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GILSONITIC PRODUCTS.

Original application filed August 28, 1919, Serial No. 320,514. Divided and this application filed April 3, 1922. Serial No. 549,186.

To all whom it may concern:

Be it known that we, CHARLES N. FORREST, of Rahway, in the county of Union and State of New Jersey, HAROLD P. HAYDEN, of Raritan Township, in the county of Middlesex and State of New Jersey, and ORIN R. DOUTHETT, of Beaver Falls, in the county of Beaver and State of Pennsylvania, citizens of the United States, have invented certain new and useful Improvements in Gilsonitic Products, whereof the following is a specification.

Our invention relates to gilsonitic products and their manufacture, and more especially to products and materials obtainable from gilsonite through sulphonation treatment. We have found that there can be obtained from gilsonite and gilsonitic substances semi-drying oils characterized by various useful properties.

This application is a division of our application, Serial No. 320,514, filed August 28, 1919, entitled "Gilsonitic products and their manufacture".

The various phases of our invention will be specifically described hereinafter in accordance with the best mode of applying them in a practical way at present known to us.

As a gilsonitic material to be treated, we ordinarily prefer gilsonite distillate to native gilsonite itself. We have obtained a much greater yield of sulphonic products from the treatment by preparing the distillate sometime in advance and allowing it to "age" for a considerable period before being treated. Such distillate may be prepared as follows:

Gilsonite as received from the mine is charged into an iron or steel still, fired with gas or oil (or otherwise suitably heated), and connected to a suitable condenser,—such as an iron pipe condenser water-cooled. Any convenient quantity of gilsonite may be charged,—say 600 pounds to several tons. The still being closed and heat applied gradually, the gilsonite will liquefy and collect in the bottom of the still, and vapor and gas evolving from it will fill the top of the still and pass over into the condenser. As the heating progresses, temperature readings should be taken from time to time on the body of vapor in the upper portion of the still, as well as on the body of liquid beneath it. (Excepting as there may be special occasion for distinguishing them, we here and hereinafter comprehend mingled gases and vapors under the single term "vapor", for the sake of brevity. For convenience, we refer to various stages of operations by the corresponding vapor temperatures, unless otherwise specially noted.) The effect of the progressive heating of the gilsonite is to gradually break it up and decompose it chemically,—whence, mainly, the evolution of vapor. The coming off of vapor from the still begins at a temperature of some 165° F., and continues up to or even beyond coking temperatures.

Up to the point where the vapor temperature approaches some 550° F., the distillation may be carried out as rapidly as the contents of the still can be made to absorb heat. At this point, however, some exothermic or other peculiar action occurs, so that the evolution of vapor in the still tends to become excessively rapid. Unless, therefore, the previous heating has been especially slow, it is necessary to reduce the application of heating very greatly as this critical point is approached, in order that undistilled liquid may not be carried over into the condenser, and clog it up so as to render it unusable. In practice, it will usually be found convenient to cut down the fire some 100° F., in advance of this temperature. Once this critical point is well passed, the fire may be increased and the distillation pushed on as rapidly as desired to its conclusion. In practice, the heating need not be carried further than a temperature of some 850° F., measured on the solid coke product collecting in the bottom of the still.

While the vapor coming off from the still may all be led into the iron pipe condenser, as above suggested, and all of the strictly vaporous portion thereof there condensed and collected as a liquid, a slightly different procedure is preferable. A minor portion of the vapor is condensable at relatively high temperatures; and at the temperature in the condenser, the corresponding condensate is of such thick, gummy consistency that it would tend to clog it up. It is desirable,

therefore, that this heavier portion of the normally liquid products be condensed and collected separately, without entering the condenser at all. This can advantageously be taken care of by making the pipe leading from the still to the condenser of substantial length and providing it with a trap. With this arrangement, the heavier portion of the normally liquid products will be condensed by the cooling effect of the atmosphere upon the pipe (which thus acts as a sort of auxiliary condenser), and will collect in the trap, whence it can be drawn off from time to time and added to the liquid products drawn from the condenser itself. The trap also affords a measure of protection against the effects of too rapid heating at the critical temperature above mentioned.

The crude distillate thus obtained contains some 2 to 5% water, which may be eliminated by settling it out in a settling tank.

