

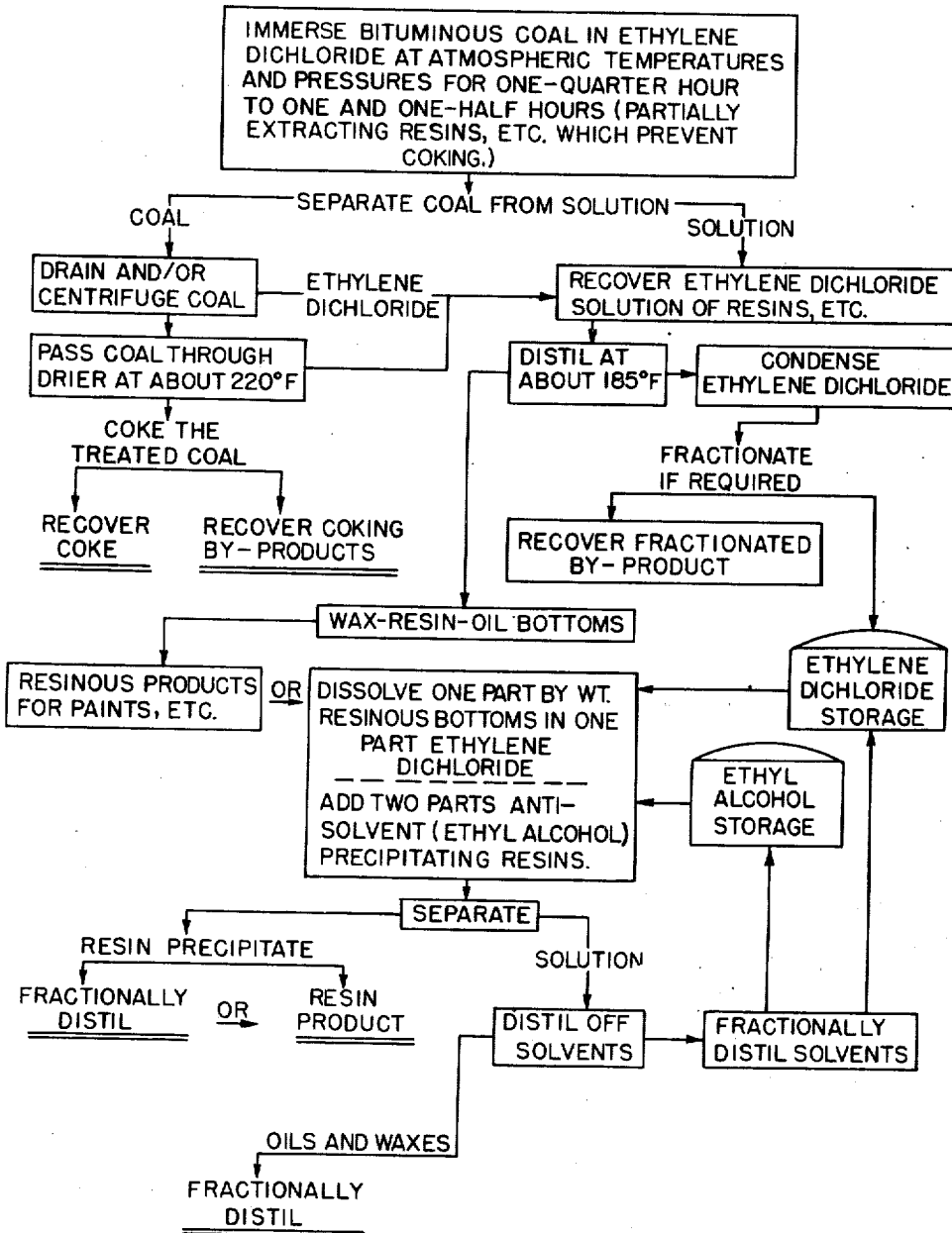
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PROCESS OF TREATING BITUMINOUS COAL

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PROCESS OF TREATING BITUMINOUS COAL

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8 Claims. (Cl. 260-107)

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This invention relates to the treatment of bituminous coals which contain an undue proportion of highly volatile material and possesses 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 poorly coking coals are represented by coals found in the State of Utah and elsewhere and are in general referred to herein as bituminous coals of the Utah type. 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.

