Patented Mar. 23, 1926. 1,578,235

UNITED STATES PATENT OFFICE.

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GILSONITIC PRODUCT AND ITS MANUFACTURE.

No Drawing. Application filed August 28, 1919. Serial No. 320,514.

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 and Their Manufacture, 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 and to processes and methods connected with such treatment. We have found that, by treatment of this character, there can be derived from gilsonite and gilsonitic substances various new and useful products of unique properties, and we have devised various novel processes, steps, and methods for accomplishing this to the best advantage. Certain of our processes and methods can also be adapted and extended to hydocarbon substances or materials other than gilsonitic ones,—especially those of mineral origin.

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, while the real scope and essence of the invention will be indicated in our claims.

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 some time in advance and allowed 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 unusuable. 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 temperatures 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° F. 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 Jan. 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 nitrogenous 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, under the usual sulphonating conditions. 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, odorless, 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 specially 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 from 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 tougher and more elastic.

The water-soluble organic sulphonic material of the middle layer gives an acid reaction, and has, in general, the useful properties of sulphonic acids. In appropriate combinations, therefore, its characteristic radical or radicals constitute a useful agent for many different purposes—acting as hydrolyzer or saponifier for oils, fats, and other glycerides or fatty substances, when employed in the usual manner, and having excellent detergent and emulsifying properties. For the first of these uses, at least, this sulphonic agent is serviceable in the impure acid form in which it exists in the middle layer, although its color characteristics and the efficiency of its hydrolyzing action are not so good as after purification. To purify it of the organic top layer material (the principal contaminating impurity), it may be neutralized, which has the effect of setting free this top layer material and allowing it to float to the surface and be readily removed. For hydrolyzing purposes, the purified salt thus obtained may be reconverted (by means of sulphuric or other acid) to yield the agent in purified free acid form; while for detergent or emulsifying purposes, the purified salt form of the agent will ordinarily be preferred to the acid form. The sulphonic material of the middle layer can also be freed from organic contamination without neutralization, by merely diluting the middle layer with water freely,—which will allow the organic material to come to the surface as described above.

If desired, the salt form of the reagent may be obtained free from both organic material and sulphates. For this purpose, the middle layer may be diluted with water and barium sulphate precipitated therefrom (some little barium salt of the reagent being unavoidably thrown down also) by addition of barium carbonate in just sufficient amount to fully satisfy the sulphuric acid; this leaves the free acid reagent in solution. After filtration, the organic material can be set free for removal from the solution as before.

In both purified and unpurified states, the sulphonic products from the later sulphonation treatments have greater hydrolyzing power than those from the earlier treatments.

It is most convenient and desirable to handle, pack, and ship an agent of this sort in the form of a dry, solid, stable salt, rather than in its more active free acid form,—which is, besides, in the present instance, more difficult to dry. It is, of course, preferable that the particular salt that is to be so used commercially be produced at the outset, in the freeing of the agent from organic contamination as described in the preceding paragraphs. For detergent and emulsifying purposes, the sodium salt will ordinarily be preferable, on account of its relatively low cost. For saponifying or hydrolyzing purposes, however, it is peculiarly advantageous to employ as the commercial material a salt with a volatile base, and to produce the active, free acid saponifier therefrom by acidulation when it is to be used,—either before or in the actual treatment of the glycerides,—on account of the facility thus afforded for securing glycerine water free from saponifier, acidulant, or other deleterious impurity. For this purpose, the ammonium salt form of the agent is especially suitable. When this is used, the glycerine water subsequently obtained will contain only acid saponifier, acidulant, (usually sulphuric acid), and ammonium salt of the acidulant. By addition to this glycerine water of a suitable base or salt (such as calcium hydrate or barium carbonate), insoluble salts of the acidulant and the saponifier will be formed and precipitated. This will leave in solution in the glycerine water, as an impurity only an unstable combination (ammonium hydroxide or carbonate) whose components can be volatilized and driven off by boiling.

As to the general properties of these gilsonitic derivative sulphonic materials, it is to be observed that the alkali salts (i. e., both amonium and alkali metal salts) are water-soluble, as well as the acid; while the alkaline earth and the other metal salts generally are water-insoluble. (These properties, it will be seen, specially adapt these materials to the modes of use described in the preceding paragraph). As it exists in the middle layer, the acid material is a thick, viscous fluid, dark or black, with a brown undertone in a thin film. Aside from the organic top layer contamination, it is soluble in alcohol. The alkali salts are also soluble in alcohol,—which fact affords another convenient method of freeing them from sulphate contamination.

We have hereinbefore spoken of sulphonating reagents, sulphonation treatment, and sulphonation reaction or sulphonic products, etc., using these expressions 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.

Returning, now, to the residual oil remaining from the last sulphonation, we desire to call attention to a mode of dealing with it alternative to that above set forth. In this method, the first step is to wash

the oil with alcohol diluted with (say) an equal or double amount of water. The oil may now be neutralized, as above described, and washed with water (without trouble from excessive emulsification) to remove the excess of alkali. If desired, it may also be distilled, as above. This mode of treatment greatly improves the color of the purified residual oil finally obtained.

