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BRIQUETTE CARBONIZING PROCESS USING
MODIFIED TAR OR PITCH BINDERS

Clayton S. Wolf, New Haven, Conn., assignor, by
mesne assignments, to American Cyanamid
Company, New York, N. Y., a corporation of
Maine

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3 Claims. (Cl. 202—34)

This invention relates to the carbonization of briquettes prepared from coking bituminous coals and more particularly relates to the use of modified tar or pitch binders in such processes.

It is well known that any coking bituminous coal can be ground to a certain degree of fineness, say to all pass through a 28 mesh screen, and without the use of any binder the ground coal can be compressed into a briquette and this briquette can be carbonized. Depending upon the method of carbonization, that is to say whether the carbonization is carried out in a so-called by-product coke oven or whether a vertical retort oven is used in which the briquettes continuously pass through the retort counter-current to a flow of heated non-oxidizing coking gas, a maximum rate of temperature rise per minute through the plastic temperature range can be determined at which rate the briquettes will not swell. Furthermore, there can be determined the maximum superimposed headload which the briquette will withstand without slumping or deforming when it is carbonized at the maximum non-swelling rate of temperature rise through the plastic temperature range.

It is also known that, if coal tar pitch or coal tar is used as a binder for making briquettes of the bituminous coals, the amount of superimposed headload which the briquette will sustain at the maximum non-swelling temperature rate will be very drastically reduced. In a practical briquette coking process it is very desirable that the briquettes can be made with a binder which will permit them to be coked at the maximum temperature rate without swelling and which at the same time will withstand appreciable headloads without undue slumping or deformation. In the past many such bituminous coals could not be compressed into briquettes, using coal tar or pitch as a binder, and subsequently carbonized with any degree of success as it was necessary that the briquettes withstand superimposed headloads.

In accordance with the present invention I have discovered a method of treating coal tars and/or pitches so that when used as a binder in making briquettes out of finely ground coking bituminous coal the briquettes can be coked and will sustain a higher or greater headload or weight without deformation than they would have sustained if the tars and/or pitches had not been so treated. In modifying the coal tars or pitches in accordance with the present invention about 8 to 15% of a moderately strong (60° Baumé) sulfuric acid is added to and stirred into the coal tar or pitch or a mixture of coal tar and

pitch, and the same is then ready for use as a briquette binder. In general, heating of the tar and/or pitch is not necessary except as the case may be to soften or make liquid in order to facilitate the mixing of the acid with it. In some instances, however, it may be possible to use a lower percentage of acid if the mixture is subjected to elevated temperatures. The amount of acid added to the coal tar or pitch will vary with different pitches and will also vary with the type of bituminous coal upon which the material is to be used as a binder. I have found, however, that percentages varying from 8 to 15% cover the best ranges. The strength of the acid (60° Baumé) is not narrowly confined and can be varied within certain limits without appreciably altering the final results. Likewise, other inorganic acids, such as nitric and mixtures of nitric and hydrochloric, are effective. However, sulfuric acid is preferred because of the consistent results obtained when it is used and also because of its cheapness.

The process of the present invention is applicable to briquetting processes using a wide variety of bituminous coals. In general, it is applicable to all classes of bituminous coals which can be economically formed into briquettes using coal tar or pitch as a binder and subsequently carbonized. Many bituminous coals have a tendency to cake and swell badly when it is attempted to carbonize them at a temperature rise of more than about 1° C. through the critical temperature range. The difficulties due to swelling and caking of such coals can be very largely overcome by pre-oxidation processes which alter the coking characteristics of the coals to such an extent that they do not swell and cake when subjected to carbonization at a temperature rise of even 2° C. per minute through the critical range. Several methods of pre-oxidizing coal are known to the art, one being that described in the co-pending application of William J. Kruppa, Serial No. 343,518, filed July 2, 1940, in which finely ground coal is subjected to air pressure of about 50 pounds per square inch for a period of about 4 hours while being maintained at a temperature of 150° C. The present invention is not specifically concerned with any method of pre-oxidizing bituminous coals but is primarily concerned with a method of carbonizing briquettes from such coals, using coal tar or pitch as a binder which has been modified by acid treatment so that the headload bearing properties of the briquettes are greater than similar briquettes made by using untreated tar as a binder. Many bituminous

