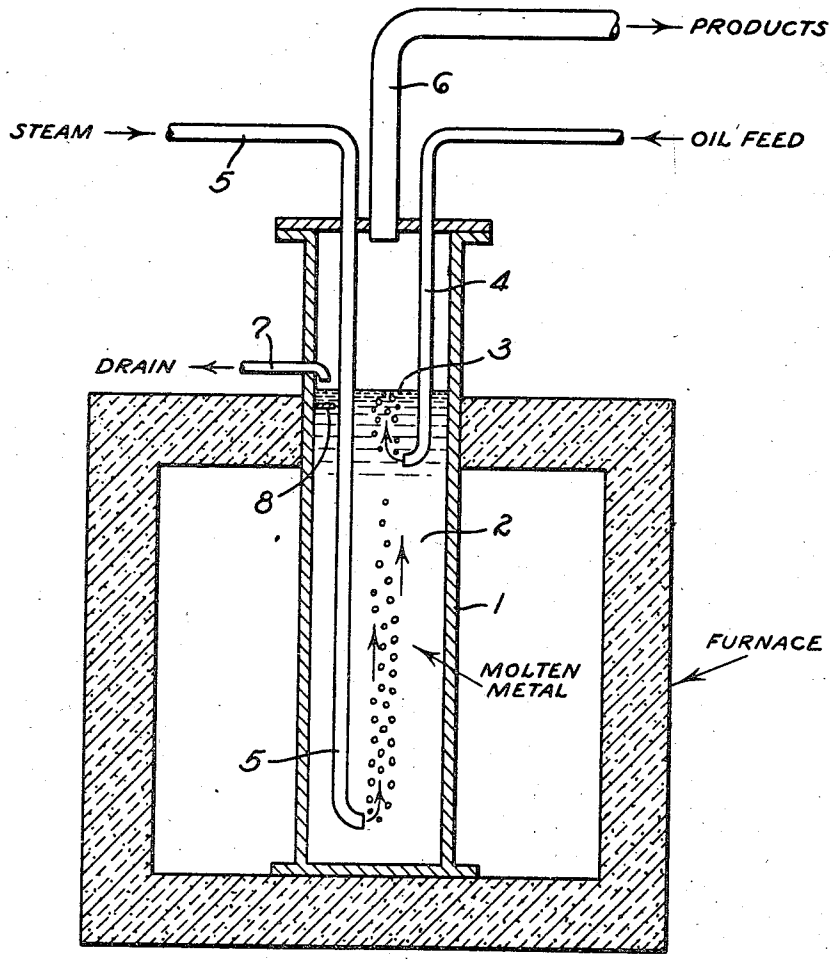
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PROCESS FOR THE CONVERSION OF ASPHALTIC HYDROCARBONS

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PROCESS FOR THE CONVERSION OF ASPHALTIC HYDROCARBONS

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This invention relates to the conversion of asphalt or asphalt-like hydrocarbons into hydrocarbon oils falling within the boiling point range of lubricating oils; this conversion being accomplished by a simple heat treatment, without the addition of hydrogen or use of chemicals. These asphaltic hydrocarbons occur in nature either as such or together with lighter hydrocarbons in petroleum, also in the destructive distillation products of coal, shale, peat, wood, etc. In such products and especially in petroleum, asphaltic bodies form the least valuable constituent and in the refining of such products for various industrial uses, the asphalt presents one of the greatest problems not only from a purely technical, but also from a commercial viewpoint.

Thus, in the separation of the various constituents of petroleum by distillation, not only are the asphaltic bodies separated with difficulty from the most valuable fractions; that is, the heavy lubricating oils, but the tendency is for the lubricating oil fractions to revert into asphalt. Moreover, the asphaltic residues may be disposed of only as low grade fuel oils or as the least desirable raw stock for cracking processes.

In the cracking of the asphaltic oils with a view of producing lighter motor fuels, formation of coke and noncondensable gases soon sets in, resulting in a yield of gasoline lower than what would be theoretically expected, taking into consideration the hydrogen content of the original stock. When overhead stocks such as kerosene, gas oil or lubricating oils are used as starting material, a much more satisfactory decomposition reaction first takes place, but eventually asphalt formation sets in, resulting ultimately in the formation of coke and noncondensable gases, whereby valuable hydrogen is lost.

