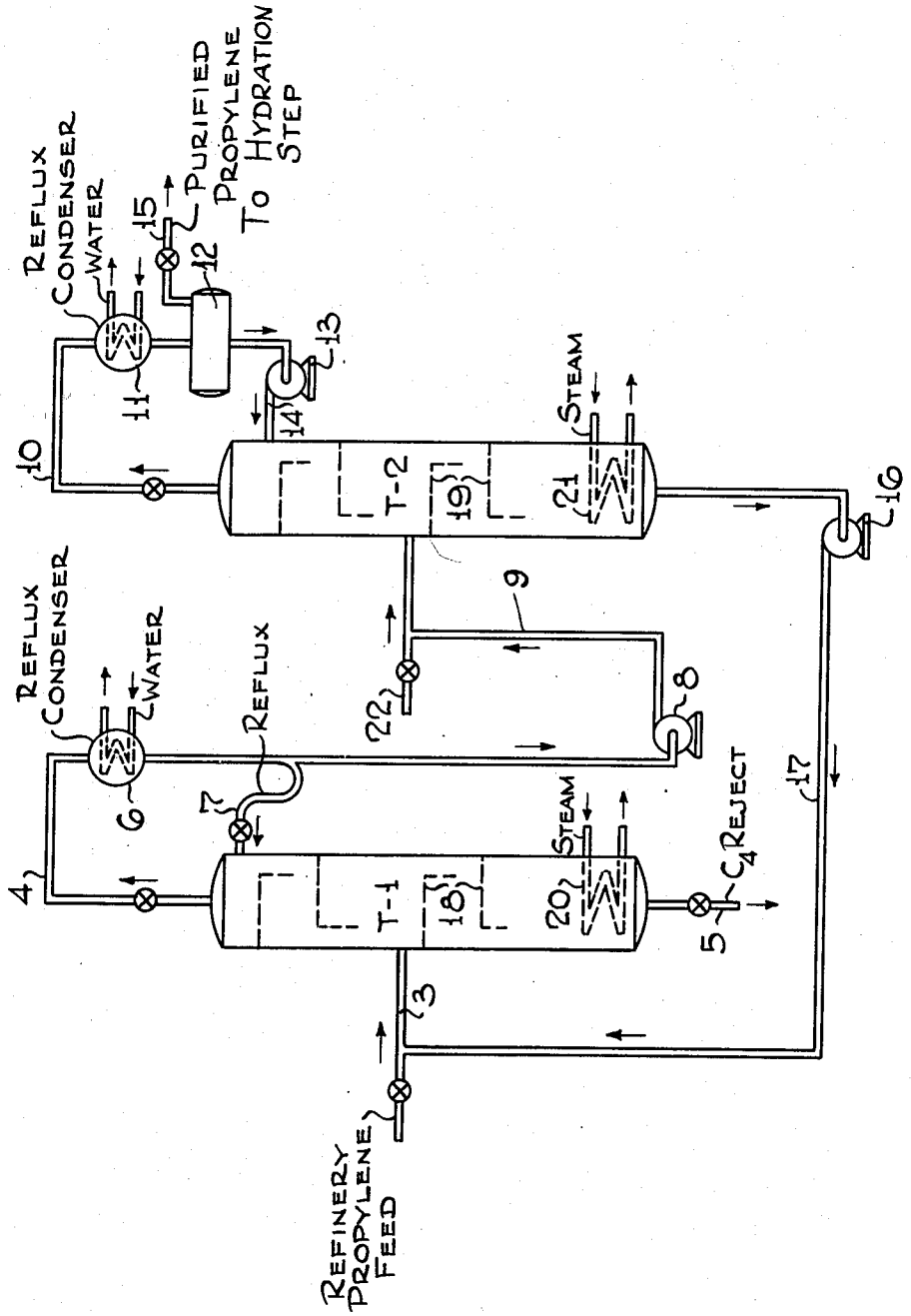
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ISOPROPYL ALCOHOL PROCESS

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Albert P. Giraitis
Mack C. Fuqua Inventors

By Henry Berk Attorney

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ISOPROPYL ALCOHOL PROCESS

Albert P. Giraitis and Mack C. Fuqua, Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

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The quality of isopropyl alcohol is improved economically by this invention through an industrially feasible method of purifying refinery propylene fractions.