coals cannot be compressed into briquettes, using a coal tar binder, and subsequently carbonized at a temperature rise of more than a fraction of a degree centigrade per minute through the plastic temperature range without badly swelling and caking. The Pittsburgh seam coals are of this type. They can, however, be subjected to pre-oxidation treatments which reduce the swelling and caking characteristics so that briquettes can be formed using coal tar or pitch as a binder and carbonized at a somewhat increased rate of temperature rise through the plastic stage. However, such briquettes have a very poor headload bearing strength and the carbonization cannot be carried out in ovens wherein the briquettes in the lower portion of the oven must bear the weight of the briquettes contained in the upper portion of the oven. The Beckley seam coals represent a second class of bituminous coals which cannot be successfully formed into briquettes using coal tar or pitch as a binder and carbonized at a reasonable rate of temperature rise through the plastic range unless the coal has first been subjected to a pre-oxidation treatment. Even after pre-oxidation these briquettes, using coal tar or pitch as a binder, have a relatively poor headload bearing strength. When these pre-oxidized coals as described above are formed into briquettes using my modified or acid treated tar as the binder, they have a much greater headload bearing strength than those using an untreated tar or pitch as a binder. This represents the outstanding feature of the present invention. The amount of modified acid binder necessary to provide sufficient bonding for the briquettes is approximately the same as the quantity of untreated coal tar or pitch previously used. Briquettes having sufficiently strong bonds are produced using as little as 5% of the modified tar based on the weight of the coal and quantities as high as 10% may be used in some cases.

Some coals which are weakly coking coals need not be preoxidized but can be formed into briquettes directly, using the modified tar or pitch binder of the present invention, to produce briquettes having greater headload bearing strength than briquettes produced from the same coal using untreated tar or pitch as the binder. In two such coals mined in England and known as "Thorne" and "Alerton Main" respectively it was found that when these coals were ground to all pass 28 mesh screen and then compressed into briquettes using about 8% of a sulfuric acid treated coal tar binder, the briquettes could be carbonized at a rate of $2\frac{1}{2}^{\circ}$ C. per minute rise through the plastic temperature range and yet sustained a superimposed headload of a 4 foot column of the briquettes, which was comparable with the same performance of these coals at the same rate wherein the briquettes were made with no binder. This is the exact opposite of results usually obtained when coal tar is used as a binder, in which instance the coal tar bound briquettes always have a much less headload bearing ability than the no binder briquettes. The results and the method of carrying out the tests described above were obtained as follows:

The quantities and specifications of tar, acid, and coals used were as follows:

40 lbs. of coal ground to all pass a 28 mesh screen.
3.2 lbs. of raw oven tar
0.32 lb. of 1.84 specific gravity H_2SO_4 diluted with
0.16 lb. of water

The procedure was as follows:

The 3.2 lbs. of tar were placed in a can which was immersed to about one-half its depth in boiling water until the tar reached a temperature of about 75° C. The diluted acid was then stirred into the tar. The ground coal was then placed in a horizontal paddle mixer or fluxer and the treated tar was poured into the coal and the whole stirred or fluxed for about ten minutes, which length of time was sufficient to thoroughly mix or flux the tar and coal. The coal and tar flux was next placed in the feed box of a typical roll briquetting press and compressed into hard strong $2\frac{1}{2}$ ounce pillow shaped briquettes. These briquettes were then carbonized in a vertical cylindrical retort which gave a column depth of briquettes of about 4 feet. The carbonization was effected by passing a stream of coal gas through the column of briquettes, said coal gas, by means of proper controls and equipment, was made to rise in temperature at a rate of $2\frac{1}{2}^{\circ}$ C. per minute. The carbonization was carried to a finishing temperature of 600° C. The carbonized briquettes were very hard and dense and showed no deformation or slumping of those at the bottom of the pile. When a straight raw tar, i. e., non-acid treated tar, was used as a binder, the maximum headload which the briquettes would sustain at the rate of $2\frac{1}{2}^{\circ}$ C. per minute was in the order of about 6 inches rather than 4 feet, without undergoing such a degree of slumping or distortion that the free void spaces between briquettes were so completely closed up that the heated carbonizing gas could not be passed through any voids and around each briquette to thereby accomplish the carbonization.

