorbed rich solvent, semi-rich and lean solvent entrained in the leached coal.

The completely leached, spent coal is not usable for coking purposes since, for one reason, the conventional coal tar by-products cannot be recovered during the coking process although the treated coal can be used as industrial or commercial fuel.

The completely leached coal was analyzed at 52% fixed C, 40% fixed volatiles, less than 6% ash and 1% S.

The rich solvent was distilled to recover the solvent for re-use and the residual oil and resins were separated by precipitation. The oils recovered and separated from the resins amounted to 7 gals. for the 250 lb. batch. The oils were fractionally distilled to obtain gasoline and the remaining light oil components.

II. COMPLETE EXTRACTION OF UN-EXPOSED SHALES

The general process set forth in Example IB was followed with an unexposed shale of the Utah type which is relatively unoxidized. The shale was ground to a particle size of coarse sand (No. 6 mesh screen to 1/4 inch) and subjected to a complete extraction for 5 hours with methylene chloride being recirculated through the shale at about 40.5° C. under a pressure of 1500 lbs. per sq. inch. Following rinsing with hot solvent under pressure and removal of the entrained solvent from the shale by vacuum, it was that the shale was substantially completely extracted of all the methylene chloride-soluble constituents.

The resulting shale was neutral, had a high affinity for tar and had a stony appearance. The separated residues comprised benzine, high grade gasoline, kerosene, fuel oil, and minor amounts of resins and waxes. The oil recovered from the extraction was measured at 7.75 gals. for the 250 lbs. of raw shale treated.

III. COMPLETE EXTRACTION OF LIGNITES

The process set forth in Example II was followed with a pulverized lignite occurring naturally in California, the only variation being that a vacuum of 28 inches was employed for removal of the solvent entrained in the spent lignite following the leaching and rinsing. It was found that complete extraction of the methylene chloride-soluble constituents was achieved by the 5 hour leaching.

The products obtained by fractional distillation were found to be as follows:

TABLE I

Products obtained by fractional distillation from leached lignite by methylene chloride

	8 mm.	760 mm.	
	°C.	°C.	°F.
Initial.....	120	258	496
1.....	138	281	538
2.....	156	303	577
3.....	170	320	608
4.....	180	332	630
5.....	186	340	644
6.....	195	349	660
7.....	200	354	669
8.....	205	360	680
9.....	210	366	691
10.....	215	371	700
11.....	221	379	714
12.....	225	383	721
13.....	224	382	719
14.....	222	380	716
15.....	218	375	707
16.....	210	360	691

Waxes
Fraction 1 Group—Refractive Index 1.513.

Montan Wax
Fraction 2 Group—Refractive Index 1.519.

Resins
Fraction 3 Group—Refractive Index 1.516.

Still temperature was 360° C. (680° F.) at close of distillation. Additional products may be obtained from the remaining pitch by cracking.

In the preferred form of the invention, the resins are not separated before making the above refraction recovery; that is, the leached out material is fractionated without first separately recovering the resin. It has been found that this can be done to great advantage in the case of a lignite containing a high percentage of resins.

IV. COMPLETE EXTRACTION OF PEATS AND PRODUCTS OBTAINED THEREBY

The process set forth in Example III was followed with a peat occurring naturally in Pennsylvania. Substantially complete extraction of the methylene chloride soluble constituents from the peat was obtained with the 5 hours leaching, the extracted products separated by fractional distillation having the following characteristics:

TABLE II

Products obtained by fractional distillation from leached lignite by methylene chloride

Waxes:

Fraction 1 Group—Refractive index 1.513.

Montan wax:

Fraction 2 Group—Refractive index 1.519.

Resins:

Fraction 3 Group—Refractive index 1.516.

Additional products may be obtained from the remaining pitch by cracking.

In the preferred form of the invention, the resins are not separated before making the above refraction recovery; that is, the leached out material is fractionated without first separately recovering the resin. It has been found that this can be done to great advantage in the case of a peat containing a high percentage of resin.

Among the general considerations and specific conditions to be observed in practicing the present invention are the following critical factors which are co-related in respect to each other.

(a) The solvent is methylene chloride which has a boiling point of about 40.5° C. This boiling point is sufficiently low to permit separation of the various soluble components without injury thereto or effect thereon from excessive heat. This specific solvent has the ability to dissolve out all the desired components in a relatively short time at low temperatures and pressures.

(b) A leaching temperature of 35 to 40.5° C. must be employed for partial extraction of coal to form a cokable coal. A temperature of approximately 40.5° C. is necessary for complete extraction of the carbonaceous materials.

