

## UNITED STATES PATENT OFFICE

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## PROCESS OF FORMING ALKYL SULPHATES

No Drawing.

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The present invention relates to the recovery of acid used for the absorption of olefines in the production of alcohol and has as its object the provision of a method whereby acid used in fixing the propylene in cracked petroleum products may be recovered in concentrated form.

It has been known to absorb olefines of cracked petroleum products in a mineral acid to form alkyl esters and to thereafter hydrolyze the esters by distillation whereby the alcohols are driven overhead and a dilute acid remains in the still. In practice, sulphuric acid is used for absorbing the olefines.

It has naturally occurred to those practicing the process just described to reconcentrate the sulphuric acid and to return to the process the acid remaining after distilling off the alcohols. It has been found, however, that the spent acid from an alcohol process treating cracked petroleum products and as heretofore practiced contains so much sulphonic acid that its reconcentration is impractical because the sulphonic acids break down and deposit carbon in the concentration of the acid.

I have found that the contaminations giving trouble in the concentration of the spent acid in question after completion of the distillation for alcohols is almost entirely derived from sulphonic acids. It appears, moreover, that these sulphonic acids are due to reactions occurring between the sulphuric acid used in absorbing the olefines and compounds of the nature of acetylenes, dienes and aromatic and other cyclic compounds which are present in the cracked petroleum material.

One object of the present invention is to provide a method of absorbing olefines while preventing the formation of sulphonic acids. The prevention of formation of the sulphonic acids during absorption of the olefines is achieved according to the present invention as to substances gaseous at atmospheric pressures and normal room temperatures by maintaining the sulphuric acid used for absorbing olefines from cracked petroleum products at a temperature of not

above 5° F. throughout the absorption step. When the acid does not rise above 5° F. substantially no sulphonic acids are formed and so little sulphonic acid remains in the spent acid after hydrolyzation that it can be readily reconcentrated for further use by methods and apparatus now in common use in concentrating sulphuric acid. Preferably, the reconcentrated acid is used over and over again for the absorption of olefines from cracked petroleum products. As to sulphonic forming substances in cracked petroleum which are normally liquid, further precautions are necessary as well appear presently.

As an illustration of a suitable complete process according to the present invention, the process may be practiced as follows:—cracked petroleum products of gaseous character are brought into contact with concentrated sulphuric acid of 66° Bé., the petroleum products as well as the acid being maintained at a temperature of not more than 5° F. throughout the period the two are in contact. Preferably, the petroleum products, if containing material gaseous or vaporous at atmospheric pressures, are maintained under superatmospheric pressure while in contact with the acid. This is not essential, however.

If the material to be treated contains unsaturated substances, and especially sulphonic acid forming substances, whose boiling points are above normal room temperatures, the acid must have its concentration reduced by the formation in it of alkyl sulphates from the gaseous olefines prior to the contact of the acid liquor with the normally liquid unsaturated substances. This is true even when the temperature of the acid liquor is not above 5° Fahrenheit. The acid liquor should have its gravity reduced by formation of alkyl sulphates from 66° Bé. to approximately 30° Bé. at 5° Fahrenheit before coming into contact with cracked petroleum material containing a mixture of normally liquid unsaturated compounds. The gravity of the liquor should preferably be below 35° Bé. before contacting it with the liquid material.