Having in mind the serious consequences attending efforts to produce coking coals and suitable domestic fuel from highly resinous, waxy and oily bituminous coals of the described Utah type, I have made the unexpected discovery that such bituminous coals may be easily solvent-treated at normal temperatures and pressures and for comparatively very brief intervals of time 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 a seven or eight inch screen. Thus, by the term "run of mine coal" or the term "coal as mined," I mean

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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.

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, above referred to as coals of the Utah type, 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 bituminous coals of the stated Utah type 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 overall 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 satisfactorily cokable coal.

This application is a continuation-in-part of my earlier application Serial No. 699,591, filed September 26, 1946.

The accompanying drawing, which is in the nature of a flow sheet, represents diagrammatically various aspects of the present invention and the sequence of steps involved in carrying on various forms and phases of the invention.

My invention resides in part in the specific discovery that bituminous coals having a content of volatile materials such as resins, waxes, oils and similar constituents which render the coals substantially non-cokable, that is, coals of the described Utah type, may be rendered cokable by

3 extraction with ethylene dichloride as a solvent, the extraction being carried on under atmospheric temperatures and pressures by immersion of the coals in the ethylene dichloride for a moderately brief interval of time which ordinarily lies between about twenty minutes and about one hour, so that sufficient of resins, waxes, oils and similar materials are extracted to render the coal products cokable, but without any over-treatment which would result in removal of tars and possibly others of the less soluble materials apparently necessary for proper coking operations. Such over-extraction deleteriously affects the coking characteristics of the product. By the term "over-extraction," I mean to indicate that, if these non-cokable coals are extracted with ethylene dichloride for long periods of time, for example ten hours or more at normal temperatures, especially at average atmospheric temperatures of around 70° F. to summer heat in the neighborhood of 100° F., such extraction removes tars and possibly other less soluble materials which apparently render the treated coal product undesirable because its coking characteristics are deleteriously affected, and also because the operations of the well established by-products recovery systems are upset and the conventional by-products desired are not obtained.

Thus, this invention is distinguished from processes heretofore known where it was sought to extract the coal with a solvent for a long period of time with or without further extraction to remove as many of the soluble constituents as possible, elevated temperatures approaching the boiling point of the solvents or above being used if required to effect maximum or other extensive extraction. According to the present invention, however, the extraction is carried on only to the optimum to produce the best coking coal and to yield coking by-products best approximating conventional by-products recovered from ordinary coking coals well known in the industry.

Considering the treatment of the described bituminous coals, the above described run of mine coal without being put through a special grinding or powdering operation, is immersed and leached in a quantity of ethylene dichloride, that is, the coal is placed in ethylene dichloride in quantity sufficient to cover the coal. Both the coal and the ethylene dichloride are preferably unheated, that is, in no instance, in accordance with this invention, are they raised above ordinary normal temperatures or summer heat temperatures such as around 70° F. to 110° F. For efficient operation of the process, operations ordinarily are carried on simply at the prevailing atmospheric temperatures, and they are likewise carried on at atmospheric pressures. Thus, if the temperature is around the average normal temperature of 60° F., 70° F., or 80° F., the coal and the solvent are both employed at such a temperature. If the temperature drops to freezing, the process is still usually carried on at the prevailing atmospheric temperature. Excellent results have been accomplished, for example, where the atmospheric temperature was about 15° F., the immersion period being only sixty minutes. However, the ethylene dichloride might then also come from ordinary storage where it could have a somewhat greater temperature, that is, anywhere up to perhaps 60° F. or 70° F., but any other ordinary temperature as above indicated, such as summer heat temperature, might be used for the solvent. Possibly, if both the coal and the solvent were at a low temperature,

such as the mentioned 15° F., it might be helpful to extend the time to perhaps an hour and one-quarter or even an hour and one-half, but even then this treatment time of a maximum of an hour and one-half is very brief compared with extraction periods of many hours as heretofore employed where the purpose has always been, as above indicated, to produce the maximum or other severe extraction of materials soluble in the extracting fluid. Thus, these intervals are sufficiently brief to avoid over-extraction and therefore avoid producing extracted coal of objectionable coking properties.

From the standpoint of operations at normal temperatures, as above indicated, another very important factor is the convenience of operating at atmospheric pressure. While it is within the scope of this invention to employ elevated pressures if desired, no important advantage is obtained, and if elevated pressures are employed the economy of operating at atmospheric pressures is lost. Similarly, if desired to keep the ethylene dichloride at average normal temperatures, for example, between about 60° F. and about 80° F., when the atmospheric temperature is lower, as when it is around freezing or lower, the solvent may be correspondingly warmed, but again the economy of operating at the existing atmospheric temperature is lost.

