

UNITED STATES PATENT OFFICE.

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SYNTHESIZING OILS.

No Drawing.

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This invention relates to synthesizing oils; and it comprises a method of making synthetic oils with the aid of aluminum chlorid wherein a gas rich in hydrogen, such as natural gas, oil still gas, coke oven or coal gas, hydrogen, etc., is heated with a body of liquid oily material rich in carbon, such as asphalt, asphalt base oils, fuel oils, etc., in the presence of anhydrous aluminum chlorid to produce useful oily bodies at the expense of both; all as more fully hereinafter set forth and as claimed.

Ordinary petroleum oils are composed of various hydrocarbons; that is, combinations of hydrogen and carbon. In a general way, it may be said that these oils carry a maximum of 14 or 15 per cent of hydrogen; the amount reaching these limits in light oils, such as gasoline, of saturated or "sweet" nature and being less in the heavier oils. Heavy oils derived from asphalt base crudes may carry considerably less. The demand for these oils, and particularly for the light oils, is increasing at a greater rate than the supply; and it is a desideratum in the art to provide new sources. It is one purpose of the present invention to provide a method of synthesizing light oils, using various gases and heavy tarry materials as joint sources. Another purpose is to improve the quality and commercial value of various oils and oily materials now available.

There are various gases available which contain much more hydrogen than do the commercial mineral oils. Natural gas of the "dry" type usually consists mainly of methane or CH_4 ; and methane carries 25 per cent hydrogen. The gases liberated from oil stills, and particularly from those used in high temperature or cracking distillations, are composed of various hydrocarbons, among them methane, ethane with 20 per cent hydrogen, propane with 18 per cent, and the various olefins with 14.3 per cent. Gases of much the same character are formed in the distillation of coal in making coke and carbonizing coal, lignite, etc., and generally these gases also carry free hydrogen in greater or less amount. In "wet" natural gas, in addition to the real gases present (methane and ethane), there are also vapors of various very volatile liquid hydrocarbons, condensable with more or less ease to form the so-called casing head gasoline; these hydrocarbons includ-

ing the pentanes (C_5H_{12}) with 16.7 per cent hydrogen, the hexanes with 16.3 per cent, etc. Butane with 17.2 per cent hydrogen also occurs in these gases and is in part condensed in the casing head gasoline recovered therefrom. This type of gasoline although difficult and dangerous to store, transport and handle because of its low boiling point is nevertheless manufactured on a large scale. The same condensable hydrocarbons are contained to a greater or less extent in still gases, escaping condensation with the gasoline in distillation because of their great volatility.

On the other hand, there are available great supplies of materials unduly rich in carbon and low in hydrogen, such as asphalts, tars, pitches, etc. Asphaltic oils, which are low in hydrogen, are available in great amounts and at a low cost, many being considered useful only as fuel oil.

In a general way it may be said that the petroleum oils most useful in the arts are materials containing a medium proportion of hydrogen, the value being the greater the greater the amount of hydrogen and often increasing inordinately with a relatively small increase in hydrogen. On the other hand, both the materials rich in hydrogen (hydrogen and hydrogen containing gases) and materials poor in hydrogen and rich in carbon (asphalts, asphaltic oils, etc.), are of considerably less value. It is a purpose of the present invention to chemically blend or average, so to speak, representatives of both classes and thereby attain material of greater value. Hydrogen is derived from cheap gases and used to improve cheap carbonaceous materials.

Aluminum chlorid is a hard, crystalline, rather volatile body easily made from aluminum and chlorin or hydrochloric acid; from chlorin, alumina (bauxite) and carbon; etc. When heated with hydrocarbon oils it displays energetic and fargoing catalytic actions, rearranging the hydrocarbons chemically; that is, redistributing the hydrogen and carbon in new combinations. The actions tend to go forward to some sort of equilibrium. The catalytic effect is now utilized on the large scale in the manufacture of gasoline, kerosene, etc., from oils of higher boiling point, such as gas oil. About 5 per cent of aluminum chlorid is added to a body of hot oil in a still and the

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 mixture vigorously agitated and distilled. There is a continuous production of low boiling oils until the activity of the aluminum chlorid is exhausted, which takes place
 5 after a time. More oil is supplied to replenish the bath as it lessens in volume by production and distillation of gasoline. The aluminum chlorid when added melts down or combines with a small portion of
 10 the oil to form a heavy liquid underlying the rest of the oil. The function of the agitation is to keep this heavy liquid suspended and offer a large area of contact. As the distillation goes on, the heavy liquid
 15 becomes more and more viscous and finally acquires an asphaltic, or even a hard, consistency. At this time, it is generally discharged and sent to chlorid recovery plants to regain the aluminum chlorid.

20 In this operation, the action of the aluminum chlorid is to produce new hydrocarbons in the oil, some lighter and more volatile and some less volatile than the oil under treatment; its action striving to produce some sort of equilibrium. The process represents a "disturbed equilibrium"; the low boiling materials are removed as fast as formed and more are produced in the effort to reinstitute equilibrium, the production thereby becoming continuous. The
 25 net result is the production, on the one hand, of volatile sweet gasoline, relatively rich in hydrogen, and, on the other hand, of non-volatile asphaltic bodies relatively
 30 poor in hydrogen and rich in carbon.