In milder cracking operations, where effort is made to convert residual oils into fuel oil of lower viscosity, into oil stock more suitable for intensive cracking operations, or even into lubricating oil, the processes now known are capable of only partial conversion of asphalt, if the actual asphalt content of the stock is taken into consideration. Moreover, if recovery of lubricating oils or other valuable oil fractions is attempted as separate distillate, a large part of the stock worked upon will remain as residue of less value than the original stock and unfit for further conversion by the same process, except under conditions where coke and gas formation takes place.

A simple, economical process for the complete conversion of asphaltic bodies into oils of the lubricating oil boiling point range, by a simple heat treatment without the use of hydrogen and without any appreciable loss or formation of any undesirable by-products, would therefore be valuable, not only from the viewpoint of lubricating values, but also from the viewpoint of overcoming refining difficulties and reducing the refining losses and from the viewpoint of producing superior fuel oils and more desirable stocks for cracking operations.

It is an object of my invention to provide a method of simple and efficient character whereby heavy hydrocarbons may be converted into lighter hydrocarbons and whereby a substantial conversion of asphalt or asphalt-like residues into lubricating oil may be obtained by pyrolytic treatment, and in general to provide a hydrocarbon conversion method for the manufacture of lubricating oils, fuel oils, or overhead cracking stocks of superior quality.

I have discovered that if asphaltic hydrocarbons are brought into contact with molten substances or at any rate with molten metals or alloys for a certain, short period of time, at a certain temperature, they are converted into lubricating oils and I have discovered means of producing and maintaining the necessary conditions as regards the time element, temperature, heat transfer, and contact, so that the reaction can be maintained indefinitely or at least to such an extent that such a process becomes of practical value.

The conversion of asphaltic hydrocarbons by this process into lighter oils falling mainly within the boiling point range of oils classed as lubricating oils, may be made highly efficient; that is, side reactions producing undesirable by-products such as fixed gases, coke or other valueless or detrimental products may be largely suppressed to give a substantially complete yield of lighter oils on the basis of the asphalt converted. However, as the time element is very short, it is difficult to establish and maintain conditions absolutely ideal as regards every particle of asphalt passing through the reaction zone, the result being that part of the asphaltic substance remains unconverted in a single passage through the process. This unconverted asphalt does not, however, differ substantially from the original material and may in most instances be converted by the same process, as by simply returning it into the process with fresh feed stock, or by treat-

ing it separately, if necessary at a higher temperature.

As stated, the necessary time element is very short. This is controlled in part at least by keeping the amount of hydrocarbon material in the reaction zone to a minimum relative to the available contact surface. If the unconverted portion of the asphalt is not removed almost immediately, or within a certain time limit, depending on the temperature employed, it will polymerize and eventually decompose with the formation of carbon or coke, which carbon or coke will rapidly foul the contact medium or metal bath, in many cases within a few minutes, to such an extent that the converesion reaction of asphalt into lubricating oil will be completely arrested, despite the fact that the time element and temperature might be suitable for conversion.

Whether the molten substance, such as molten metal or alloy, called here the contact medium, acts in the process disclosed here in the role of a catalyst, is not certain. As a rule, the reactions produced by catalysis are specific to certain substances, whereas to my knowledge the conversion reaction disclosed here can be brought about by contact with any molten substance, as far as a substance is used that does not enter into chemical reaction with the asphalt and thus make it difficult to determine the cause of the reactions produced. At any rate, I have successfully used tin, lead, and zinc, both singly and in combination, one with another, and in combination with antimony.

On the other hand, the rapidity with which heat is transferable from the molten metal to the small globules or films of asphalt material may be an important factor in the process. The depolymerization or conversion reaction by which asphalt is converted into lubricating oil may be initiated at elevated temperatures, but is apparently endothermic in character, and a continued and rapid input of heat is required to maintain this reaction in ascendancy over undesirable side-reactions leading to degraded products, coke etc. Attempts to obtain this rapid heat transfer through poorly conducting surfaces, e. g., solid surfaces, would require such a high temperature differential as to result in local over-heating and surface deposition of coke, thus defeating further conversion. By the use of molten metal, however, conversions at a hydrocarbon temperature of 275° to 375° C. may be maintained with a temperature differential such for example that the metal temperature need be only 450° to 550° C. The rapidity of heat transfer is further aided by the agitation or circulation of the molten metal, whereby rapid convection as well as rapid conduction of the heat is obtained.