Various ramifications of the process within the limits above indicated may be employed accordingly as operating conditions may indicate to be desirable. For example, batch operation effected by soaking the coal in an adequate amount of ethylene dichloride sufficient at least to immerse the coal may be employed, the soaking continuing for the required time interval as above indicated, with recycling of the solution if desired. Again, the operation may be continuous, and this probably will be most economical in nearly all installations, especially large installations. If desired, for any particular purpose, combinations of batch and continuous operation may be used. In the case of continuous operation, the coal may be passed by mechanical conveyors from one end of a long tank to another at such a rate as to provide the required extraction. In such a case the ethylene dichloride solvent itself may be supplied in batches, coal being passed therethrough until any desired concentration of extracted resins, waxes, oils and other soluble constituents of the coal is attained, whereupon a fresh batch of the solvent will be introduced after running off the "rich" solution. In any event, the treated coal preferably is given a final rinse with fresh or "lean" ethylene dichloride. On the other hand, where mechanical conveyors are employed for moving the coal through an elongated tank, fresh or "lean" ethylene dichloride may, if preferred, be continuously introduced at the discharge end of the tank, and the "rich" ethylene dichloride solution withdrawn from the coal-feed end of the tank, the rate of introduction and withdrawal of the ethylene dichloride and the coal being proportioned to the amount of coal being passed through the ethylene dichloride so that the desired concentration of extracted material is reached at the time of withdrawal. As will be apparent to those skilled in the extraction art, the solution would not be permitted to become so concentrated as to produce unsatisfactory extraction.

From the standpoint of the size of the coal being treated, this ordinarily will be run of mine

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coal, that is, coal as mined, without, however, excessively large lumps, as previously indicated. In no instance should all the coal be crushed or ground to a powder. Thus, while run of mine coal will commonly contain a considerable portion which may run as fine as one hundred mesh or finer, although such proportion does not deleteriously affect coking, nevertheless, if all of the coal were to be reduced to such a degree of fineness, the treated product would not coke properly. It is necessary and desirable that a considerable proportion of the coal be of appreciably larger sizes, such as about one inch size to three inch size, or larger, or too large to pass a one-half inch screen. Moreover, a considerable proportion of the coal may be of still larger sizes, and coal has been successfully treated where lumps were present running up to seven inches in their smallest or transverse dimension, or, in other words, coal passing a seven or eight inch screen. As previously defined, the terms "run of mine" and "coal as mined," as used herein, are intended to indicate a coal of ordinary run of mine characteristics in which there are not many large lumps in excess of about seven inches in transverse dimension. Preferably, any such larger lumps should be broken into pieces ranging in the order of one inch to four or five inches, or up to about seven inches in transverse dimensions so that all of the coal may be within sizes that may be classed within the above run of mine definition. Powdered coal, that is, coal in the order of one hundred mesh and finer tends toward over-extraction which is apparently offset to some extent by more limited removal of some of the (less soluble) constituents in the larger sizes, for example those running between about two inches and seven inches in their transverse dimensions. As a consequence, treatment of run of mine coal with ethylene dichloride at atmospheric temperatures and pressures as above defined, and within treating times of about fifteen minutes to not over about one hour and one-half, produces good coking coals from non-cokable bituminous coals of the Utah type herein described.

In general, the longer times between about an hour and one and one-half hours are employed where treating coals at temperatures below freezing, and the shorter periods, for example twenty minutes, have been found satisfactory where treating under summer heats, for example around 90° F. to 100° F. However, should any particular run of mine coal tend to run in the larger sizes rather than in the smaller sizes it may, at least for some coals, be preferable to use the longer treating time, that is, around one hour to as much as about one and one-half hours, even though operating in the upper portion of the indicated temperature range.

When the treated coal is to be removed from the solution of the extracts in ethylene dichloride, as much of the ethylene dichloride solution is removed as possible by any convenient operation. Thus, if a strictly batch treatment is employed, and the solution is drained from the coal, an adequate time will be allowed for drainage of the solution out of the tank and, if desired, auxiliary means, such as blowing, may be employed.