We prefer not to treat the water-freed primary, crude distillate thus produced directly, in gross, but to separate it into a plurality of different portions by fractionation or reduction. The following examples (wherein the temperatures given are the vapor temperatures in the still, unless otherwise stated) will sufficiently illustrate the most convenient methods of redistillation:

(1) Condense separately the vapors coming from the still up to 475° F. and from 475° to 600° F.,—subsequently drawing off as residuum the oil unvaporized at the latter temperature, or allowing it to remain and mix with the next charge of crude oil.

(2) Condense separately the vapors up to 475° F.; from 475° F. to 650° F.; and from 650° F. until the temperature of the material in the bottom of the still is about 850° F. By this procedure, an amount of coke equal to about 2% of the crude oil charge will be produced.

In either of these cases, considerable destructive action occurs in the production of the higher fractions,—especially the last.

(3) Three fractions nearly similar to those described under (2) may be obtained at temperatures some 100° F. lower than those mentioned by carrying out the redistillation as described in U. S. Patent 877,620, granted January 28, 1908, to Wells, blowing carbon dioxide or other inert permanent gas through the liquid in the still. In this case, the destructive action is much less. It is advantageous to pass the gas and vapor coming off through a filter of fuller's earth in the dome of the still, on its way to the condenser. A residuum of heavy oil will preferably be left in the still, as described under (1).

The gas from the primary distillation contains ammonia, which can be segregated as ammonium sulphate by a sulphuric scrubbing operation. The coke from both distillations also has a nitrogeneous content recoverable by a similar operation in connection with conversion thereof into fuel gas by incomplete combustion in a by-product gas-producer. The water eliminated from the crude distillate also contains ammonia in solution, which may, if desired be also converted into ammonium sulphate. For these operations for recovery of ammonia may be used the unconsumed portion of the sulphuric reagent employed in the purification and sulphonation treatments hereinafter described.

Of the distillates thus produced, we generally prefer to treat the intermediate one. Prior to sulphonation treatment, however, we prefer to subject the gilsonitic material to preliminary purifying treatment with a sulphuric reagent, thus removing therefrom organic bases, olefines, and other impurities that might alter or impair the character and utility of the final products. This preliminary sulphuric treatment may be carried out by agitation of the gilsonitic material with about 5% of sulphuric acid of oil of vitriol grade,—i. e., about 66° Bé.,—for about one half hour. It is desirable to repeat the operation (using fresh acid) one or more times.

After this preliminary step, "sulphonation" treatment may be carried out by subjecting the purified gilsonitic oil to the action of a sulphonating reagent. The sulphonating reagents which we prefer to use are oil of vitriol, such as mentioned above, and fuming sulphuric acid or "oleum." It is desirable to conduct this treatment in a cast iron vessel, using mechanical agitation rather than air agitation in order to avoid such contamination with atmospheric moisture as might interfere with the desired reaction.

We have found that the quality of the final products is improved by carrying out this treatment progressively, with successive portions of reagent, and segregating the reaction products, as formed, from the material being treated, so that each of the successively acting portions of reagent shall be perfectly fresh and untainted with such reaction products. Further improvement can be obtained by starting with relatively weak reagent, and using more and more reactive or energetic reagent as the treatment progresses. This may be done in a succession of separate operations upon a single lot of material with different portions of reagent, rather than in one single operation,—say four such treatments, each with an amount of reagent equal to 20% of the material treated. Thus for the first treatment, the reagent may be oil of vitriol alone; for the second, a mixture of 15 parts oil of vitriol and 5 parts oleum; for the third, a mixture of oil of vitriol and oleum in equal parts;

for the fourth, a mixture of 5 parts oil of vitriol and 15 parts oleum. Each of these treatments may last about two hours.

If, on the other hand, it is desired to carry out sulphonation treatment all at once, in a single operation, rather than progressively, it may be done by mechanical agitation for some eight hours,—using, say, an amount of sulphonating reagent equal to 80% of the material treated and consisting of 50 parts oil of vitriol and 30 parts oleum.

At the end of each treatment or operation, the charge in the agitator is allowed to stand an hour or more, when it will be found to have separated into two distinct layers; a top layer of residual or mother oil, and a bottom layer of acid sludge. This latter should be drawn off and thus segregated prior to the next treatment of the mother material.