In some instances it is advantageous to provide for the more or less abrupt heating of the asphalt to the desired conversion temperature; i. e., to avoid preheating or other pretreatment involving heating of the stock to elevated temperatures. For example, asphaltic crude oils are sometimes more amenable to conversion than are topped residual fractions obtained therefrom. In other instances, however, preheating of the conversion stock immediately prior to conversion induces no noticeable change and is of advantage in reducing the heat load on the molten metal.

To specify the actual time element necessary for the asphalt lubricating oil reaction, that is, to specify it in units of time, is difficult, as the contact time necessary for conversion is very short, is partly dependent on the exact nature of the asphaltic oil stock worked upon, on the temperature of the contact medium, on the temperature of the incoming oil, etc. However, the procedure necessary in each case will be made clear from the disclosures given further on. In general, the contact period should be sufficiently short to insure that the hydrocarbon material, typically unconverted asphalt, is not substantially decomposed into coke, fixed gas etc., such decomposition being prevented by removing the asphalt before it reaches excessive temperatures or before substantial decomposition sets in due to protracted contact at elevated temperatures, or both.

The proper, short time element for contact is accomplished, first by introducing the asphalt or oil containing it either upon the surface of the metal bath or a short distance below it, such as a few inches, and second by rapid or immediate removal of the converted products from contact with the bath by rapid or immediate volatilization, induced by maintaining a sufficiently high temperature in the molten bath and employing any known means capable of increasing the volatility of the oils produced, such as vacuum and/or carrier gases, but especially steam, inert gases, and the like, which I have found most effective and economical.

The use of steam or other effective means of increasing volatility, is especially important from the viewpoint of immediately removing any unconverted asphalt from contact with the bath, if temperatures appreciably above 400° C. are maintained in the bath. If temperatures below 400° C. are maintained in the bath, it is however possible to allow the asphalt to remain in contact with the bath a somewhat longer period, so that it may be allowed to float on top of the bath and is drained off as rapidly as possible. The steam may be introduced into the molten bath at any level, preferably at a lower level than the asphaltic raw stock. The steam does not decompose or enter into reaction with the oil; the water recovered in the condensate is equal to the water fed in as steam.

The feed stock need not be preheated when temperatures appreciably over 400° C. are maintained in the bath, but with lower temperatures, preheating of the stock becomes advisable; in which case a preheat temperature of about 250° C. is sufficient to insure a high degree of conversion. Due to the short contact period the temperature of the oil or oil vapors is not brought up to the temperature of the contact medium or bath, in fact a contact period should be established of only sufficient duration to heat the stock to a point where the converted products, and in case of higher temperatures in the bath also the unconverted asphalt, are volatilized with the aid of steam. The temperature of the vapors is usually around 300° C. It is to be stated here that with a high temperature in the bath, such as for instance 450° C. and over, any unconverted asphalt is readily volatilized together with the converted products, provided sufficient steam or other carrying gases and/or vacuum are used, despite the fact that the temperature of the vapors may not be over 300° C. This volatilization of asphalt under such conditions may not be due to actual vaporization, but to mechanical carrying over, such as in the form of a fog.

I have found that in many instances my invention may be advantageously practiced with the molten metal at a temperature of 450° to 550°

C. and a contact time such that the asphaltic hydrocarbon leaves the molten metal at a temperature between 275° and 375° C.