Tests were also carried out on oxidized Beckley seam coal and on oxidized Pittsburgh seam coals, and in all cases the briquettes using acid treated coal tar or pitch as a binder had a much greater headload bearing ability than briquettes prepared from the same coal using untreated tar or pitch as a binder. Tests were also conducted on the coals described in the test above in which the proportion of sulfuric acid added to the coal tar or pitch was about 8%, 12%, and 15%. The results were, in general, comparable to those in which 10% sulfuric acid was used, and in all cases the briquettes had a greater headload bearing strength than briquettes carbonized under the same conditions but using untreated coal tar as the binder.

As pointed out heretofore, coking bituminous coal briquettes bound with coal tars and/or pitches have been carbonized in many ways, and it is invariably true that such briquettes during the softening range of carbonization (about 300° to 500° C.) could sustain only a relatively small superimposed headload without undergoing deformation or slumping of the briquettes. In using the process of this invention, the acid treated tars and/or pitches permit increases in superimposed loads in the order of 5 to 10 times as much as the prior methods. In a preferred carbonization process, in accordance with the present invention, the finely ground coking bituminous coals compressed into briquettes using my acid treated tar as a binder, is the process in which the briquettes are carbonized in a vertical retort wherein the briquettes flow continuously down through the retort counter-current to an ascending stream of a heated, non-oxidizing gas. In this process it is obviously an advantage that the briquettes passing through the 300° to 500° C. range have the ability to sustain the

maximum possible headload without deformation. This process is of real commercial importance because it permits the use of the coal tar and/or pitch, which are by-products in coking operations, under conditions which compare favorably with more expensive binders such as sulfite liquor and under conditions which coal tar or pitches could not heretofore be successfully employed.

What I claim is:

1. A method of making briquettes having increased strength during the coking operation, from swelling bituminous coking coals capable of being compressed into briquettes, using coal tar as a binder and carbonized without undue swelling at a temperature rise through the plastic temperature range of at least 2° C. per minute which comprises forming a briquette of such coal, using from 5 to 10% of the binder comprising a mixture of sulfuric acid with a substance included in the group consisting of coal tars, coal pitches, and mixtures of coal tar and coal pitches, and subjecting said briquette to a carbonization process in which the temperature rise is at least 2° C. per minute through the plastic temperature range, said binder containing from 8 to 15% sulfuric acid.

2. A method of making briquettes having increased strength during the coking operation, from swelling bituminous coking coals capable of being compressed into briquettes, using coal tar as a binder and carbonized without undue swell-

ing at a temperature rise through the plastic temperature range of at least 2° C. per minute which comprises forming a briquette of such coal, using from 5 to 10% of a binder a mixture of sulfuric acid with a substance included in the group consisting of coal tars, coal pitches, and mixtures of coal tar and coal pitches, and subjecting said briquette to a carbonization process in which the temperature rise is at least 2° C. per minute through the plastic temperature range, said binder having from 8 to 15% sulfuric acid.

3. A method of carbonizing bituminous coal briquettes having increased strength during the coking operation which comprises finely grinding the coal, mixing the ground coal with from 5 to 10% of a binder comprising a mixture of sulfuric acid and a substance included in the group consisting of coal tar, coal pitches and mixtures of coal tar and coal pitches, compressing into briquettes and subjecting said briquettes to carbonization, at a temperature rise through the plastic stage of about 2° C. per minute, in a vertical retort wherein the briquettes flow continuously down through the retort counter-current to an ascending stream of heated non-oxidizing gas, said briquettes being capable of sustaining about a 4 foot column of briquettes superimposed thereon while passing through the plastic stage without undue deformation, said binder containing from 8 to 15% sulfuric acid.

CLAYTON S. WOLF.

CERTIFICATE OF CORRECTION.

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CLAYTON S. WOLF.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows, Page 3, second column, line 4, before "a mixture" insert "--comprising--"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of May, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.