The production of a high quality isopropyl alcohol product, from the standpoint of purity and odor, made by the hydration of propylene with sulfuric acid as catalyst, is achieved by removing C_4 hydrocarbons from a propylene fraction prior to absorption in the acid; also, by removing simultaneously the highly unsaturated C_3 hydrocarbons, methylacetylene and propadiene from the fraction.

The production of a chemically pure isopropanol is desirable when the alcohol is to be used for preparing other chemicals, for use in cosmetics and toilet goods, for rubbing alcohol, or for use as a sterilizing agent.

The commercial propylene fraction is generally a cracked hydrocarbon product obtained by close fractionation which leaves the propylene contaminated by other C_3 hydrocarbons and small amounts of C_4 hydrocarbons.

The removal of the contaminants that cause degrading of the isopropyl alcohol product is efficiently accomplished by a method which will be further described in detail.

Earlier studies did not show any certain correlation between C_4 components in the propylene feed stream to the acid absorber and the finished alcohol product. Now the failure to learn about this correlation can be ascribed to the rather long hold-up of impurities in the conventional alcohol plant operations.

Work has now been carried out to determine which, if any, of the C_4 and C_3 hydrocarbons, difficult to remove, produce the undesirable odor that often degraded the ispropyl alcohol product requiring an expensive washing and finishing treatment for removal.

In order to make the terms used understandable, a brief description of the process for isopropanol manufacture is given herewith. The propylene feed stock is fed at a suitable pressure to an absorber containing sulfuric acid of suitable strength and temperature and the sulfuric acid reacts with the propylene to form an isopropyl sulfate-sulfuric acid mixture also containing some free alcohol and isopropyl ether. This mixture is fed to a stripper where dilution water is added and steam introduced to remove all alcohol and other volatile components from the diluted acid. After caustic scrubbing for removal of acidic components from the crude alcohol, the alcohol is sent to storage from which it is fed to the finishing section. The isopropanol finishing section consists of a column for removing low

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boiling impurities and some alcohol overhead and and alcohol-water mixture with some impurities boiling higher than the alcohol as bottoms. The overhead stream is washed with water and the insoluble portion consisting primarily of isopropyl ether and high boiling impurities soluble in the ether is sent to storage. The water alcohol layer from this ether washer is returned to the above mentioned column for recovery of the alcohol. The bottoms from the above mentioned tower are fed to a second distillation tower for concentration and purification of the alcohol. A portion of the lower boiling constituents from the column are recycled to the first column. This stream is referred to as recycle stock.

An isopropyl sulfate, sulfuric acid mixture of the usual strength made in the alcohol plants was prepared by adding sulfuric acid and water to isopropyl alcohol of high grade with no odor. C_4 hydrocarbons of different types were then absorbed in separate portions of the isopropyl sulfate-sulfuric acid mixtures to the extent of approximately 1 mole percent of propylene (or isopropyl alcohol) in the extract. The absorption was carried out by passing each of the gaseous C_4 hydrocarbons through a separate sample of the extract at 80° C. and atmospheric pressure until a predetermined amount was absorbed. One sample was allowed to absorb a large amount of one of the C_4 hydrocarbons. Two control samples containing no C_4 were prepared, one heated at 80° C. and the other at 100° C. for the same length of time and finished in the same way as the other samples. The finished alcohol product was prepared from this steam distillate by distillation in the usual manner. The products of the samples were classified according to odor as follows:

TABLE I

Hydrocarbon Added	Alcohol Product Odor
Butadiene	Heavy.
Isobutylene	Moderately heavy.
Butylene 1	Do.
Butylene 2	Do.
Isobutane	Slight.
N-Butane	Good.
Butadiene (large amount)	Very heavy.
Control (80° C.)	Good.
Control (100° C.)	Do.

Each of the samples, including even the control, produced a recycle stock that had odor, the recycle stock being the usual fractional condensate that is condensed from the overhead isopropyl alcohol vapors of the finishing still.

As shown by the foregoing experiments, the

absorption of the butylenes and of butadiene in the extract produced characteristic undesirable odor. The absorbed isobutane produced some odor. The strongest odors were approximately as strong as those obtained in plant production. It was not found how to isolate the odoriferous compound or compounds. In studies made for the purpose of concentrating and possibly isolating the odoriferous products from the isopropyl alcohol product, isopropyl alcohol having odor was carefully fractionated and separate small fractions were examined. It was found that the odor components were both somewhat higher and somewhat lower boiling than the isopropyl alcohol itself and could not be removed by fractionation.