The reduction in concentration of the acid just mentioned is readily accomplished if the cracked petroleum material is passed upwardly through two tower sections in succession counter-current to the acid and acid liquor, both tower sections being maintained at 5° F. or below. Acid of 66° Bé., or like concentrated sulphuric acid, is passed into the top of one section, out at its bottom and then into the top and out of the bottom of the other section. The cracked petroleum material is passed into the bottom of the section from which the acid liquor issues last and out at the top of this section. The normally liquid petroleum material is then separated from the normally gaseous petroleum material by well-known means and only normally gaseous material is passed into the bottom of the section into which the acid enters first. In this way the concentrated acid is prevented from coming into contact with the normally liquid olefines and sulphonic acid forming substances in the cracked petroleum as it is not at all difficult to operate the tower section into which the acid is first introduced so that the acid liquor shall pass out of its bottom tray at 30° Bé. or thereabout. At temperatures of 5° F. and below practically all of the olefines in the petroleum material, except the ethylene, react with the sulphuric acid to form alkyl esters. The speed of the reaction, while less than at temperatures about 32° F. 0° C., is high enough for commercial purposes. The petroleum material is kept in contact with the acid at a temperature below 5° F. until at least a major portion of the propylene contained therein has reacted with the sulphuric acid to form either acid or normal isopropyl sulphate. Preferably, the acid and petroleum material are kept in contact until substantially all the propylene has combined with the sulphuric acid. The amount of polymers formed during absorption of the olefines is very small and substantially no sulphonic acids are formed. The absence of sulphonic acids in the alkyl sulphate mixtures results not only in a spent acid capable of re-concentration by ordinary methods, but in an isopropyl cut free from the familiar "straw" odor noticeable in ordinary crude isopropyl alcohol. I have found that the "straw" odor noticeable in ordinary crude isopropyl is produced by the products of decomposition of certain sulphonic acids which decompose during the usual distillation following the absorption of the olefines. The sulphonic acids not decomposable by continued heating at temperatures of 212° F. (100° C.) and lower, would remain in the acid and hinder or prevent its re-concentration as above mentioned.

After absorption of the olefines is suf-

ficiently complete, the alkyl sulphates and any uncombined acid are then separated from the petroleum material and diluted with water. Preferably four volumes of water to one of esters is employed. A wide range of water to esters, however, is permissible. The diluted alkyl sulphates may then be distilled for the production of alcohols which are driven over-head, dilute or spent acid remaining in the still. However, if desired the diluted alkyl sulphates may be hydrolyzed prior to distillation by heating with agitation. Preferably the distillation for alcohols is performed as soon as possible after the absorption or hydrolysis.

The alcohols having been driven off, the dilute acid remaining in the still is thereupon reconcentrated for further use by any ordinary or preferred method. While it is convenient to use the reconcentrated acid in the further absorption of olefines from cracked petroleum products for the production of alcohols, the present invention is not limited to any given use of the concentrated acid.

If preferred, the absorption of the propylene may be conducted separately from the absorption of butylene or heavier olefines. The separate absorption of the propylene as just mentioned is described in Born and Isham Patent 1,744,207 granted January 21st, 1930 on an application filed May 1st, 1919. In said application, however, the propylene scrubber or scrubbers is operated at 50° F. (10° C.), whereas, according to the present invention, it must be kept below the temperatures at which substantial amounts of sulphonic acids are formed. Whether the propylene is absorbed with the butylene or not, the lessened speed of reaction of the propylene with the sulphuric acid when operating at the temperatures necessary to avoid formation of sulphonic acids is off-set by contacting the acid with the petroleum material for a long enough time to absorb substantially all the propylene. The length of contact for this purpose with any given strength of acid and petroleum material can best be determined by preliminary routine tests. The ethylene may be absorbed, if desired, in a body or stream of acid separate from that used to absorb the propylene. As is well known, sulphuric acid must be hot in order to absorb ethylene at commercial rates of speed. If the ethylene is to be used for the production of denatured alcohol, the presence of bad odors in the alcohol due to the formation and decomposition of sulphonic acids in the absorption and distillation of the olefine and alkyl sulphates or alcohols is not material. However, the substances in the petroleum material forming sulphonic acids with sulphuric acid are nec-