The organic material dissolved or extracted from the residual oil by the alcohol appears to be the cause of the emulsifying property of the oil; for when recovered (by distillation of the alcohol), it itself presents this same property. As thus obtained, this extract derivative is an acid substance, brown to black in color, and with slight odor. Appropriate combinations of its characteristic radical or radicals present useful properties similar to those of our other sulphonic agent described above,—though somewhat superior in degree,—and are serviceable for the same purposes and in the same way. We have no proof, however, that it is a true sulphonic substance or sulphonation product, or that its characteristic radical is sulphonic. In both acid and salt forms, this gilsonitic sulphonic agent is similar to the other as regards water-solubilities; but with respect to organic solvents, it is sharply distinguished. Thus both the acid and salt forms are soluble in most organic solvents,—such as benzole, alcohol, petroleum naphtha, or other distillates,—and both salt and acid forms are more freely soluble in such solvents than in water. The dissolution of the acid material in water is peculiar (probably owing to impurity), in that as water is gradually added to the material, it first gelatinizes and then goes more freely into solution. The relative hydrolyzing, detergent, and emulsifying properties of these gilsonitic derivative sulphonic materials (i. e., acid and salts) are similar to those of the others.

Having thus described our invention, we claim:—

1. The process which consists in purifying gilsonitic material by sulphuric treatment; subjecting the purified product to the action of a sulphonating reagent under sulphonating conditions and segregating the resultant sludge; segregating the sulphonic products in the sludge from the remainder thereof; and freeing the segregated sulphonic products from contaminating impurity.

2. The process which consists in purifying gilsonitic material by sulphuric treatment; subjecting the purified product to the action of a sulphonating reagent under sulphonating conditions and segregating the resultant sludge; dissolving the unconsumed reagent in the sludge with a solvent, and thus causing reaction products in the sludge to separate from one another and from the solution of reagent by gravity.

3. The process which consists in subjecting gilsonitic material to the action of a sulphonating reagent under sulphonating conditions, and segregating the resultant sludge; and separating reaction products in the sludge from one another and from the unconsumed sulphonating reagent by addition to the sludge of a solvent of such reagent.

4. The process which consists in treating gilsonitic material with a sulphonating reagent under sulphonating conditions, dissolving products of the reaction in an excess of such reagent; segregating the resultant sludge solution from the mother material; removing the excess of sulphonating reagent from said sludge solution by solution of such excess of sulphonating reagent with another solvent; and separating said reaction products from one another and from the solution of solvents by gravity.

5. The process of preparing sulphonation reaction products from gilsonitic material which comprises subjecting the gilsonitic material to sulphuric purification, thereby removing organic bases, olefines, or other impurities; and subjecting the thus purified material to the action of a sulphonating reagent under sulphonating conditions.

6. The process of preparing sulphonation reaction products from gilsonitic material which comprises purifying the gilsonitic material with oil of vitriol grade sulphuric acid and subjecting the thus purified material to the action of a sulphonating reagent under sulphonating conditions.

7. The step in the manufacture of sulphonation reaction products from hydrocarbon material which consists in subjecting said material to successive sulphonation treatments with different portions of sulphonating reagent, segregating the sludge of each treatment from the mother material prior to the next treatment of said material.

8. The step in the manufacture of sulphonation reaction products from hydrocarbon material which consists in subjecting said material to successive sulphonation treatments with portions of sulphonating reagent of successively increasing reactivity, segregating the sludge of each treatment from the mother material prior to the next treatment of said material.

9. The method which consists in subjecting gilsonitic distillate oil to progressive sulphonation treatment with successive portions of fresh sulphonating reagent, each untainted with reaction products of such treatment.

10. The method which consists in subjecting gilsonitic material to progressive sulphonation treatment with fresh sulphonating reagent of greater and greater reactivity,

segregating the reaction products, as formed, from the material being treated.

11. The method of manufacturing hydrocarbon sulphonation sludge products which consists in producing separate lots of such sludge by a plurality of successive sulphonation treatments of a single lot of hydrocarbon material with different portions of sulphonating reagent, and further treating such lots of sludge individually.

12. The method of manufacturing gilsonitic sulphonation sludge products which consists in separately preparing and working up a plurality of lots of such sludge from a single lot of gilsonitic material.

13. The method of treating gilsonitic sulphonation sludge which consists in segregating the sulphonic products therein from the remainder of said sludge by addition to the sludge of a solvent of the sulphonating reagent.

14. The method of treating gilsonitic sulphonation sludge which consists in dissolving the unconsumed sulphonating reagent therein with a solvent, and separating the sulphonic and other reaction products in the sludge from one another and from the solution of reagent by gravity.

15. A gilsonitic sulphonic material; serviceable as an agent for the hydrolysis of glycerides; detergent: and characterized by a radical whose alkali salts and free acid are water-soluble, but whose alkaline earth salts are water-insoluble.

16. A sulphonation product derived from gilsonite distillate; having generally the useful properties of true sulphonic substances; and characterized by a radical whose alkali salts and free acid are water-soluble, but whose alkaline earth and other metallic salts generally are water-insoluble.

17. A sulphonic material derived from gilsonitic sulphonation sludge as a water-soluble separation product; characterized by a radical whose alkali salts and free acid are water-soluble, but whose alkaline earth salts are water-insoluble.

18. A sulphonic derivative of sulphurically purified gilsonitic material; having, in general, the useful properties of true sulphonic substances.

19. A sulphonic derivative of the residual from antecedent sulphonation treatment of gilsonitic material; having, in general, the useful properties of true sulphonic substances; and characterized by superior hydrolyzing power as compared with the corresponding product from such antecedent sulphonation treatment.

20. A sulphonic derivative of the residual from antecedent sulphonation treatment of sulphurically purified gilsonite distillate.

21. A gilsonitic sulphonic material serviceable as an agent for the hydrolysis of glycerides; comprising a salt of a volatile base which yields, when acidulated, an active water-soluble saponifier.

22. A gilsonitic sulphonic material serviceable as an agent for the hydrolysis of glycerides; comprising a water-soluble ammonium salt which yields, when acidulated an active water-soluble saponifier.

In testimony whereof, we have hereunto signed our names at Maurer, N. J., this 25th day of August, 1919.

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