

UNITED STATES PATENT OFFICE.

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TO SETH B. HUNT, TRUSTEE, OF MOUNT KISCO, NEW YORK.

ACID LIQUOR AND PROCESS OF PRODUCING SAME.

1,365,044.

Specification of Letters Patent.

Patented Jan. 11, 1921.

No Drawing.

Application filed June 26, 1917. Serial No. 177,058.

To all whom it may concern:

Be it known that I, CARLETON ELLIS, a citizen of the United States, and a resident of Montclair, county of Essex, and State of New Jersey, have invented certain new and useful Improvements in Acid Liquor and Process of Producing Same, of which the following is a specification.

This invention relates to the production of acid liquor by the treatment of olefin material with an extractive acid, such as sulfuric acid, and the process of its production.

The term "olefins" is used to include unsaturated hydrocarbon material capable of reacting in the general manner hereinafter set forth. Such olefin material may be substantially pure or may be comprised in material containing saturated and unsaturated material, such as cracked oils, including cracked petroleum oils.

In treating such material with a reactive acid, such as sulfuric acid, the unsaturated bodies are taken up to a greater or less extent by the acid and an acid liquor is produced. So far as reaction occurs between the acid and the olefins, it is desirable, preferably in order to obtain materials suitable for subsequent treatment to produce products of value, that the reaction be directed substantially to sulfation and that it be carried on under sulfating conditions, by which is meant conditions whereby the reaction is substantially directed to the production of sulfated products and reactions productive of tarry, resinous and charred products in substantial proportions are avoided, so far as practicable. When such undesirable reactions are permitted to take place freely, as in ordinary oil refinement practice, the materials produced are not suitably reactive for further treatment, and according to the present invention preferably the production of such objectionable bodies is avoided, though the same may and usually does take place to some extent. The taking up of the unsaturated components of the olefin containing materials may also include dissolving, absorption, etc., of the unsaturated materials by the acid.

When the acid is added to the olefin containing materials, as, for example, to light hydrocarbon fluid obtained by compressing the gases of petroleum stills or to other forms of cracked oils, the extraction may be carried out by adding the acid slowly and

preferably keeping the material cool and by continued agitation during the mixing of the acid with the hydrocarbons. As the treatment proceeds, acid extract or liquor is formed and the power of the acid to extract olefins from the olefin containing material is reduced, as is also the readiness with which the olefins are absorbed or extracted by the acid, so that the ability of the acid to extract olefins from the olefin containing material is apparently limited, and when the acid extract is withdrawn from the hydrocarbon fluid the latter still contains a substantial quantity of olefins unextracted.

I have found that upon withdrawing the acid extract or liquor from the hydrocarbon material and entering it into fresh olefin containing hydrocarbon material, additional quantities of unsaturated material may be extracted. Care is taken to prevent undesirable reactions taking place as far as possible, preferably about as in the case of extracting with the sulfuric acid in the first place, but when extracting fresh cracked gasolene or other olefin containing material with the acid liquor obtained from extracting previous batches thereof with acid, it is generally not necessary to exercise so great a degree of care to prevent the reaction going too far. The acid extract obtained by the first extraction may be strengthened, if desired, by addition of fresh acid thereto prior to the second extraction.

Also I have found that upon withdrawing the acid liquor from the hydrocarbon material it is possible to extract still further quantities of the unsaturated components thereof by extracting it in substantially the manner already referred to, that is to say, under sulfating conditions, with fresh sulfuric acid, and the acid extract so obtained may be used, as in the case of the acid extract previously referred to, to extract additional quantities of unsaturated components from unsaturated containing materials, as cracked gasolene, by using the acid liquor as an extracting medium in place of the acid itself.

Further, even after as great a degree of saturation of the acid with the unsaturated materials has been secured as is obtainable with any one or more of the modes already set forth, the acid is present in the acid liquor in excess and is capable of dissolving further quantities of unsaturated materials,

and by adding to the acid liquor so obtained the unsaturated materials in substantially the pure form, or reversing the addition and adding the acid to the substantially pure unsaturated materials, it is possible to obtain a degree of saturation of the acid with the olefins which is substantially complete, the acid being substantially completely saturated with olefin material so that its capacity for absorbing olefins is exhausted. Reextraction in any of the modes referred to may be carried out repeatedly, if desired, but ordinarily the first and second extractions are sufficient for all practical purposes.

