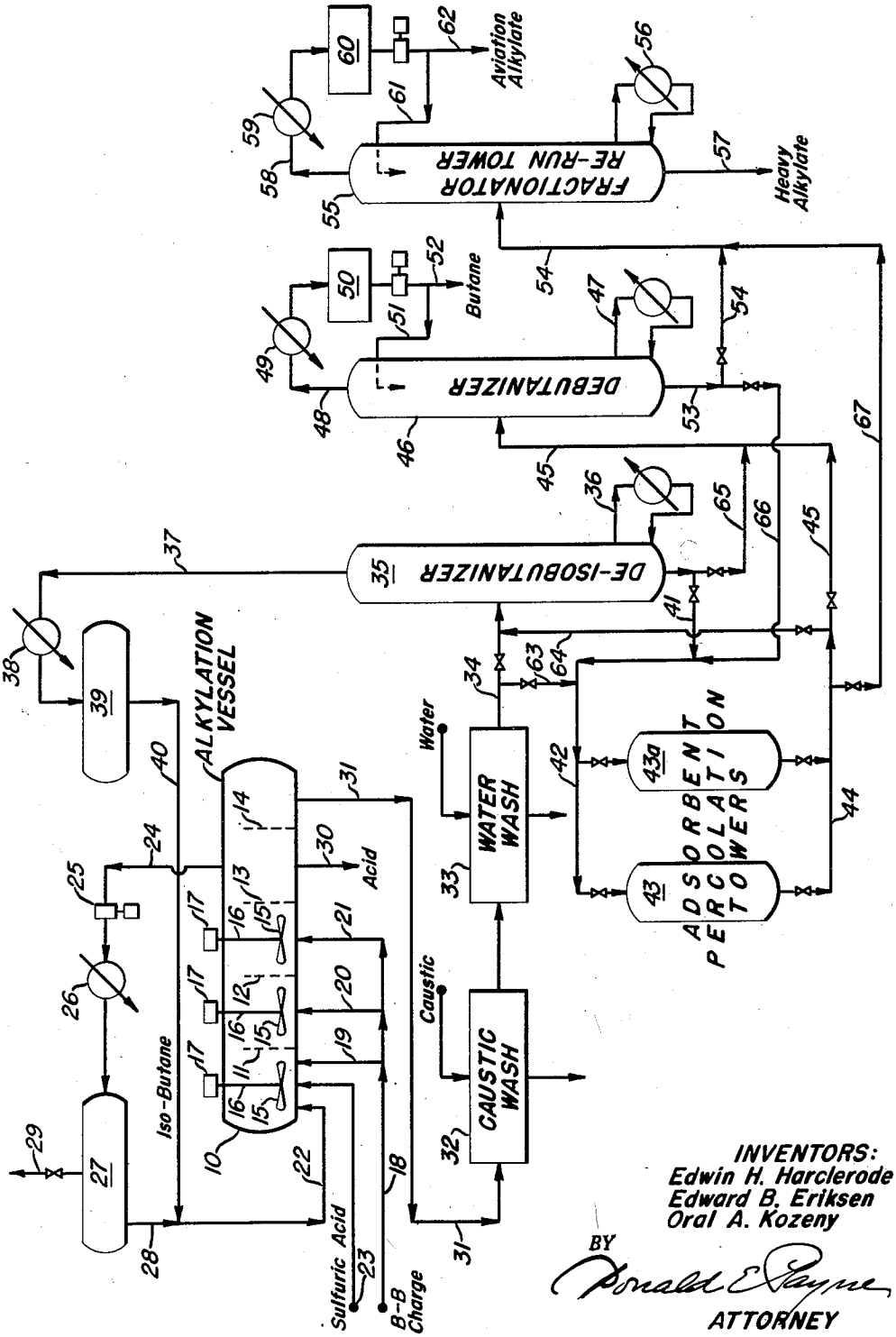
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PREVENTION OF REBOILER FOULING IN SULFURIC ACID PROCESS FOR ALKYLATING ISOBUTANE WITH OLEFINS

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PREVENTION OF REBOILER FOULING IN SULFURIC ACID PROCESS FOR ALKYLATING ISOBUTANE WITH OLEFINS

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7 Claims. (Cl. 260—683.4)

This invention relates to a sulfuric acid process for alkylating isobutane with olefins having 3 to 5 carbon atoms per molecule wherein the formation of heavy alkylate requires fractionation of the alkylate product and it pertains more particularly to inhibiting deposit formation on the reboiler heating surfaces employed in the fractionation step.

When isobutane is alkylated with C_3—C_5 olefins such as a butylene mixture in a so-called "cascade" type of alkylation unit (note U. S. 2,429,205), a considerable amount of the alkylate is higher boiling than gasoline so that a rerunning or fractionation step is required. In such operations the reboiler tubes in the rerun or fractionator tower became so heavily coated with deposits that after an operation of about two weeks it was necessary to shut down the unit and clean said reboiler tubes. This difficulty was not encountered in other types of alkylation units and the addition of corrosion inhibitors to the crude alkylate stream (which was all that was required for successful operation of other types of alkylation units) was ineffective in preventing the fouling of the fractionator reboiler tubes. The object of this invention is to provide a method and means for inhibiting deposit formation in such reboiler tubes.