As the conversion process disclosed here consists of a simple heat treatment and as all the constituents of the oil stock are volatilized or in any case the lubricating oils and other lighter constituents present, the process can at the same time be employed to a great advantage as a distillation process; in fact, the process should whenever possible be employed on the original crudes as a distillation process, and in any case the asphaltic material should preferably not have previously gone through any heat treatment by which its composition might have been changed due to partial decomposition or polymerization. The process is of special value in distilling of heavy, high-asphalt crudes, whereby the heavy residues which would result in an ordinary distillation process, are converted into oils more suitable as fuel oils or cracking stock; also, asphaltic bodies formed during cracking operations, may be converted into superior fuel oils or made suitable for further cracking. It is also of value in distilling crudes which are used for the manufacture of lubricants. In case of such oils, the asphalt content of the crude is usually low, but in the distillation of the crude by ordinary methods, not only is some asphalt carried over with the lubricating oil, but the tendency is for the lubricating oils to revert into asphalt, the result being that expensive and wasteful refining operations are necessary such as acid refining, solvent extraction, etc., whereas if the crude is distilled by the method disclosed here, these refining operations can at least be modified and simplified and in many cases even dispensed with entirely, so that the oils may be finished with such a simple procedure as treatment with absorptive clays.

The accompanying diagrammatic drawing will more clearly illustrate the fundamental principles of the process and will be of assistance in connection with further specifications and examples given below. The apparatus comprises a steel cylinder 1 placed in a suitable furnace. The cylinder is filled with molten metal 2 up to a level 3, for example about 12 inches from the top. Oil feed pipe 4 extends down a short distance below the surface, suitably to a level about 4 inches below the surface of the molten metal, though the oil may also be introduced on the surface of the metal. Steam line 5 extends down to the bottom of the apparatus, though the steam may also be introduced at higher levels and at several levels simultaneously. Vapor line 6 leads directly into a condenser or fractionating column. An outlet 7 is for draining out residues in cases where the temperature of the bath is kept so low that the unconverted asphalt will not volatilize. This outlet should be as close to the surface of the metal as possible and a baffle 8 is placed below it to prevent the molten metal from being thrown into the drain line, as the metal bath is being agitated by the rising steam and oil vapors. This drain line leads of course into a trap or seal to prevent the escape of oil vapors.

What temperature should be maintained in the metal bath depends in each case on the exact nature of the crude oil to be distilled or treated and also on the exact nature of the oil desired in each case. In accordance with the principles disclosed above, a temperature in the bath, a manner of introducing the oil, and means of accelerating the volatilization are selected to insure the proper, short contact time and rapid transfer of heat in each case. Crude oil with a low asphalt content, such as is usually used for the purpose of manufacturing lubricants, can be distilled by maintaining in the bath a temperature from about 425° to 500° C. Oils containing a high percentage of asphalt can also be treated with similar or somewhat higher temperature in the bath, yet a small amount of carbon or coke may form in such cases. While the amount of this carbon or coke may be so small, such as one per cent, as not to affect the economical value of the process and while this carbon or coke may readily be removed, there is a tendency in many cases for this carbon or coke to adhere to the metal, forming a slag of sponge-like structure, so that considerable metal is carried away with the carbon or coke removed. I have found that in such cases it is of advantage to maintain the metal bath at a temperature of about 375° C. or lower. If sufficient steam or other means for volatilization, agitation, and rapid heat transfer is provided, a high degree of conversion is accomplished. To insure a high degree of conversion, it is also advisable in such cases to preheat the oil, preferably to about 250° C. The portion of asphalt remaining unconverted in a single passage through the reaction zone will not volatilize; that is, it is not carried away with the oil or steam vapors, but is drained out as rapidly as possible through the outlet provided for such purpose.

A few examples of specific cases may further illustrate the principles on which the method disclosed here is based and how they may be put in practice in each particular case.

Example No. 1

A heavy, asphalt base California crude petroleum containing, as determined by distillation analysis, 16% crude naphtha, 19% gas oil, 14% lubricating oil, and 51% asphalt was passed in a continuous process through molten lead, in an apparatus similar to the one described above. The temperature of the lead bath was maintained at 500° C. and the oil was introduced 4 inches below the surface of the metal. Steam amounting to 20% of the crude oil was introduced into the bottom of the apparatus. The oil was all volatilized including the asphalt remaining unconverted. It was roughly estimated that the contact period was less than one second, although the actual period of contact could not be determined exactly and is best described as "substantially momentary." The vapors were led into a condenser and the combined distillate measured and fractionally distilled to determine the yields and degree of conversion. The total distillate amounted to 98% by weight of the crude oil treated, 1% of carbon and 1% of non-condensable gases being produced. The converted distillate contained 19% of crude naphtha, 18% gas oil, 56% lubricating oil, and 7% asphaltic residue as determined by the usual distillation methods. The asphalt content was reduced from 51% in the crude oil down to 7% in the treated oil, and the lubricating oil content was correspondingly increased from 14% in the crude to 56% in the treated oil. The crude oil was black, highly viscous, hardly mobile, while the treated oil was of a much lower viscosity, suitable for fuel oil, and possessed a rich green bloom characteristic of high grade lubricating oils or paraffine base crude oils. By leading the oil vapors into a fractionating column and re-