Such blowing may include hot air blowing for the purpose of further removal, as by volatilization, of the ethylene dichloride. Where the coal being treated is carried through the ethylene dichloride bath by mechanical conveyors, whether

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by counter-current flow of ethylene dichloride or otherwise, the coal will be allowed to drain adequately and may then be passed to centrifuges for removal of all excess liquid ethylene dichloride possible, the coal being then passed through steam heated units for volatilization of the remaining ethylene dichloride. Such units may be heated, for example, to the boiling point of ethylene dichloride, namely, about 185° F., or somewhat above that temperature, for example, around 200° F. to 212° F. The hot, dried coal is then passed as desired through cooling means, or otherwise, to tipple screens or to cars or other transportation means, or to stock piles.

The ethylene dichloride evaporated from the coal, as indicated, is recovered by condensation for further use. Upon drying of the coal of its ethylene dichloride content, the surface of the coal particles is found to be covered with an almost infinitesimally thin layer of the resinous and waxy materials extracted from the coal particles and pieces, which layer acts to reduce dust formation and also reduces the hazard of spontaneous combustion of the coal.

The ethylene dichloride solution removed from the coal by drainage, by centrifuging or by removal from the coal-feed end of the treating tanks, and, therefore, containing constituents extracted from the coal, may be passed to an appropriate still heated to appropriate temperatures such as from about 185° F. to about 195° F., in order that the ethylene dichloride may be recovered and reused.

However, the ethylene dichloride solution sometimes contains extracted fractions from the coal whose distillation temperatures are so close to the distillation temperature of ethylene dichloride at atmospheric pressure that, when desired to recover these fractions, fractional distillation may be employed. Such distillation may be effected at the time of removal of the solvent from the resins and other residue-forming materials, or the solvent including the desired low boiling extracted fractions may be first distilled off from the resins and other residue-forming materials, and then fractionated.

The ethylene dichloride distilled from the extracted fractions represented by the resins and other extracted materials is recovered by condensation for further use in treating fresh coal.

The resinous residues recovered upon removal of the ethylene dichloride are in a solid to a semi-solid condition and may be used without further treatment in the preparation of paints or varnishes, or in connection with the plastic industries, or for any other purposes to which resinous and waxy materials are adaptable, or, they may be further refined or decolorized for appropriate uses. Alternatively, these resinous bottoms may be fractionated into their various constituents for various purposes. The first separation stage may be effected at atmospheric temperatures and pressures by selective solvent extraction and precipitation. Thus, according to one method of separation, one part by weight of the resinous bottoms recovered upon distilling off the ethylene dichloride, is dissolved in one part by weight of lean ethylene dichloride, and two parts by weight of 95% ethyl alcohol, or denatured ethyl alcohol, are added to the ethylene dichloride solution, whereupon certain of the resins are precipitated out. In another method of separation the ethylene dichloride is distilled until the still bottoms contain approximately 50% of ethylene dichloride (approximately 1.66 specific

gravity at 60° F.). Then about two parts by weight of denatured alcohol are added for each part of ethylene dichloride by weight. Other anti-solvents such as methyl alcohol, propyl alcohol and iso-propyl alcohol may be substituted for the above mentioned alcohol.

After precipitation has been completed, the precipitated resins and associated materials are settled and separately recovered. The precipitate may then be used as a resinous product for paints and varnishes and other purposes as above indicated, or otherwise, or it may be fractionated by heat, that is, fractionally distilled.

The supernatant liquid separated from the precipitate produced by the addition of ethyl or other alcohol as above described, is then distilled to remove the ethylene dichloride solvent and the alcohol, their separation being fractional. Separated lean ethylene dichloride may then be passed to storage with the other recovered ethylene dichloride separated from the treated coal, and the alcohol returned to storage to be used for further precipitation of resins.

The bottoms remaining following removal of the ethylene dichloride and the ethyl alcohol are oils and waxes, and they may be further separated into fractions by vacuum distillation.

In general, the resinous, waxy, oily and similar materials recovered from bituminous coals of the stated Utah type commonly run from around sixty-five pounds to one hundred pounds or more per ton, the greater proportion of this extract being precipitable with ethyl alcohol from ethylene dichloride solution as above described.