The residual oil remaining after the last treatment may be neutralized, as with sodium hydrate solution (preferably of specific gravity greater than 30° Bé., in order to avoid emulsification). After the excess of caustic has been drawn off, the resultant alkaline oil should preferably not be washed, on account of its emulsifying tendency; but it may instead be distilled with steam, in order to improve its color, and filtered through fuller's earth for the same purpose. This gilsonitic sulphonation residual oil as thus purified is a thin, clear oil; substantially colorless, orderless, and tasteless; and suitable for about the same uses as highly refined petroleum. If desired, the distillation above mentioned may be carried out fractionally, so as to yield different oils more especially suitable for particular purposes.

It is preferable that the lots of sludge obtained from different sulphonation treatments be further treated or worked up individually, since the various treatments yield final products having somewhat different properties. This sulphonation sludge contains, as principal components, unconsumed sulphonating reagent, water-soluble organic sulphonic products, and oil produced from the mother oil by chemical action incident to the sulphonation treatment. It also contains, as impurity, an inconsiderable amount of the mother oil itself (which may, if subsequently segregated, be neutralized along with that obtained as above described), and some small amount of other organic products. The proportions of the sulphonic and other reaction products in different lots of sludge vary considerably; the oil reaction product, in particular, may be entirely absent from the sludge of the last sulphonation treatments. The condition of the materials in the sludge is that of solution in the unconsumed sulphonating reagent.

We have found that separation of the sulphonic material mentioned above fron the rest of the sludge can be effected by addition thereto of a solvent of the sulphonating reagent: for this purpose, the sludge may be diluted with an equal weight of water. Preferably the water is placed in a lead-lined, water-jacketed vessel, and the sludge gradually introduced at such a rate that the temperature shall not rise excessively,—110° F., being a perfectly safe limit. The operation is decidedly exothermic, and sulphur dioxide is copiously evolved. The dilute sludge is allowed to stand some eight to twelve hours,—more or less,—at a temperature of 150°F., or thereabout. During this period, separation into three distinct layers takes place, and these may be successively drawn off and thus segregated. The bottom layer is a dilute aqueous solution of the excess of sulphonating reagent, discolored by some slight amount of organic impurity; the middle layer comprises the water-soluble organic sulphonic material, contaminated with an inconsiderable amount of the solution that forms the bottom layer and with a small portion of the ingredients of the top layer; and the top layer contains the reaction oil component and the residual mother oil impurity, etc., mentioned above. (In some cases, as indicated above, the "top layer" may be entirely absent).

Coming, now, to the further disposition or treatment of these separation products,—the dilute acid of the bottom layer may be used for the recovery of ammonia as above described. The "top layer" (when present) may be neutralized with sodium hydrate and washed with water until free from alkali. The resulting gilsonitic sulphonation sludge oil is a viscous liquid; of slow-drying or "semi-drying" character; and usually of dark, reddish-brown color and slight, inoffensive odor, somewhat suggesting that of vaseline. It is soluble in benzole or naphtha and insoluble in alcohol, when freshly prepared; and vice-versa after sufficiently prolonged exposure to the air. Not only is it adapted for general use as a semi-drying oil; but when mixed with boiled linseed oil, it so modifies the drying properties of the latter that it dries homogeneously, without formation of the usual surface film. It also seems to render the fully dried linseed oil tougher and more elastic.

We have hereinbefore spoken of sulphonating reagents, sulphonation treatment, and sulphonation reaction or sulphonic products, etc., using these expression in reference to the chemical character and mode of use of the reagent employed in the principal treatment described above, or to the useful properties of products resulting therefrom. We do not, however, mean

by this language that our sulphonic products are true sulphonic substances in the sense of having sulphonic radicals,—since we are without clear evidence on this point.

Having thus described our invention, we claim:

1. A semi-drying, viscous, gilsonitic sulphonation sludge oil.

2. A gilsonitic oil; viscous and slow-drying; soluble in benzole and naphtha and insoluble in alcohol when fresh, and vice versa when dried.

3. A semi-drying, viscous gilsonitic oil; having the property, in admixture, of causing boiled linseed oil to dry homogeneously instead of with a surface film.

In testimony whereof, we have hereunto signed our names at Maurer, N. J., this 29th day of March 1922.

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Witnesses:
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