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PROCESS OF CRACKING OR TREATING OILS AND OTHER SIMILAR HYDROCARBONS.

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Our invention is a method or process of cracking or treating oils and other similar hydrocarbons, in stills or containers, with the use of natural or prepared colloid cracking agents.

In the process of treating hydrocarbons such as crude oil, for example, to obtain therefrom the more salable and useful compounds, such as gasoline, kerosene and lubricating oil, it has heretofore been the custom to employ heat, applying the same to the hydrocarbon undergoing treatment within a container at normal atmosphere or higher pressure; the heat and pressure application is given to the hydrocarbon while it is in either the liquid or gaseous state, or both.

The prime object of many of such processes is the production of so-called gasoline or motor spirit and the attempt is made to regulate the above factors so that a greater proportion of gasoline may be obtained from the heavier and less expensive hydrocarbons than can be produced by the straight distillation process without special heat application or the use of chemicals.

In bringing about the above result it has been the custom to apply in practice 80 to 900 pounds pressure and varying intensities of heat in the stills or treaters used, said pressure being thought by many engaged in the art of so-called "oil refining," as dangerous or requiring expensive equipment to produce the desired commercial results: namely an increased quantity of gasoline, or motor spirit.

Further in increasing the yields of gasoline and other lighter liquid hydrocarbons in the practice of the above art, it has been the custom to introduce into the liquid or gaseous phase within the apparatus so used an anhydrous prepared chemical compound to further the purpose of the art, whereby larger quantities of gasoline, motor spirit and other liquid hydrocarbons are produced at lower temperatures and pressures. For instance, pure or contaminated anhydrous aluminum chlorid is found suitable as an addition agent added as hereinbefore described, wherein and whereby there is produced from liquid hydrocarbons, (for instance: fuel oil, still cuts, or residium), the lower boiling products gasoline, motor spirit, and other hydrocarbons liquid at normal pressures and temperatures, which otherwise could not be produced by methods now practiced in the art, excepting by the use of higher pressures and temperatures, which practice is hereinafter designated as the high pressure art, and hereinafter the present practice of using anhydrous aluminum chloride, is referred to as the low pressure chemical art, as connected with the art of distilling crude oil, or its products or their treatment under heat and pressure.

We have made a discovery whereby we can produce more gasoline, motor spirit, or other liquid hydrocarbons from natural or manufactured hydrocarbons of a higher boiling point, or combination of higher and lower hydrocarbons, for instance, crude oil, than can be produced by simple distillation, without using our discovery, and, whereby results and products simulating or surpassing in quality and quantity those brought about by the employment of high pressure art, and low pressure chemical art, as at present employed, are accomplished. In carrying out our discovery it has been our practice to incorporate with the product to be treated (for instance, black asphalt, or paraffine base, crude oil, or manufactured hydrocarbon, for instance, kerosene, gas oil, lubricating oil, tar residium, etc.), a natural product in its crude state or so prepared by mechanical or chemical treatment as to meet our needs, said incorporation being carried out before or during the process of distillation or other treatment by heat, or during intervals of interruption in said process or treatment.

Of the natural products, i. e. those products occurring in nature, we have found that those which are naturally colloidal, i. e. those which occur all or partly colloidal in the natural state or as in the raw state as mined, (in contrast to materials which are rendered colloidal by artificial or manufacturing means), or those which may be made colloidal by mechanical grinding or by the addition of heat, and addition of water, or alcohol, or any other suitable dispersing agent, or by treatment with chemicals, or colloided with peptonizing agents, are useful for our purpose, and are hereinafter referred to as natural colloidal cracking agents. In preparing the cracking agent we find a convenient way to be to pour pure alcohol over

the lumps of material; this causes the material to go rapidly of its own accord into a very fine state of sub-division in which state it remains as a dry smooth powder after the alcohol has been distilled off and recovered to be used over again; this dry powder is so fine that it will stay in suspension by mere agitation.

In particular our invention relates to the use of bentonite, which is a name given to a group or series of clay-like materials having a content of SiO_2 ranging around 58%, and a content of Al_2O_3 ranging around 22%, together with the small contents of Fe_2O_3, CaO, MgO, K_2O, and so forth. Bentonites available for use in the present invention are characterized by very strong colloidal properties in order to provide for the necessary dispersion of the material throughout the hydrocarbon under treatment, and to afford the necessary surface for the deposition of carbon forced out during the cracking operation.