The treated coal dried as above described presents a shiny appearance resulting apparently from a very thin film of resinous material with which the surface of the coal is coated after the ethylene dichloride has been dried out and thus freed from the coal. By reason of the treatment of the coal and the presence of this thin film of resinous material the tendency of the coal to form dust is almost entirely eliminated. As a consequence of this non-dusting property and the removal of the soluble extracts by the ethylene dichloride, it becomes a very valuable fuel for use in home furnaces and for similar purposes. However, its greatest value lies perhaps in its usefulness for coking, especially since it produces good metallurgical coke. The improvement of the coal both from a coking standpoint and as a fuel is in part represented by the marked increase in B. t. u.'s per pound, which increase for different coals runs from about 300 B. t. u.'s per pound to about 900 B. t. u.'s per pound. For example, in one particular instance the B. t. u. rating per pound was increased from about 12,800 for the untreated coal to 13,700 for the treated coal. In this latter instance, the fixed carbon content was correspondingly increased from 48.4% to 49.6%. At the same time, the volatile matter content, the ash content, and the sulfur content were all reduced. The improvement in the coal for both domestic fuel purposes and coking purposes is further illustrated by the actual loss in weight of the coal due to the removal of the valuable by-products, which if left in the coal are objectionable and, moreover, are wasted in burning.

Where the treated coal is to be used for coking, it is fed to a conventional coking furnace in a conventional manner and coked in a conventional manner. The by-products of the coking operation are passed to and treated in any standard or conventional by-products apparatus for

the separation and recovery of the usual by-products from coking plants. Such treatment is entirely feasible because the specific extraction process of the present invention yield for coking purposes a coal which does not upset the usual operation of the coking plant and its by-products recovery unit.

OPERATION EXAMPLES

As examples of operation according to this invention, run of mine coal from the Deer Creek coal field in Utah and from the Geneva Steel coal fields in Utah, which coals are bituminous coals of fairly high resin content, were employed. These coals contained no lumps larger than about six inches in their shorter or transverse dimension. As has been previously indicated, the term "run of mine coal" is intended to signify a coal which has no lumps larger than about seven inches in transverse dimension, and, if any appreciable portion of larger lumps is encountered, it is preferable to break or remove these lumps. For complete uniformity of treatment it might sometimes be deemed desirable that there be no lumps larger than three or four inches in greatest dimension, but as has been previously shown, this is not necessary to produce a coal having entirely satisfactory coking qualities.

Where batch treatment is employed, the coal may be immersed in ethylene dichloride contained in an appropriate tank. The amount of ethylene dichloride should be sufficient to cover all of the coal being treated.

In a specific instance, using coal from the Deer Creek field in Utah, immersion of the coal at about 70° F. in ethylene dichloride at a temperature of about 70° F. was maintained for about forty minutes, whereupon the ethylene dichloride solution was drained off and passed to another tank for similar immersion of another batch of coal. Several similar quantities of coal were treated with the same ethylene dichloride solution. Commonly such treatment is continued until the ethylene dichloride contains from about 20% to about 35% of resinous, waxy, oily and similar materials extracted from the coal.

As another example of extracting bituminous coals of the Utah type, a quantity of coal from the Geneva Steel coal field of Utah was placed in a tank and submerged in ethylene dichloride which was continuously recirculated by drawing from the bottom and returning at the top. Here, the operating temperature ranged between about 15° F. and about 20° F., and the treatment was continued for approximately sixty minutes. The solution was then drawn off, and the coal given a brief rinse with lean ethylene dichloride to wash off excess resinous material on the surface of the coal.

In each instance, the treated coal, which possessed a shiny appearance due to a very thin coating of resinous material remaining upon the surface of the particles, was passed to a standard coking plant and coked. The coke was found to possess the conventional characteristics for metallurgical coke, and the by-products of the coking operation were found to be successfully treated in the usual by-products recovery unit of the coking plant without upsetting the economics of the system or the operation of the system. No substantial distinction over the usual coking coal was found, either in the coking qualities or in the by-products production of the various coals treated as above described. These various cokes successfully withstood the usual

sieve test, rumbler test and shatter test. These statements apply as well to coal containing seven inch lumps as to coals which have been reduced to sizes containing lumps not over about two inches.

For the purposes of this invention, all extraction requirements with the ethylene dichloride are met when extracting within the above stated time and temperature ranges at atmospheric pressures, this being the result of the unexpected discovery that ethylene dichloride is the only solvent satisfactory for these purposes and conditions.

As a specific example showing the beneficial effects of my process, the following test data are furnished for Deer Creek coal treated by the batch process as above described. It will be observed that these data show in the treated coal a reduction in the volatile matter, the ash, and the sulfur content, together with an increase in the fixed carbon content and in the B. t. u. value. These data also indicate the coke yield and the coke by-products together with the yield of the coke by-products.