The acid liquor so obtained in any one or more of the foregoing ways, may be used for any purpose for which it is adapted. For example, it may be entered into water and distilled whereby it becomes hydrolyzed, producing mixtures of alcohols corresponding to the olefins of the cracked oils originally treated, or it may be directly treated to form mixtures of esters corresponding to the esters of olefins contained in the original material treated, or it may be made use of for other purposes. This invention, however, relates to the acid liquid and the mode of its production and is not concerned with its subsequent utilization which may be performed in any way desired, the uses to which reference has been made having been mentioned only for the purpose of giving an understanding of modes in which the acid liquor produced in accordance with the present invention may be utilized.

Preferably material of the nature of sulfuric acid of substantially 1.8 or 1.84 specific gravity is used, although as already stated, reactive oxygen containing mineral acids may be used, and the sulfuric acid when used may be of different gravities. With some olefin materials oleum or pyrosulfuric acid may be used and ordinary commercial acid, and sulfuric acid of 95%, 98%, 100% and fuming acid of say 105%, but ordinarily the greater the strength of acid used, the lower the temperatures to be used in order to maintain sulfating conditions. The specific gravity of the olefins is generally much less than that of the acid. Usually the specific gravities of the olefins are considerably less than one, so that the degree of saturation of the acid with the olefins can readily be gaged, at least in a rough way, by noting the specific gravity of the acid liquor. For example, while the gravity may vary considerably, according to the present invention it becomes possible to ob-

tain acid liquor extracted by the acid from olefins having a specific gravity ranging in the neighborhood of 1.3 or 1.2 or thereabout.

The acid extract formed in any or all of the preceding modes is immiscible in fluid saturated hydrocarbon material, as gasolene, and may be readily withdrawn therefrom as by settling and drawing off from the bottom. This is of particular advantage, for example, where acid liquor is to be produced by extraction of olefins from material as cracked gasolene, containing but a small percentage of olefins or other unsaturated bodies.

Having thus described my invention, I claim:

1. The process of making reactive acid liquor which comprises treating hydrocarbon material containing olefins and liquid saturated hydrocarbons with sulfuric acid under sulfating conditions, and using the acid extract so obtained for treatment of other olefin material, whereby acid liquor highly saturated with olefins is obtained.

2. The process of making reactive acid liquor which comprises gradually entering sulfuric acid of about 1.8 specific gravity into hydrocarbon material containing olefins and liquid saturated hydrocarbons, with agitation and cooling, separating the acid extract formed, and using the acid extract so obtained for treatment of additional olefin material, whereby acid liquor highly saturated with olefins content is obtained.

3. The process of producing a reactive acid liquor which comprises extracting hydrocarbon material containing olefins and liquid saturated hydrocarbons with sulfuric acid under sulfating conditions, reextracting further olefin material with the first extract, and bringing the extract up to substantial saturation with olefins by the addition of substantially pure olefin material.

4. The process of producing a reactive acid liquor which comprises extracting hydrocarbon material containing olefins and liquid saturated hydrocarbons with sulfuric acid under sulfating conditions, separating out the acid extract formed, reextracting further olefin material with the first extract, and bringing the acid extract up to substantial saturation with addition of substantially pure olefin material.

In testimony that I claim the foregoing, I hereto set my hand, this 23rd day of June, 1917.

CARLETON ELLIS.

It is hereby certified that in Letters Patent No. 1,365,044, granted January 11, 1921, upon the application of Carleton Ellis, of Montclair, New Jersey, for an improvement in "Acid Liquor and Processes of Producing Same," errors appear in the printed specification requiring correction as follows: Page 2, line 27, for the word "liquid" read *liquor*; same page, line 37, before the word "material" insert the word *acid*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of June, A. D., 1921.

[SEAL.]

KARL FENNING,

Acting Commissioner of Patents

Cl. 23—24.