Bentonite, as mined in the crude state, has the appearance of soft rock, evidently because the particles composing the material are compacted together. When, however, water or alcohol is added to the material, they penetrate between the particles and separate them so that the materials become jelly-like in consistency and the particles are sufficiently separated to be dispersed in a liquid by moderately violent agitation. For our purpose it is desirable to disperse the particles of the colloid throughout the oil to be cracked so that the particles may act as nuclei for deposition of carbon.

The bentonite which we have found particularly and in the most conspicuous degree adapted to our purpose is that which when mined and placed in water, with freedom to swell, does so, absorbing water up to three or more volumes of itself, on which it appears as a jelly-like mass. This mass may then be added to the oil; a satisfactory method being grinding or stirring the jelly-like mass of bentonite with the oil to be distilled, until thoroughly emulsified with the oil, after which the process of distillation may be completed in the usual way, or oil emulsified with bentonite, may be mixed with the oil to be distilled before or during distillation or added thereto.

Thorough emulsification and dispersion of bentonite, as mined, may be brought about by proper grinding with the oil or other product and introduced into the still or other apparatus to accomplish the purpose desired without the use of an intervening medium of water.

Of the various types of bentonite those carrying notable percentages of iron are particularly indicated in the treatment of high sulphur black oils.

Bentonite is found widely scattered through the formations of the earth, more particularly the sedimentary formations, and so occurs very near or with the actual oil to be treated, as in the States of Wyoming, Montana and California. The economic feature of this process is the close occurrence of bentonite to crude oil, and oil refineries, its abundance and readiness with which it is available—whereby cheap operation and production of the desired light products is possible,—for instance, in Wyoming there are bentonite deposits occurring near oil wells where the bentonite can be delivered at the oil source for less than one dollar per ton. This is readily understood where it is known that frequently oil well drillers penetrate strata or deposits of one to one hundred feet of bentonite before or after striking oil.

The term bentonite has roughly been applied to those natural earthy clays that absorb moisture and expand to a notable extent over the natural bulk similarly to dry glue and gelatine, and on then shaking with water a more or less proportion of said product stays in temporary or permanent suspension and which we will designate in the present specification as natural colloidal cracking agents. This term is intended to include not only the true bentonites listed in the present geological classifications but other material closely allied in chemical composition to the bentonites and having the same colloidal properties which render the true bentonites available for use in the present invention.

Asphaltic base oils treated by the herein described cracking process using natural colloid cracking agents, may be made to yield asphalts resembling natural asphalts in character, by conducting the process or distilling to such a point that the residue may still be withdrawn from the still as a liquid. Asphalt so produced more nearly resembles natural asphalt on account of the inclusion of dispersed colloid mineral material, as in natural asphalt, thus altering to a favorable extent the asphalt thus produced by distilling without the natural colloid cracking agent.

In many portions of the world oils exist that on withdrawal from their natural reservoirs are found to be so viscous as to present difficulties in transportation through pipe lines. We have found it possible to overcome this difficulty by adding to the oil in the herein described manner, a natural colloid cracking agent, and the addition of heat, whereby our purpose is accomplished This operation of lowering the viscosity of oils may well be conducted in a closed vessel. the natural colloid cracking agent being brought into the operation as herein described in connection with distilling.

By heating viscous oils in vessels with the

natural colloid cracking agents their viscosity is lowered on account of the production of lower boiling compounds, and as indicated under distilling, the production of these compounds is influenced by the time, temperature, pressure, and colloid used; all of which may be varied for the accomplishment of said purpose.

By chemical or mechanical means the natural colloid cracking agent may, if desired, be removed before passing to the refining plant or point of consumption.

During treatment a certain portion of the lighter boiling hydrocarbons may be removed if desired.

Though we do not limit ourselves in the herein described process of operation to the use of 65 pounds pressure, but claim the right to use any pressure, in connection with the heat and the natural colloid cracking agents, we find that a very satisfactory method of operation is to operate at pressure under 65 pounds, within this limit being able to produce substantial cracking, with the following modus operandii, starting with crude oil.