turning the heavy, asphaltic bottoms back into the process with fresh feed stock, a complete conversion of the asphalt present in the crude oil was accomplished. The converted distillate or asphalt-free overhead therefrom could be variously utilized The lubricating oil fractions were equal or superior to the lubricating oil originally associated with the crude, and also constituted an excellent cracking stock for liquid or vapor phase cracking, as well as a blending stock for fuel oils.

Example No. 2

The same crude oil as in Example No. 1 was treated by passing it through a molten alloy, consisting of 90% of lead and 10% of antimony, this alloy having a melting point sufficiently far below the temperature employed in this case to keep it sufficiently fluid at all times. The oil was preheated at 250° C. and introduced into the molten alloy 4 inches below the surface. The alloy was kept at a temperature of 370° C. and steam amounting to 40% of the crude was introduced through another feed line, also 4 inches below the surface. In this case, due to the low temperature maintained in the alloy, the portion of asphalt remaining unconverted was not volatilized or carried over by the vapors, but remained on top of the alloy and was continuously drained out as rapidly as possible. With such a low temperature in the alloy, the asphalt will not coke in the time required for draining despite the fact that under such conditions it remains in contact with the bath a longer period than in cases where the asphalt is removed by volatilization. The asphalt or residue drained off the surface of the alloy amounted to 15% of the crude oil treated. The combined distillate was free from asphalt. The asphalt content was therefore reduced from 51% to 15%, the lubricating oil was increased from 14% to 50%. No coke or gas formation took place and the total yield of oil and asphaltic residue was 100%. It was found that the remaining asphalt drained off the surface of the bath could not be converted by returning it back into the process with fresh feed stock. However, conversion of this residue was accomplished by employing a procedure similar to the one given under Example No. 1 and maintaining in the bath a temperature of about 550° C.

Example No. 3

An Oklahoma crude petroleum was used in this case. This crude is extensively used for the manufacture of lubricating oils, but contains about 5% of asphalt and when distilled in the ordinary manner produces lubricating oil stocks which require acid refining, with consequent heavy losses, before they can be finished to a proper color with absorptive clays. This oil was distilled in a manner similar to the one given under Example No. 1, except that the temperature of the lead bath was maintained at 425° C. and the amount of steam used was 40%. The yield of oil recovered was approximately 100% and no carbon or coke formation took place. The lubricating oil stock produced was then treated with absorptive clays without a preliminary acid refining and an oil with a standard color was obtained, while the lubricating oil stock obtained from the same crude by ordinary distillation methods could not be treated and finished with absorptive clays without preliminary acid refining.

This application is a continuation-in-part of my copending applications, Serial Nos. 142,560 and 166,307.

I claim as my invention:

1. A method of converting asphaltic hydrocarbon of the character described to lubricating oil, comprising the steps of: bringing said asphaltic hydrocarbon into substantially momentary contact with a body of molten metal maintained at such a temperature in the range of 450° to 550° C. that said asphaltic hydrocarbon will be brought to a temperature within the range of 275° to 375° C.; and disengaging the asphaltic hydrocarbon and resulting converted products brought to said temperature from further contact with the molten metal by volatilization and atomization in a concurrent flow of both volatilized and nonvolatilized portions with steam so adjusted that substantially no converted or unconverted asphaltic hydrocarbon is left in contact with the molten metal for periods exceeding the desired momentary contact.

2. A method of converting asphaltic hydrocarbon of the character described to lubricating oil, comprising the steps of: bringing said asphaltic hydrocarbon into substantially momentary contact with a body of molten metal maintained at such temperature that said asphaltic hydrocarbon will be brought to a temperature within its temperature range of conversion as the result of said contact with molten metal, whereby a substantially complete conversion of asphaltic substance to lubricating oil is obtained without substantial formation of coke, gas, or other reversion products; and disengaging the asphaltic hydrocarbon and resulting converted products brought to said temperature from further contact with the molten metal by volatilization and atomization in a concurrent flow of both volatilized and nonvolatilized portions with steam so adjusted that substantially no converted or unconverted asphaltic hydrocarbon is left in contact with the molten metal for periods in excess of the desired momentary contact.