UTAH BITUMINOUS COAL—DEER CREEK FIELD

Untreated

Volatile 43.56%; ash 7.38%; sulfur 1.16%; fixed carbon 48.40%. B. t. u./lb. 12,831.

Leach with ethylene dichloride

Treated coal:	Ethylene dichloride solution.
Volatile 42.67%; ash 6.06%; sulfur 1.01%; fixed carbon 49.90%; B. t. u./lb. 13,721.	

Coke yield 63.55%

Ash 10.24%; volatile 3.67%; fixed carbon 86.09%; sulfur .83%.

Coke by-products

Gas 10,991 cu. ft. total per ton of coal

B. t. u./lb. of coal	3,378
B. t. u./cu. ft. gas	677
Illuminants	per cent. 7.3
Hydrogen	do 49.4
CO	do 11.5
Methane	do 28.4
Nitrogen	do .8
Ethane	do 2.6

Other by-products

Water	per cent. 7.66
CO ₂	do 3.66
H ₂ S	do .23
Naphthalene	do .16
Ammonium sulfate per ton coal	pounds 28.36
Tar per ton coal	gallons 12.66
Light oil	do 3.63

Ethylene dichloride solution distilled at 185° F.

Resin and oil residue—66.1 lb./ton coal=3.3%. Dissolve in equal weight ethylene dichloride; add 2 parts by weight 95% ethyl alcohol to precipitate resin.

Decant

Precipitate	Alcohol Solution
Fractionally distil.	Remove alcohol and ethylene dichloride. Fractionally distil residue.

Variations of the generic invention herein disclosed doubtless will occur to others skilled in the art, and it is intended to protect all such mod-

ifications as fall within the scope of the claims.

I claim as my invention:

1. A process comprising: leaching bituminous poorly cokable coal of the type containing resinous and other soluble constituents which render the coal poorly cokable, the leaching being performed by immersing the coal in ethylene dichloride under atmospheric temperature and pressure ranges for a brief period of time between about one-quarter of an hour and one and one-half hours to remove from the coal resinous and other ethylene-dichloride-soluble materials to yield a coal having good coking properties; separating the treated coal from the ethylene dichloride solution to recover the resultant cokable coal; and recovering from the solution the resinous and other constituents of the coal dissolved therein.

2. A process as in claim 1 wherein the leaching step is carried on at temperatures between about 60° F. and about 80° F. and for a period of time between about fifteen minutes and about fifty minutes.

3. A process as in claim 1 wherein the leaching step is carried on between about 15° F. and about 110° F. for a period of time approximating fifteen minutes to one and one-half hours.

4. A process as in claim 1 wherein the leaching step is carried on below about 32° F. for a period of time between about fifty minutes and about one and one-half hours.

5. A process as in claim 1 wherein the leaching step is carried on at summer heat temperatures for a period of time approximating twenty minutes.

6. A process comprising: leaching a bituminous non-cokable coal of the Utah type containing resinous and other soluble constituents which render the coal non-cokable for metallurgical purposes, the leaching being performed by immersing the coal in ethylene dichloride at approximately atmospheric temperatures and pressures for a brief time approximating forty to sixty minutes to remove from the coal resinous and other ethylene-dichloride-soluble materials, to yield a coal having good coking properties; separating the treated coal from the ethylene dichloride solution to recover the resultant cokable coal; and recovering from the solution the resinous, waxy, oily and other materials dissolved therein.

7. A process comprising: leaching a bituminous poorly cokable coal containing resinous and other soluble constituents which render the coal poorly cokable, the leaching being performed by immersing the coal in ethylene dichloride within atmospheric temperature ranges between summer heat temperatures and winter temperatures below freezing approximating 15° F. for a time between about fifteen minutes and about one and one-half hours to remove from the coal resinous and other materials soluble in ethylene dichloride to yield a coal having good coking properties; separating the resultant ethylene dichloride solution from the treated coal; recovering in solution in ethylene dichloride the materials dissolved from the coal; and separating the dissolved materials from such solution.

8. A method comprising: leaching a bituminous poorly cokable coal of the Utah type containing resinous and other soluble constituents which render the coal poorly cokable, the leaching being performed by immersing the coal in unheated ethylene dichloride at atmospheric temperatures and pressures for a brief time ap-

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proximating twenty minutes to remove from the coal resinous and other ethylene-dichloride-soluble materials to yield a coal having good coking properties; separating the treated coal from the ethylene dichloride solution to recover the resultant cokable coal; and recovering from the solution the resinous and other materials dissolved therein.

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

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