

I. G. Farbenindustrie A. G.  
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~~PATENT APPLICATION FOR THE PROCESS OF MANUFACTURING MOTOR FUEL.~~

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A process has been developed which permits to use mixtures of olefins containing a large amount of paraffin for alkylation. The olefins are separated from the n-paraffin by contacting the mixture with sulphuric acid of a concentration of 80-90%, preferably acid containing 86 - 88%  $H_2SO_4$ . The olefins form with the sulphuric acid mainly diesters with a small amount of monoesters. The n-paraffin hydrocarbons extract the diesters from the acid layer and the diesters are recovered by distillation of the hydrocarbon layer after separation from the acid. It is best to contact a liquid mixture of paraffins and olefins with sulphuric acid. For purposes of alkylation the diester is then reacted with isoparaffin.

The mixture of olefins and n-paraffin hydrocarbons to be treated can also contain isoparaffins. In this case the mixture of vapors obtained by distillation of the hydrocarbon mixture after acid treatment contains n-paraffin hydrocarbons as well as isoparaffins and the distillation can be conducted in such a way that the n-paraffins are condensed as liquid, whereas the isoparaffins leave the column in the form of vapors; the isoparaffins can then be subsequently reacted with the sulphuric acid diesters.

In order to obtain diesters the gases containing the olefins are contacted with sulphuric acid at low temperatures, preferably not exceeding  $41^\circ F$ . The formation of diesters is, furthermore, favored by the use of an excess of olefins as compared to sulphuric acid. The molar ratio of olefins to  $H_2SO_4$  should be at least 2:1 and it is advantageous to increase this molar ratio to as high as 5:1.

In the process described above the liquefied n-paraffin hydrocarbons extract the diesters from the sulphuric acid, the paraffins having a sufficiently high solvency for the diesters. In this way it is possible to separate the diesters by continuously adding liquefied feed gases and contacting them counter-currently with sulphuric acid; the diesters can subsequently be reacted with isoparaffin.

The process can also be practiced in that way that the feed stock is treated with an insufficient amount of acid which results in forming a solution of the diesters in a mixture of liquefied n-paraffin hydrocarbons and non-reacted olefins. This method of operation will be useful when a feed stock is used which is very rich in olefins. In this case a sufficient amount of acid may also be used and additional quantities of paraffins may be added in case that the amount of paraffins present in the original mixture should not be sufficient to extract the amount of diesters formed.

The liquefied feed gases are advantageously contacted in several reactors with recycled acid of increasing concentration. The acid leaving the first extraction vessel which has the lowest concentration can be regenerated by mixing it with spent alkylation acid or with an acid which has been obtained by regeneration of part of the spent acid. It is advantageous to recover the olefins which are present as sulphuric acid monoester, e.g. by polymerization at elevated temperature or by hydrolysis to the corresponding alcohol.

### Example

The butane fraction obtained from the tail gases from a high-pressure hydrogenation plant is distilled in column 1 and n-butane and isobutane are obtained. The n-butane is passed through line 2 into the dehydrogenation unit 3 in which it is dehydrogenated to n-butylene. In this way a dehydrogenation gas is obtained which contains 53.9% n-butane, 17.6% n-butylene, 20.8% hydrogen, 4.3% C<sub>1</sub> - C<sub>3</sub> hydrocarbons and 3.4% residual gas (O<sub>2</sub>, CO, N<sub>2</sub>). This gas is passed through line 4 into unit 5 for the preparation of a pure C<sub>4</sub> fraction.

The pure liquefied C<sub>4</sub> fraction is passed through line 6 into a distributing apparatus, e.g. a nozzle, which is arranged in the lower part of the main extraction unit 7; in this unit the bulk of the n-butylene is converted into dibutylsulphate by means of sulphuric acid. The unit consists mainly of a pressure- and acid-resistant packed tower into which sulphuric acid containing 80 - 90% H<sub>2</sub>SO<sub>4</sub>, preferably 86 - 88% H<sub>2</sub>SO<sub>4</sub>, is pumped by means of pump 8 and line 9; the acid used contains still a certain amount of butylester. Pressure and temperature are regulated in such a way that the hydrocarbons are contacted in liquid phase counter-currently with the sulphuric acid. In the absorption tower very good mixing and fine dispersion of the reactants is obtained due to high surface activity. The mixture of sulphuric acid, liquid hydrocarbons and butylesters then enters through line 10 into the pressure- and acid-resistant separator 11. The reaction mixture separates here into a lower layer consisting of sulphuric acid and monobutylester and an upper layer consisting of a solution of dibutylesters in C<sub>4</sub> hydrocarbons, mainly n-butane. The upper layer is kept in the liquid phase by suitable control of temperature and pressure. The extraction of the dibutylester from the mixture of liquids by means of liquid butane which had started in the absorber 7 is brought to completion in the separator. The upper layer is drawn off through line 12 and introduced into the evaporator 13 in which the n-butane which contains residual butylene is separated from the neutral ester. The gas enters at elevated or atmospheric pressure through the line 14 into an after-extraction unit for the removal of residual n-butylene; this extraction unit consists preferably of two absorbers in series. The gas enters first the absorber 16 into which 86 - 88% sulphuric acid is introduced by pump 16 at line 17. This acid also contains a certain amount of butylester but less than the acid drawn off from absorption tower 15. N-butane is now passed through line 18 into the absorber 19 where it is freed from the last traces of n-butylene, and is then returned through line 20 into the dehydrogenation unit 3.