I have discovered that this action can be, so to speak, reversed—instead of being so conducted as to split a body of oil into two fractions, one more volatile and richer in
 40 hydrogen and the other less volatile and poorer, still more volatile bodies (which is to say, gaseous hydrocarbons or even hydrogen) can be condensed with materials rich in carbon (asphaltic materials, etc.)
 45 to form an averaged composition. There is a synthesis of oils of a medium hydrogen content. The equilibrating powers of the aluminum chlorid are used for blending or amalgamating, instead of being utilized in
 50 a splitting operation. New oils or oily hydrocarbons are formed at the expense, on the one hand, of the hydrogen of the gas and, on the other hand, of the carbon of the asphalt or asphaltic oils. As will be seen,
 55 considering for the moment gas to be the equivalent of gasoline, the operation just stated is exactly the reverse of the gasoline making process. Instead of breaking down oil into two classes of products, the two
 60 classes of products are united to form oil.

The stated discovery is applicable in very many ways in the oil industry. By it, low grade asphaltic oils, useful mainly for fuel or producing asphalt, can be converted into
 65 high grade petroleum oils. Part of the

new high grade oil comes from the oil under treatment and part comes from the gas; the proportion of course depending on the amount of gas taken up. Both the gas and the low grade oil are converted into high
 70 grade products. In a similar way, asphalts, tars, pitches, etc., can be used as a source of carbon in producing oils from various gases now only locally useful as fuels. Where the gas used, like a wet nat-
 75 ural gas or like some of the still gases, contains vapors of unduly volatile hydrocarbons, such as those of casing head gasoline, these take part in the action and contribute to the new body of oil. The new
 80 oils produced can be used for any ordinary purposes, including the manufacture of gasoline with the aid of aluminum chlorid in the method briefly described ante; that is, oils of medium composition like ordi-
 85 nary petroleum oils can be synthesized from cheaper high-carbon materials and low-carbon materials and then, like such ordinary oils, can be used in making gas-
 90 oline.

A minor but particularly useful embodiment of my invention is in rehabilitating the activity of spent aluminum chlorid, which, for the present purposes, can be regarded as
 95 a mixture of aluminum chlorid and oily high-carbon material. As stated, after a period of action, the aluminum chlorid occurs in an asphaltic or sludgy composition, which is usually treated by a baking operation to distil off the aluminum chlorid in
 100 condition for reuse. In this embodiment of the present method, the spent sludge is simply treated with hydrocarbon gas under pressure, at a temperature of, say 300-500° F. The gas is taken up and the asphaltic bodies
 105 associated with the aluminum chlorid are reconverted into oil giving a mixture of oil and aluminum chlorid. If the amount of new oil formed is sufficient, the mixture may be simply redistilled to produce gasoline in the method stated ante. Commonly, however, the oils so produced by the synthesis are not sufficient in amount to re-exhaust the chlorid and more must be added from another source. In one methodical way of operating a body of asphaltic oil may be dis-
 110 tilled with chlorid to give such gasoline as it will, the heavy residue treated with gas to give a new body of oil of better quality and active chlorid, this again distilled and so
 120 on, diminution of volume by removal of gasoline being of course compensated by additions of more asphaltic oil.

In this embodiment of my invention the spent, or partly spent, residues are used both to furnish carbon-rich heavy oils or asphalts and to furnish aluminum chlorid.

In another embodiment of my invention, the stated production of asphalt in the formation and distillation of gasoline may be

indefinitely delayed by the simple expedient of supplying a certain amount of gas to the body of oil and aluminum chlorid during the distillation. This gas takes part in the reaction and serves to furnish hydrogen, replenishing the supply depleted in the formation of gasoline.

I regard the present invention as covering broadly the olefying or improvement of asphalt and pitchy bodies, whether existing as such or contained in oils or residues, with the aid of hydrogen-rich gases, whether these gases be natural gas, still gases, coal gases or hydrogen itself. Gases containing oxygen or oxygen compounds (CO , CO_2 , H_2O , etc.) or negative radicals, such as chlorin, etc., produce other actions than are here sought and are not desired in the present cases. Many other petroleum oils, other than those strictly classifiable as asphaltic or asphaltic base oils, are susceptible of improvement by the use of gas under the present invention. By the term "hydrogen containing gas" in the accompanying claims, I mean to include any type of hydrocarbon gas, or hydrogen itself, or any kind of hydrogen-rich vapor or semi-gas. In a reciprocal way, I regard it as covering the olefying of gases with the aid of carbon-rich products of the nature of asphalts, etc.

I often use pressure to hasten the absorption of gas, ordinarily using the more pressure the less carbon the gas contains. This is for the reason that the solubility of these gases in oily and tarry matters, in a general way, is the less the richer they are in hydrogen. Hydrogen itself is but little soluble in oils and particularly when hot, so that rather high pressure, say, 100 pounds or so, in its use is desirable to promote speed of reaction. The reaction goes forward without pressure, but more slowly.

