

DEPARTMENTAL CORRESPONDENCE

DATE August 29, 1968SUBJECT ISOBUTYLENE CRACKING PROCESS PATENT SEARCH, AUGUST 28, 1968To Harry A. Brown DEPT President - PetrochemicalFROM Lange Hoffman DEPT Legal - Houston

I am forwarding herewith a copy of Jeff Giller's letter concerning the subject patent search, along with a copy of his letter to Messrs. Cushman, Darby & Cushman.

Jeff Giller states that in his opinion there will be no infringement of any United States Patent issued prior to August 15, 1968 in the operation of the plant described in his letter of July 26, 1968 to Cushman, et al.

Giller does not, however, render any opinion with respect to the use of the molecular sieve since as of this date he has not received the requisite report from his searchers.

LH:ph
Attachment

FULBRIGHT, CROOKER, FREEMAN, BATES & JAWORSKI
ATTORNEYS AT LAW
BANK OF THE SOUTHWEST BUILDING
HOUSTON, TEXAS 77002

JEFFERSON D. GILLER
PARTNER

August 28, 1968

Re: D-3088 - Production of Isobutylene

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Coastal States Petrochemical Company
6th Floor, Lincoln Liberty Life Building
777 Polk Avenue
Houston, Texas 77002

Attention: Mr. Lange Hoffman

Gentlemen:

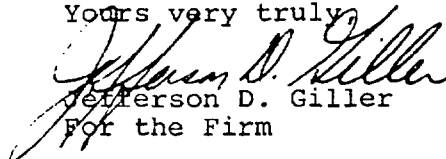
You have asked for our opinion as to whether the operation of the isobutylene plant which you propose to build will infringe any United States patents. In order to render our opinion, we have had a collection search made of United States patents by Messrs. Cushman, Darby & Cushman, Washington, D. C. who are our regular searchers and upon whom we believe we can rely. Their search and our opinion is upon the plant described in our letter of July 26, 1968 to Cushman, Darby & Cushman, a copy of which letter is attached.

Based upon an examination of the patents collected in that search and a conference held with Mr. George Adams and your Mr. John Brown, we are of the opinion there will be no infringement of any United States Patent issued prior to August 15, 1968 in the operation of the plant described in the attached letter of July 26, 1968 down to the processing of material through the molecular sieve unit. We have not yet received a report from our searchers with respect to the use of a molecular sieve in this process and so are not presently in position to render an opinion with respect to its use.

No search was made nor is any opinion here given with respect to the individual pieces of equipment themselves as we understand they, with the possible exception of the molecular sieve unit, are all conventional.

If you care to have the patents developed on this search, we will be happy to forward them to you.

Yours very truly,


Jefferson D. Giller
For the Firm

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HOUSTON
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JDG:eg
Encl.

CED0006963

July 26, 1968

Re: D-3088 - Method of Producing Isobutylene -
Infringement Search

Messrs. Cushman, Darby & Cushman
American Security Building
730 Fifteenth Street, N.W.
Washington, D. C. 20005

Gentlemen:

A client of ours is proposing to build a plant for the production of isobutylene from a stream of liquid butane containing at least 85% isobutane. Would you please make a collection search of United States patents in order that we may examine them and determine the probabilities of patent infringement by the process described below. No search need be made with respect to the equipment itself -- only with respect to the process.

We believe that if there are infringement problems, they will be with the cracking process that takes place in the pyrolysis furnace 6, later described, or with respect to the purification of the C₄ hydrocarbons after the C₄ hydrocarbons have been separated from the other hydrocarbons.

Referring now to the attached drawing, a stream of liquid butane containing at least 85% isobutane is fed to the pump 3 which pressurizes this stream to 250-400 psig and forces it through a pyrolysis furnace 6. This is a conventional hydrocarbon pyrolysis furnace having a convection section 4 and a cracking zone 7. In the convection section 4, the liquid butane is vaporized and combined with diluent steam added at a pressure of 250-400 psig from the line 5 in a ratio of between one-fourth to one pound of steam per pound of butane. The combined steam and butane stream passes through the cracking zone in approximately 0.1 to 10.0 seconds and has an outlet pressure from the pyrolysis furnace of 150-350 psig and an outlet temperature of 1200-1400° F. The products of the reaction in the cracking zone include C₃ and heavier hydrocarbons, isobutylene,

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unreacted isobutane, C_3 hydrocarbons, and C_2 and lighter hydrocarbons.