The natural colloid cracking agent is emulsified with and dispersed in the whole or portion of the oil and kept in stock tanks, from which it is conducted to a still or, whereby on the addition of heat and with or without pressure the gasoline naturally present in the oil is removed, after which by increased heat and pressure applied to the oil, the higher boiling fractions in the still are thereby cracked. If for any reason the effectiveness of the colloid remaining in the still is not satisfactory more may be added to the still incorporated in oil or in its natural form or ground or jelled with water, whereby further cracking is accomplished—even to the nearly complete conversion of heavier fractions to lighter fractions, all of which may be regulated by the operator, by regulating temperature, pressure, colloid, and removal of lighter fractions.

We find our natural colloid cracking agent of more universal service than aluminum chloride, for aluminum chloride is not effective on oils containing moisture, whereas, water may be incorporated with our natural colloidal cracking agent, and be effective on oils containing water, or the dry natural colloid cracking agent may be added to either wet or dry oil without in any way losing its effectiveness, for our purpose, namely the production of lighter or lower boiling hydrocarbons from heavier or higher boiling hydrocarbons by heat or by heat and pressure herein referred to by the term cracking.

In attempting to account for the cracking of oil by bentonite and other natural colloid cracking agents, it has been noticed that the speed, extent and character of the cracking are largely influenced by the colloid character of the product used, and the extent to which they may be placed in a suspended or dispersed state within the oil being cracked.

The bentonite which we have found especially useful in carrying out our invention is that which lies in or above the Benton shales.

Through the practice of our invention we find it possible to produce gasoline, motor fuel and compounds of lower boiling points that do not exist as such under normal conditions in the material treated; to crack oils that cannot be treated by the low pressure chemical art on account of moisture; to crack high sulphur oil and the removal therefrom of a large amount of sulphur which otherwise would be found in the finished product under normal distillation; to crack oils at pressure below and above 65 pounds; to crack oils up to and above 900 pounds pressure and within widely varying limits of temperature with natural colloid cracking agents; to crack oils at atmospheric pressure to motor fuel by separating the motor spirits produced from each cracking distillation by ordinary fractionating methods and redistilling the residual portions in the presence of the colloid bentonite or the natural colloid cracking agent in the oil; to produce cracking of any natural crude oil or any similar hydrocarbon in one operation, to any degree of gravity of motor fuel desired at the will of the operator by regulating the percent of colloid cracking agent, the time of addition to the oil, and the back pressure on the still; to produce motor spirits or motor fuel from crude oil or other hydrocarbon in quantities greater than existed in the original raw material; to obtain the complete or partial removal or alteration of the character of sulphur in crude asphalt base oils during the process of distilling, so that the condensates are lower in sulphur; to crack viscous oils with natural cracking agents without removing any or only a part of the lighter specific gravity products so produced to make an oil that is less viscous than the original oil.

What we claim is:

1. The process of treating hydrocarbon under conditions of temperature and pressure condusive to cracking, which includes the dispersion throughout the hydrocarbon of a previously prepared gel composed of a natural colloidal cracking agent having catalytic properties and water, substantially as described.

2. The process of treating hydrocarbon under conditions of temperature and pressure condusive to cracking, which consists in forming a gel composed of bentonite and water, and thereafter introducing said gel into the mass of hydrocarbon subject to cracking conditions, substantially as described.

3. The process of treating hydrocarbon to promote cracking, which includes the dispersion throughout the hydrocarbon of a previously prepared mixture of a natural colloidal cracking agent having catalytic properties and water, substantially as described.

4. The process of treating hydrocarbon to promote cracking which consists in forming a mixture of bentonite and water, and thereafter introducing said mixture into the mass of hydrocarbon, substantially as described.

5. The process of treating hydrocarbon to promote cracking in order to obtain gasoline and the more salable distillates, which includes the incorporation with the hydrocarbon to be treated of a mixture composed of water and any natural earthy element in colloidal form having the characteristic catalytic action of bentonite when reduced to the colloidal state, substantially as described.

6. The process of treating hydrocarbon to promote cracking which includes the mixing with the hydrocarbon of a previously prepared mixture consisting of a natural colloidal cracking agent having the characteristic catalytic action of bentonite when reduced to the colloidal state, and a non-oleaginous liquid having the dispersive properties of water, substantially as described.

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