The adverse effect of the C_4 hydrocarbons on odor is also usually accompanied by other undesired manifestations such as, acetone build up, increase of high boiling compounds that accumulate in the fractionating tower plates above the feed plate in the alcohol finishing still, and lowered finishing rates.

A plant scale study which shows the necessity for making the propylene feed free of C_3 acetylenes to produce a high quality isopropyl alcohol product is furnished by the following tabulated data of Table II:

TABLE II

Acetylenes in Feed, p.p.m.	Acetone in Alcohol heads, Wt. Percent	High Boiling Compounds in Ether Product, Wt. Percent
396	4.4	1.8
550	5.6	2.0
585	8.0	2.0
744	5.2	3.0
744	7.2	4.0
865	8.2	3.4
510	6.0	1.9

The effects of C_4 hydrocarbons in the propylene feed on product quality and formation of undesired acetone and high boiling by-products is shown by data on typical plant runs presented in Table III.

TABLE III

Effects of C_4 hydrocarbon in propylene feed

C_4 in Feed, Wt. Percent	Acetone, Wt. Percent	High boilers in Ether Product, Wt. Percent	Odor of Alcohol Product
0.0	3.2	2.0	Good
0.01	----------	----------	Good
0.04	----------	----------	Fair
0.1	----------	----------	Poor
0.34	8.0	6.0	Poor
1.0	14.0	7.0	Poor

The data in Tables II and III indicate that the tolerable limit for both the C_4 compounds and acetylenes in the C_3 feed is not more than 0.10% and 0.05%, respectively, if a high quality alcohol is to be obtained. They also show how the acetone and high boiling by-products increase as these impurities in the feed increase.

Thus it can be fully appreciated that an efficient method of reducing the C_3 acetylene content, preferably to less than 0.05%, while reducing the C_4 content of the C_3 propylene feed to less than 0.10% is a very important asset for producing high quality isopropyl alcohol economically.

A satisfactory method for removing the harmful C_3 and C_4 hydrocarbon impurities of the propylene fraction will be described with reference to the accompanying flow diagram.

In the drawing, the unit shown has two fractionating towers, low pressure tower T—1 and high pressure tower T—2. The crude propylene fraction containing excessive amounts of the harmful C_3 and C_4 hydrocarbons, such as present in a cracked hydrocarbon propane-propylene cut, is passed by line 3 into an intermediate part of the fractional distillation zone in T—1. An overhead vapor comprising the propylene and a small proportion of the C_4 impurities that enter T—1 is withdrawn by line 4. A bottoms product comprising the C_4 impurities is withdrawn from T—1 by line 5.

The overhead vapor from T—1 is cooled and condensed by indirect heat exchange with water in condenser 6. A portion of the overhead vapor condensate is returned as reflux by line 7 to the top of T—1 and the remaining portion of condensate is passed by pump 8 through line 9 into an intermediate part of the fractionating zone of T—2.

In T—2, the temperature and pressure conditions are controlled to make the liquid bottoms contain a substantial amount of C_3 hydrocarbons with the liquid C_4 impurities, so that vapors that pass overhead from T—2 through line 10 are essentially free of C_3 acetylene and C_4 hydrocarbons. The overhead vapors from T—2 are partially condensed in water cooled condenser 11. The condensate collects in receiver 12 and is returned by pump 13 and line 14 as reflux to the top of T—2. Purified propylene product is withdrawn from receiver 12 by line 15 to be passed to an alcohol producing unit, e. g., into a sulfuric acid absorption tower. The bottoms withdrawn from T—2 are recycled by pump 16 through line 17 to the low pressure tower T—1.

The towers T—1 and T—2 are equipped with vapor-liquid contacting means, e. g., plates 18 and 19, reboiling heat exchangers 20 and 21 and other usual fractionating tower equipment.

For the type of operation described, suitable conditions in the fractionating zones are:

TABLE IV

Tower	T-1	T-2
Top Temperature, ° F	130	130
Bottom Temperature, ° F	240	180
Pressure, p. s. i. g	330	350

The temperatures and pressures given are close approximations but may vary slightly with the feed composition. In general, the top temperature of both towers is held preferably at about 130° F.; the pressure for T—1 is in the range of 300 to 330 p. s. i. g. with a T—1 bottom temperature in the range of 240 to 255° F.; and the pressure for T—2 is in the range of 330 to 350 p. s. i. g. with a T—2 bottom temperature in the range of 180 to 220° F.