These reaction products leave the pyrolysis furnace 6 by a line 8 and are immediately cooled to stop the cracking reaction. This cooling may be done by any of several ways such as by quenching with a water spray at 10 to approximately 1000° F. After this cooling, the reaction products are further cooled in a heat exchanger 12 by indirect heat exchange with water to produce some of the diluent steam and then further cooled in a water-cooled heat exchanger 14 to the proper temperature to reduce the amount of products in the vapor state and improve recovery of liquids in a gravity-type separator 16. Of course, if desired, all this cooling can be done in less or more than three steps.

Water is withdrawn from the bottom of the gravity separator 16 through the line 18 and the liquid hydrocarbons passed through the line 20 and the gaseous hydrocarbons through the line 21 to the absorber-stripper 22. The absorber-stripper 22 is of the tray type and receives the gaseous effluent from the line 21 in its absorber section and the liquid reaction products from the line 20 in its stripper section. It is operated at 150-300 psig and a bottom temperature of 200-300° F. Under these conditions, the overhead gas leaving the absorber-stripper 22 from the line 24 is principally C_2 and lighter hydrocarbons.

Some liquid from the absorber section is recirculated through the line 20a back to the line 8 immediately upstream of the gravity separator 16 and some gas from the stripper section is recirculated through the line 20b also to the line 8 immediately upstream of the gravity separator 16.

The bottoms from the absorber-stripper 22 pass through the line 26 to a tray-type fractionating tower 28. The tower 28 is operated at 100-200 psig and a bottom temperature of 400-550° F. Under these conditions, the bulk of the C_3 and C_4 reaction products are separated from the C_5 and heavier material with the C_3 and C_4 leaving the tower 28 as overhead through the line 30. The C_5 and heavier hydrocarbons are removed as bottoms through the line 31. A portion of these bottoms are returned to the

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absorber-stripper 22 as lean oil through the line 32 and cooler 32a with makeup lean oil added at 34a, which makeup lean oil is C₅ and heavier such as gasoline, naptha, or kerosene.

The overhead from the fractionating tower 28 passes to the tray-type fractionating tower 36, which tower 36 is operated at 250-350 psig and a bottom temperature of 170-275° F. Under these conditions, there is a separation of the C₃ from the C₄ hydrocarbons. The C₃ hydrocarbons leave as overhead through line 38 and the C₄ hydrocarbons leave as bottoms through the line 40.

The C₃ hydrocarbons in line 38 are treated to separate the propylene from other C₃ hydrocarbons by a tray-type fractionating tower 42 with propylene leaving the upper section of the fractionating tower 42 by the line 46 and the remaining C₃ hydrocarbons leaving from the lower portion by the line 44.

The bottoms in the line 40 from the fractionating tower 36 are principally isobutylene and unreacted isobutane. This material is fed into the tray-type fractionating tower 48 operating at 100-200 psig and a bottom temperature of 200-300° F. At a point approximately midway between the center and the top outlet of the tower 48, a stream of furfural (a solvent) is introduced by the line 49 in a ratio of approximately 10 mols of furfural per mol of hydrocarbon feed to the tower. The original supply and the makeup furfural are placed in the line 49 by the line 51. Under these conditions, most of the unreacted isobutane is separated and passed as a liquid overhead through the line 50 to the feed line 2 at a point immediately upstream of the pump 3 for recycle.

The bottoms from the fractionation column 48 are withdrawn by the line 52 and pass to the tray-type fractionating tower 54 which is operated at 100-200 psig with a bottom temperature of 400-500° F. Under these conditions, the hydrocarbons contained in the bottoms from the tower 48 are stripped from the furfural and withdrawn from the top of the tower 54 by the line 58. The furfural is withdrawn from tower 54 by the line 49 and recycled to tower 48. The material leaving tower 54 as overhead by line 58 is principally isobutylene.

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The furfural which is introduced into the fractionation tower 48 is a selective solvent and is chosen because it has the property of increasing the difference in volatility between isobutane and isobutylene and the property of a lower volatility than either isobutane or isobutylene.

The material in line 58 passes through the molecular sieve unit 60 which is a type manufactured for the absorption of straight chain hydrocarbon molecules and passage of branch chain hydrocarbon molecules. Some butene-1, butene-2 and normal butane will probably be included in the reaction products and be in the line 58 leading to the molecular sieve 60 together with the isobutylene. The molecular sieve 60 will remove this butene-1, butene-2 and normal butane by absorption.

Yours very truly,

Jefferson D. Giller
For the Firm

JDG:eg
Attachment

cc: Mr. George F. Adams
Mr. John Brown
Mr. Lange Hoffman