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essarily absorbed in the hot sulphuric acid at the same time as the ethylene, unless their presence during the absorption of the ethylene is prevented. The reconcentration of 5 the acid used for the ethyl alcohol manufacture thereby becomes impossible for reasons explained above. It is practical, however, to make a relatively clean and good smelling ethyl alcohol from the ethylene in 10 petroleum material by absorbing the sulphonate acid forming substances in a body of acid separate from that used for absorbing the ethylene. The substances in the petroleum material capable of forming sulphonate 15 acids react with the sulphuric acid at temperatures considerably below those commercially feasible for the absorption of ethylene, assuming that some reaction between the acid and ethylene may occur at relatively 20 low temperatures. When other than denatured alcohol is to be made from the ethylene according to the present invention, it is preferred to pass the petroleum material 25 from the scrubber in which the propylene has been absorbed into a body or stream of sulphuric acid of 66° Bé. maintained at slightly above room temperatures. The substances forming sulphonate acids are readily absorbed by the acid at room temperatures 30 or above, but little or no ethylene is absorbed by the acid in the time necessary for absorption of the sulphonate acid forming substances. After the absorption of the sulphonate acid forming substances, the ethylene 35 containing material is passed into a body or stream of sulphuric acid maintained at between 176° F. (80° C.) and 248° F. (120° C.), and preferably about 212° F. (100° C.). The ethylene containing material is maintained 40 in contact with the acid at 212° F. (100° C.) until substantially all the ethylene has been absorbed by the acid to form acid ethyl or di-ethyl sulphate.

The body of acid used for absorption of 45 the sulphonate acid forming substances may be treated for recovery of sulphonate acids, if desired. Whether or not sulphonate acids are recovered from the sulphuric acid used for absorbing acetylenes and like substances, 50 there is a material saving in acid achieved by absorbing these sulphonate acid forming substances in a separate body of acid as compared to absorbing them with the ethylene. 55 In the latter case, the acid can be used only once, while the sulphonate acid forming substances in a given quantity of petroleum material can be absorbed in an amount of acid much less than that required to absorb the ethylene from said given petroleum material.

The ethylene sulphuric acid or diethyl sulphate formed by the absorption of the ethylene in the acid may be converted into alcohol 65 by known methods or may be used for other

purposes, as desired. If desired, the acid liquor from the ethylene absorption, where containing no sulphonate acids, may be used to absorb olefines from normally liquid petroleum material, either in the tower section 70 previously mentioned, or in other suitable apparatus. Of course the acid liquor from the ethylene absorption should be cooled to 5° F. or below before being used with the liquid olefines as just mentioned. When the 75 acid liquor from the ethylene absorption is used for absorbing the liquid olefines, it may be unnecessary to use the acid liquor from the propylene absorption for this purpose.

While I have described in detail a process 80 embodying the present invention it will be understood that I do not limit myself to details of the foregoing description. In particular, it is within the present invention to absorb the olefines heavier than propylene 85 prior to the absorption of the propylene.

Having thus described my invention I claim:

1. In the manufacture of alcohols by contacting cracked petroleum materials with sulphuric acid, the process which comprises contacting gaseous cracked petroleum material containing a mixture of propylene and normally gaseous substances which form sulphonate acids with sulphuric acid at normal room temperatures with sulphuric acid initially of 66° Bé. gravity, maintaining the temperature during said contacting at approximately and not above 5° F. whereby no substantial formation of sulphonate acids occurs, continuing said contacting for a time sufficient to cause the absorption of the major portion of the propylene and until the gravity of said sulphuric acid has been reduced below 35° Bé. by the formation of alkyl sulphates, thereafter contacting the resulting acid liquor with normally liquid cracked petroleum products containing olefins and substances which form sulphonate acids with sulphuric acid at normal room 90 temperatures, and maintaining the contacting materials during said latter contacting not above 5° F. whereby an acid liquor containing alkyl sulphates and substantially 95 free of sulphonate acids is produced.

2. In the production of alcohols from cracked petroleum materials by contacting such materials with sulphuric acid, the process which comprises contacting gaseous cracked petroleum material containing a mixture of propylene and normally gaseous substances which form sulphonate acids with sulphuric acid at normal room temperatures with sulphuric acid initially of 66° Bé. gravity, maintaining the temperature during the said contacting at approximately and not above 5° F. whereby no substantial formation of sulphonate acids occurs, and continuing said contacting for a time suf- 100 105 110 115 120 125 130

ficient to cause the absorption of the major portion of the propylene and until the gravity of the sulphuric acid has been substantially reduced by the formation of propylene sulphates.

In testimony whereof I affix my signature.

**SYLVAN R. MERLEY.**

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