3. A process for converting asphaltic stock of the character described into lubricating oil, comprising: maintaining a body of molten metal in a reaction zone at a temperature from about 375° to about 550° C.; agitating said metal by introducing therein a stream of carrier gas and permitting said gas to escape from the upper surface of the metal; continuously bringing the asphaltic stock into said reaction zone to contact the molten metal at a level not lower than a few inches below the upper surface of the metal; adjusting the stream of carrier gas to volatilize lubricating oil fractions present in the stock and formed by conversion thereof to produce an effluent stream of gas and hydrocarbon vapor having a temperature not greatly in excess of 300° C.; and continuously removing any non-volatile asphalt from the upper surface of the metal to prevent protracted contact thereof with the molten metal.

4. A process as in claim 3 in which the asphaltic stock is introduced into the reaction zone at a level not lower than four inches below the surface of the molten metal.

5. A process for converting asphaltic stock of the character described into lubricating oil, comprising: maintaining a body of molten metal at a temperature from about 375° to about 450° C.; introducing the asphaltic stock into said metal at a depth of not over a few inches from the upper surface thereof; introducing a stream of carrier gas into the body of molten metal to cause agitation thereof and to aid in the volatilization of the lubricating oil; adjusting the relative rates of introduction of asphaltic stock and carrier gas

into the molten metal to cause complete and continuous volatilization at temperatures not greatly in excess of 300° C. of lubricating oil fractions produced by conversion of the asphalt in the presence of the molten metal; and continuously withdrawing non-volatile fractions accumulating on the upper surface of the molten metal.

6. A process for converting asphaltic hydrocarbons into lubricating oil, comprising the steps of: maintaining a body of molten metal in a reaction zone at a temperature from about 450° to about 550° C.; passing a current of steam therethrough; introducing the asphaltic hydrocarbon into said reaction zone at a level not lower than a few inches below the surface of the molten metal to contact the metal and induce at least partial conversion thereof into lubricating oil; and adjusting the current of steam to remove the asphalt and conversion products from the molten metal in a concurrent stream of vapors and atomized particles.

7. A method of converting asphaltic hydrocarbons into lubricating oils, which comprises the steps of: continuously bringing said asphaltic hydrocarbons into contact with the surface of a body of molten metal; maintaining the temperature of the metal in the range from about 450 to 550° C.; and continuously disengaging the resulting converted product and any unconverted hydrocarbon from contact with the molten metal by volatilization and atomization in a concurrent flow of both volatilized and unvolatilized portions with a stream of a carrier gas, so adjusted that substantially no converted or unconverted hydrocarbons are left in contact with the molten metal beyond a momentary period.

8. A method as in claim 7 in which the stream of carrier gas is adjusted to scavenge the surface of the molten metal and maintain it substantially clean, whereby the quantity of hydrocarbon material in contact with the molten metal at a given instant is minimized.

9. A method of converting asphaltic hydrocarbons of the character described into lubricating oils, comprising: continuously bringing the asphaltic hydrocarbons into contact with the surface of a body of molten metal; maintaining the temperature of the metal above 450° C.; and removing the converted and any unconverted hydrocarbons from contact with the metal by volatilization and atomization in a concurrent flow with a stream of a carrier gas so adjusted that the temperature of the effluent stream of vapor and gas does not substantially exceed 300° C.

10. A method of converting asphaltic hydrocarbons of the character described into lubricating oil, which comprises: bringing the asphaltic hydrocarbons continuously into contact with the surface of a body of molten metal maintaining the temperature of the metal in a range from about 350° C. to 450° C.; agitating said metal with a current of carrier gas adjusted to produce an effluent stream comprising gas and hydrocarbon vapor, the temperature of said stream being not greatly in excess of 300° C.; and continuously removing any non volatile asphalt from the upper surface of the metal to prevent protracted contact thereof with the molten metal.

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