We have discovered that the deposits on the fractionator reboiler tubes consist essentially of a mixture of coke and scale held together by an asphalt-like binder and that it is different in kind from the scale on deisobutanizer and debutanizer reboilers which contain water-soluble salts and which can largely be removed by water-washing. We have found that the fouling of the fractionator reboiler tubes may be prevented by percolating the alkylate product through an adsorbent material, such as silica gel, before said product is heated to a temperature higher than 300° F. in the fractionator reboiler. While all adsorbent materials are not equivalent and best results are obtained by percolation through a bed of silica gel, other known adsorbents such as adsorbent clays (fuller's earth, montmorillonite clay, adsorptive alumina and the like) may be employed. The contacting may be effected immediately after the conventional caustic and water-wash steps or after the deisobutanizing step or after the debutanizing step and may be effected at ambient temperature to at any temperature between about 50 to 250° F. employing a percolation rate in the range of about 1 to 30 barrels per hour per ton of adsorbent material. Two percolation vessels are preferably employed so that the contact material in one may be replaced and/or regenerated while the contact material in the other is on-stream, each on-stream run being in the range of about 10 to 400 or usually in the range of about 15 to 50 barrels per ton.

In attacking the problem of the fouling of fractionator reboiler tubes, a sample of crude alkylate obtained in a cascade unit was distilled in an Oldershaw column and some cuts taken during the course of the distillation were carefully examined. It was found that at temperatures above 300° F. there was an evolution of sulfur dioxide. At this point approximately 65 percent of the total alkylate had been distilled. The residue from this distillation was a black carbonaceous material resembling that found in the fractionator reboiler. When another sample of crude alkylate from the cascade unit was percolated through a bed of silica gel prior to distillation in the Oldershaw column, no SO_2 or residue was obtained. It is interesting to note that samples of crude alkylate from another type of alkylation unit did not evolve SO_2 or deposit the black carbonaceous residue when distilled in the Oldershaw column so that the problem appears to be associated with the cascade-type alkylation unit.

The charge to the cascade alkylation unit was substantially free from sulfur compounds and diolefins so that the problem is apparently not one of ordinary gum formation. It has heretofore been proposed to clay an alkylate after distillation to remove odor (U. S. 2,626,976) but for such operation alumina and silica gel are not operative. It has also been proposed to remove sulfur from a residual butane-butylene stream (separated from sulfuric acid in a polymerization unit) by contact with adsorptive materials but such a percolation was on a different type of material and was not prior to a distillation step or for the purpose of avoiding the fouling of fractionator reboilers.

The invention will be more clearly understood from the following description of a specific example thereof read in conjunction with the accompanying drawing which is a schematic flow diagram of our improved cascade-type alkylation unit.

Alkylation vessel **10** is divided by baffles **11**, **12** and **13** into three successive mixing chambers and a settling chamber. Baffle **14** in the settling chamber facilitates separation of spent acid from alkylate. In each of the mixing chambers there is a stirrer or mixing pump diagrammatically represented by mixing blades **15**, rotated by shaft **16** which in turn is driven by motor **17**. The charging stock which is introduced by line **18** is preferably a so-called BB stream which may contain about 45 percent isobutane, 15 percent isobutylene, 15 to 23 percent of normal butane, 23 to 15 percent of normal butenes and about 2 percent of lighter and heavier hydrocarbons. In this example where reactor **10** is a vessel about 10 feet in diameter and 30 feet long and the charge rate is 1500 barrels per day, about 500 barrels per day is introduced through line **19** at the base of the first mixing zone, 500 barrels per day is introduced through line **20** and 500 barrels per day through line **21**. Isobutane is introduced into the first mixer through line **22** at the rate of about 5,000 to 7,000 barrels per day. Sulfuric acid of 98 percent concentration is introduced through line **23** at the rate of about .5 to 1 pound per gallon of charge. The introduced streams are intimately admixed in the first reaction zone at a temperature of about 35° F. and a pressure of about 2 to 15 p. s. i. g., the external isobutane to olefin ratio being in the range of about 5:1 to 9:1 and the internal isobutane to olefin ratio being in the range of about 200:1 to 600:1. The olefin space velocity is in the range of about .15 to .4 or about .25 volume of introduced olefin per hour per volume of acid.

Part of the emulsion formed in the first reaction zone flows over baffle **11** into the second reaction zone into which about one-third of the total olefin charge is introduced. Likewise, emulsion from the second reaction zone flows over baffle **12** to the third reaction zone wherein the remainder of the olefin charge is introduced. A part of the isobutene vaporizes to control the reaction temperature; the butane vapors are removed by line **24**, compressed by compressor **25** and passed through condenser

26 to receiver 27 from which the refrigerant isobutane is recycled by line 28 to line 22, any accumulated propane being vented from the system through line 29. Spent acid is withdrawn from the system through line 30.