In a typical specific embodiment of my invention as applied to low grade oil, an asphaltic Mexican oil is topped to free it of such volatiles as may be naturally present and, incidentally, to dry it. Moisture is injurious to aluminum chlorid. A body or batch of the hot topped oil is placed in a still provided with stirring arrangements and 5 to 10 per cent of aluminum chlorid added. Spent residues arising from a gasoline-making operation may be employed in lieu of fresh chlorid, as they will be regenerated by the process itself. The still and its contents are heated, usually to 500°F . or higher, and still gas is pumped in; the rate of introduction being usually proportional to the speed of absorption as indicated by a pressure gage. The pressure may be held at a point depending upon the character of the gas used. With still gas from cracking stills or tar stills, I may use 15 to 50 pounds gage pressure; with hydrogen, gases containing hydrogen, or natural gas rich in methane, I

ordinarily use more pressure. High pressure is not necessary, but is, as stated, convenient. The still may carry the usual back-trapping arrangements connected to a water-cooled condenser with a pressure valve located either between the still and the condenser or beyond the condenser. This condensing arrangement takes care of any gasoline that may be incidentally formed in the operation and allows its recovery. Instead of allowing the gasoline to escape, it may be held in the sphere of reaction. It is often a useful expedient to allow a flow of gases through the oil under treatment, gas passing beyond being collected and returned. It is of course sometimes expedient in dealing with gases containing more or less easily absorbable constituents to allow the gas to flow through but once, taking up the most reactive constituents only.

As the feed of gas goes on, the character of the oil gradually changes and if the improvement be carried on to the end, the asphaltic oil is converted into a much lighter and less viscous oil of the nature of certain high grade crudes. The operation may be stopped at any time, however, to produce any character of oil desired, and the improved oil separated from the aluminum chlorid, which is simply allowed to settle out. In a general way, the more hydrogen is introduced into the oil, the lighter will be its character. To produce high yields of gasoline, ordinarily more gas is used than when the result sought is improved lubricating oils and heavy products. The improved oil may be sent to the refinery for any appropriate treatment. It may be refined in the usual ways applicable to high grade crudes for the production of gasoline, kerosene, lubricating oils, paraffin, etc., or it may be used as a source of gasoline in the operation described ante. By stopping the improving operation at an appropriate point, an oil may be produced of any grade between the original asphaltic oil and high quality paraffin base crude.

In another valuable specific embodiment of this invention in recovering aluminum chlorid from spent residues, particularly valuable in the case of residues containing much carbon as coke, I simply distil the residues in a slow current of hydrocarbon gas in a suitable retort. The passing gas enables the distillation of such oil as may be present by lowering the partial pressure of its vapors, it carries off the aluminum chlorid for the same reason, and it converts asphaltic hydrocarbons combined with the chlorid, which might otherwise retard its volatilization, into lighter oils which go forward with it. The material in the retort is quickly stripped of its values, leaving nothing behind but a solid residue of carbon, etc. A temperature of 200 or 300°F . is suitable in

this operation, although higher temperatures may be employed.

In the manufacture of synthetic oils under the present invention, in starting with thick or viscous materials it is often desirable to add a little oil initially to make a bath liquid enough to enable easy and thorough contacting of the gas supplied and promote its absorption.

19 What I claim is:—

1. In the improvement of petroleum oils by increasing their hydrogen content, the process which comprises heating a body of an asphaltic petroleum oil with gas rich in hydrogen in the presence of aluminum chlorid.

2. In the improvement of petroleum oils by increasing their hydrogen content, the process which comprises heating a body of an asphaltic petroleum oil with gas rich in hydrogen in the presence of aluminum chlorid until contained asphalt substantially disappears.

3. In the conversion of gases rich in hydrogen into oils of the petroleum type, the process which comprises heating such gases with anhydrous aluminum chlorid in the presence of a body of oily matter of asphaltic type.

4. In the conversion of gases rich in hydrogen into oils of the petroleum type with incident reactivation of anhydrous alumi-

num chlorid, the process which comprises heating such gases with anhydrous aluminum chlorid in the presence of a body of oily matter of asphaltic type, said oily matter being intimately associated with said aluminum chlorid.

5. In the conversion of gases rich in hydrogen into oils of the petroleum type, the process which comprises heating such gases with anhydrous aluminum chlorid under pressure in the presence of a body of oily matter of asphaltic type.

6. In the conversion of gases rich in hydrogen into oils of the petroleum type with incident reactivation of anhydrous aluminum chlorid, the process which comprises heating such gases with anhydrous aluminum chlorid under pressure in the presence of a body of oily matter of asphaltic type, said oily matter being intimately associated with said aluminum chlorid.

7. In the production of low boiling oils, the process which comprises heating an oil poor in hydrogen with a gas rich in hydrogen in the presence of aluminum chlorid until an oil of medium composition is produced and thereafter distilling such oil with such aluminum chlorid to form low boiling oils.

In testimony whereof, I have hereunto affixed my signature.

ALMER McDUFFIE McAFEE