(c) Substantially complete extraction can be obtained by forcing the methylene chloride under recirculation through the material at a pressure of 100 to 1500 lbs. per sq. inch depending on the size and porosity of the raw carbonaceous material particles and upon the compactness and amount of material being leached in the extraction. In the case of an extractor having a capacity of 20 to 40 tons, the maximum pressure is required. Likewise, in the case of partial extraction of coal in large lumps of the order of 7 inches, the high pressures are required to force the recirculating solvent through the material, at less than pressures of 100 lbs. per sq. inch, complete extraction cannot be achieved under the aforementioned conditions.

(d) Leaching periods of 1-2 hours are required for partial extraction of a poorly cokable bitu-

minous coal in order to obtain a cokable coal. Greater periods than 2 hours result in over-extraction and a coal which is not cokable.

(e) Substantially complete extraction is obtainable with an extraction period of only 5 hours time, although the extraction time may be shortened to slightly less than 5 hours where finely ground materials in small batches are employed.

(f) Substantially complete extraction may be obtained with particle sizes approximating those of coarse sand, or $\frac{1}{4}$ inch to No. 6 mesh screen size. Partial extraction of coal to form cokable coals may be had with particle sizes up to 7 inches in transverse dimension.

(g) Solvent removal of entrained solvent is preferably accomplished by vacuum of about 28 to 30 inches mercury.

It will be understood by those skilled in the art that I have provided a process which will achieve the maximum extraction of practically all hydrocarbons and other organic materials of the valuable oil, wax and resin type from the naturally occurring carbonaceous materials coal, shale, peat and lignite, which process employs the solvent methylene chloride capable of dissolving the said materials in high capacity at a minimum temperature in a minimum period of time and under a minimum leaching pressure, all without modifying the character of the extractable components. The process is adaptable for efficient, large scale operations which render it economically practical. The by-products of the coal, lignite and peat are useful as industrial and commercial fuels and may be compressed into briquette form. The shale by-products are useful as building and road aggregates.

It will be understood that the invention may be practiced with various modifications occurring to those skilled in the art and it is intended to cover all such modifications as fall within the spirit and scope of the appended claims.

I claim:

1. A process for the extraction of methylene chloride-soluble constituents from unexposed oil-bearing shale not spent by oxidation which comprises forcing methylene chloride at a temperature ranging from about 35° to 40.5° C. through said shale under pressure ranging from 100 to 1500 pounds per square inch for a period of time ranging from about one to five hours, sufficient to leach out the desired amount of the desired said constituents, separating the leached material from the resulting methylene chloride solution rich in said dissolved constituents, and recovering from the solution the said constituents dissolved therein.

2. A process for the extraction of methylene chloride-soluble constituents from unexposed oil-bearing shale not spent by oxidation which comprises forcing methylene chloride at a temperature ranging from about 35° to 40.5° C. through said shale under pressure ranging from 100 to

1500 pounds per square inch for a period of time approximating five hours to leach out the desired amount of the desired constituents, separating the leached material from the resulting methylene chloride solution rich in said dissolved constituents and recovering from the solution the said constituents dissolved therein.

3. A process for the extraction of methylene chloride-soluble constituents from unexposed oil-bearing shale not spent by oxidation which comprises forcing methylene chloride at a temperature ranging from about 35° to 40.5° C. through said shale under pressure approximating about 1500 pounds per square inch for a period of time ranging from about one to five hours to leach out the desired amount of the desired said constituents, separating the leached material from the resulting methylene chloride solution rich in said dissolved constituents and recovering from the solution the said constituents dissolved therein.

4. A process for the extraction of methylene chloride-soluble constituents from unexposed oil-bearing shale not spent by oxidation which comprises reducing said shale to a particle size of about one-fourth inch to No. 6 mesh screen size, forcing methylene chloride at a temperature ranging from about 35° to 40.5° C. through said material under pressure ranging from 100 to 1500 pounds per square inch for a period of time ranging from about one to five hours to leach out the desired amount of the desired said constituents, separating the leached material from the resulting methylene chloride solution rich in said dissolved constituents and recovering from the solution the said constituents dissolved therein.

5. A process for the extraction of methylene chloride-soluble constituents from unexposed oil-bearing shale not spent by oxidation which comprises reducing said shale to a particle size of about one-fourth inch to No. 6 mesh screen size, forcing methylene chloride at a temperature ranging from about 35° to 40.5° C. through said material under pressure ranging from 100 to 1500 pounds per square inch for a period of time approximating five hours to leach out the desired amount of the desired said constituents, separating the leached material from the resulting methylene chloride solution rich in said dissolved constituents and recovering from the solution the said constituents dissolved therein.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,836,020	Freytag	Dec. 15, 1931
1,978,010	Carlisle	Oct. 23, 1934
2,453,543	Schabelitz	Nov. 9, 1948