The alkylate is withdrawn from reactor 10 through line 31 and is first washed with aqueous caustic in wash system 32 and then washed with water in wash system 33. The caustic wash removes any entrained acid or acidic materials and the water wash insures removal of caustic and water-soluble solids. The water washed alkylate may then be passed through line 34 to deisobutanizer tower 35 which is provided with a reboiler 36 at its base. The isobutene is withdrawn through line 37 and condenser 38 to receiver 39 from which a part of the isobutane may be returned to the top of tower 35 to supply reflux and from which the net recovered isobutane is returned through line 40 to line 22.

The deisobutanized alkylate is preferably introduced by line 41 and header 42 to percolation tower 43 or 43*a* wherein it is percolated through a bed of silica gel at the rate of about 5 barrels per hour per ton of silica gel. The percolated alkylate is introduced from outlet manifold 44 through line 45 to debutanizer 46 which is provided with reboiler 47. Debutanizer overhead is withdrawn through line 48 and condenser 49 to receiver 50 from which a part of the condensate may be returned through line 51 to serve as reflux in tower 46, the net amount of normal butane being withdrawn through line 52.

The debutanized alkylate passes by lines 53 and 54 to the fractionator or rerun tower 55 which is provided at its base with reboiler 56. It is the tubes of this reboiler 56 which normally tend to become fouled because of the formation of deposits at the rate of about 20 pounds per day. However, the percolation through silicon gel avoids the formation of such deposits and thus eliminates the frequent shutdowns which would otherwise be necessary. Heavy alkylate is withdrawn from the base of tower 55 through line 57 and may amount to as much as 10 to 15 percent of the total alkylate. Aviation grade alkylate is taken overhead through line 58 and condenser 59 to receiver 60, a part of the condensate being returned to line 61 to supply reflux at the top of the fractionator, and the net aviation grade alkylate is withdrawn from the system through line 62.

In the foregoing example the percolation of the alkylate was effected after the removal of isobutane therefrom and this is the preferred operation because it avoids the necessity of passing enormous amounts of isobutane through the percolation towers. However, the water-washed alkylate may be passed to header 42 by line 63

(the valve in line 34 being closed) and the percolated alkylate may be introduced from header 44 by line 64 to the deisobutanizer tower 46 in which case the valve in line 41 will be closed and the bottoms from tower 35 will be introduced through line 65 to line 45 and thence to the debutanizer.

As another alternative, the valves in lines 63 and 41 may be closed and the bottoms from the debutanizer may be passed by line 66 to header 42, in which case the percolated alkylate will be returned through line 67 to line 54 and fractionator 55. The important consideration is to effect percolation of the alkylate before it is subjected to a temperature higher than about 300° F. and prior to its introduction into the tubes of fractionator reboiler 56.

While the invention has been described in considerable detail with respect to a specific example thereof, it should be understood that alternative arrangements and operating conditions will be apparent from the above description to those skilled in the art.

We claim:

1. In a cascade sulfuric acid system for alkylating isobutane with a C_3 to C_5 olefin wherein the formation of heavy alkylate requires fractionation of the alkylate product and deposits tend to be formed on the heating surfaces employed for supplying heat at the base of the fractionation zone, the method of inhibiting said deposit formation which comprises percolating said alkylate product through a mass of solid adsorbent material before the temperature of said alkylate exceeds 300° F. and prior to its contact with said heating surfaces.

2. The method of claim 1 wherein the olefin is a mixture of butenes.

3. The method of claim 1 wherein the adsorbent material is silica gel.

4. The method of claim 1 wherein the adsorbent material is adsorbent clay.

5. The method of claim 1 wherein the adsorbent material is fuller's earth.

6. The method of claim 1 wherein the percolation is after caustic and water washing and prior to deisobutanizing.

7. The method of claim 1 wherein the percolation is after deisobutanizing and prior to final fractionation.

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U. S. DEPARTMENT OF COMMERCE

PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,818,458 December 31, 1957

Edwin H. Harclerode et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 70, and column 3, line 13, for "isobutene", each occurrence, read -- isobutane --; same column 3, line 35, for "silicon" read -- silica --.

Signed and sealed this 20th day of May 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

Disclaimer

2,818,458.—*Edwin H. Harclerode*, *Edward B. Eriksen*, and *Oral A. Kozeny*, Neodesha, Kans. PREVENTION OF REBOILER FOULING IN SULFURIC ACID PROCESS FOR ALKYLATING ISOBUTANE WITH OLEFINS. Patent dated Dec. 31, 1957. Disclaimer filed May 7, 1962, by the assignee, *Standard Oil Company*.

Hereby enters this disclaimer to claims 1 and 2 of said patent.

[*Official Gazette June 12, 1962.*]