The neutral butylsulphate which has been freed from n-butane and traces of n-butylene in the evaporator 13 is introduced into the pressure- and acid-resistant mixing vessel 22 through line 21. In this mixing vessel gaseous isobutane is introduced from the distillation column 1 through line 23. Alkylation is now carried out in the usual way. The alkylation product contains about 75 - 85% of hydrocarbons boiling in the octane boiling range dependent upon the velocity of feed of the neutral ester. The non-reacted isobutane is recycled by means of the blower 24 and line 25, whereas the alkylation product is drawn off by line 26.

Clean alkylation acid in the form of the neutral ester is continuously introduced into the alkylation stage because the formation of the ester can be considered as purification of the acid which forms the lower layer in separator 11 and from which the n-butane extracts continuously 100% sulphuric acid in the form of the neutral butyl sulphuric acid ester. The asphalt-like sludge concentrates in the lower layer of separator 11 and the lower layer consists, besides sludge, mainly of dilute butyl esters which are monoesters and thereby correspond to 86 - 88% sulphuric acid.

Part of this comparatively weak acid which contains butylene in the form of acidic sulphuric acid esters is introduced in the absorber 19 through pump 30, line 31, and mixer 35. Since the sulphuric acid moves counter-currently to the n-butane containing n-butylene, the acid strength must decrease in the same order so that in absorber 19 the last traces of n-butylene can be removed. The acid strength at this point is about 95%. In order to maintain the strength of the acid, the 98% acid which settles in the mixing vessel 22 is mixed with the 50 - 80% acid from the separator 11 in the mixer 35 into which it is pumped by means of pump 32 and line 33.

Another part of the relatively dilute acid obtained in separator 11 is drawn off continuously from the separator 11 by means of pump 27 and line 28. In this way the concentration of undesirable asphaltic decomposition products in the acid can be maintained at any desired level. In order to utilize the butylene in the acid drawn off, it can be polymerized by heating the acid; the polymer can be hydrogenated by means of the hydrogen made during dehydrogenation. The butylene can also be hydrolyzed to butyl alcohol. The impure acid obtained in this way can be regenerated by heating, provided its carbon content does not exceed 6% by weight. In this way 80 - 95% sulphuric acid is obtained besides carbon monoxide, sulphur dioxide, coke, water and carbon dioxide. The regenerated acid is passed into the mixer 35 by means of line 34 and from the mixer it is introduced into wash tower 19, together with the acid coming from lines 31 and 33. When the carbon content of the acid exceeds about 6% by weight, the acid is completely used for the oxidation of the carbonaceous matter when the acid is heated. (In this case only waste gas is obtained besides acid coke and the other gaseous components mentioned above; no purified acid can be made.)

The process is advantageous insofar that side reactions, especially polymerization, are avoided to a large extent and a complete sulphuric acid cycle is obtained. In this way it is possible to minimize acid losses so that only a small amount of fresh acid has to be introduced into the process.

### Claims

1. Process for the manufacture of valuable motor fuel by reaction of low-molecular weight olefins with low-molecular weight isoparaffin, characterized by extracting the low-molecular weight olefins from the mixture by means of sulphuric acid of 80 - 90% concentration, preferably 86 - 88% concentration. Extraction is controlled in such a way that, besides monesters, mainly diesters of the sulphuric acid are formed and the n-paraffin hydrocarbons in liquid phase extract the diesters from the acid. The diesters are separated from the hydrocarbons by distillation. The diesters are subsequently reacted with isoparaffins.
2. Process according to Claim 1 characterized by the extraction of the olefins in several reactors in series which are filled with acid of increasing concentration.
3. Process according to Claims 1 and 2 characterized by mixing the spent extraction acid with highly concentrated alkylation acid and/or with acid regenerated by heating. The mixture obtained in this way is used again for extraction.

4. Process according to Claims 1 - 3 characterized by converting the olefins contained in the spent acid in the form of monoesters into a polymer by heating or into alcohol by hydrolysis.
5. Process according to Claims 1 - 4 characterized by isomerizing the n-paraffin separated from the olefins and isoparaffin and reacting the isomerized n-paraffin with the diesters obtained by extraction.