In operating the towers at the higher part of their pressure ranges, the bottoms liquid recycled from the pressure tower T—2 to T—1 will contain 30 to 80% by weight of liquid C_3 hydrocarbons (propylene and propane). In operating the towers in the lower part of their pressure ranges the bottoms liquid recycled from T—2 to T—1 will contain 10 to 30% by weight of these liquid C_3 hydrocarbons.

The operation in the lower part of the pres-

sure ranges is permitted when the initial feed has a low content of the C_3 acetylenes and C_4 hydrocarbons, e. g., 0.1 to 0.2 weight per cent, and such a feed may be supplied to the unit through line 22 so as to enter the high pressure tower T—2 first.

In the operations described the C_3 acetylenes are present in the C_4 bottoms withdrawn from the low pressure tower T—1, but if desired a portion of the bottoms liquid passed from T—2 to T—1 may be purged or treated to obtain a selective removal of acetylenes.

The invention claimed is:

1. The process of separating C_4 hydrocarbons and C_3 acetylene contaminants from a C_3 hydrocarbon propylene fraction to obtain purified propylene suitable for producing high quality isopropyl alcohol, which comprises distilling substantially all propylene and propane from said fraction together with a minor portion of the C_4 hydrocarbons in a fractional distillation zone, passing thus distilled hydrocarbons into a higher pressure fractional distillation zone, condensing substantially all C_4 hydrocarbons and acetylenes with a substantial portion of C_3 hydrocarbons in said higher pressure fractional distillation zone, withdrawing overhead from said higher pressure fractional distillation zone propylene vapors substantially free of acetylenes and C_4 hydrocarbon impurities, returning to the first mentioned fractional distillation zone liquid bottoms from the higher pressure fractional distillation zone, and removing separated C_4 hydrocarbons and C_3 acetylenes in liquid bottoms withdrawn from the first mentioned fractional distillation zone.

2. In the preparation of a propylene feed suitable for hydration to odorless isopropyl alcohol, the steps of separating C_4 hydrocarbon impurities from a C_3 hydrocarbon fraction of propylene and propane, which comprises distilling from said C_3 hydrocarbon fraction substantially all its propylene and propane components with a minor amount of the C_4 hydrocarbons under a pressure in the range of 300 to 330 pounds per square inch gauge, passing resulting distillate from said fractional to a higher pressure fractional distillation zone, distilling propylene and propane substantially free of C_4 hydrocarbons from the distillate in said higher pressure fractional distillation zone at a pressure in the range of 330 to 350 pounds per square inch gauge, passing bottoms liquid containing a substantial amount of C_3 hydrocarbons from said higher pressure fractional distillation zone to the first mentioned fractional distillation zone, and withdrawing bottoms liquid containing separated C_4 hydrocarbons from said first mentioned fractional distillation zone.

3. The process of separating C_3 acetylenes and C_4 hydrocarbon impurities from a C_3 hydrocarbon fraction of propylene and propane, which comprises fractionally distilling propylene and propane with a minor portion of said impurities under a pressure in the range of about 300 to 330 pounds per square inch gauge in a fractional distillation zone having a top temperature of 130° F. and a bottoms temperature in the range of 240° to 255° F., refluxing a portion of the resulting distillate in the upper part of said fractional distillation zone, passing a remaining portion of the resulting distillate into an intermediate part of a higher pressure fractional distillation zone in which a pressure of 330 to 350 pounds per square inch gauge is maintained with top temperature of 130° F. and a bottom temperature in the range of 180° to 220° F., removing propylene and propane vapors from said higher pressure fractional distillation zone, partially condensing overhead vapors from said higher pressure fractional distillation zone into condensate, separating uncondensed propylene and propane vapors from said condensate, refluxing said condensate to an upper part of said higher pressure fractional distillation zone, passing bottoms liquid from the higher pressure fractional distillation zone into said first mentioned fractional distillation zone and withdrawing liquid bottoms containing separated C_4 hydrocarbons and C_3 acetylenes therefrom.

4. In a production of high quality isopropyl alcohol from propylene in the presence of sulfuric acid, the steps of pretreating a propylene fraction that contains small amounts of C_4 hydrocarbons and C_3 acetylenes as impurities which comprises distilling the propylene from said fraction with a minor portion of said impurities in a relatively lower pressure fractional distillation zone under a pressure which maintains the major portion of the C_4 hydrocarbons and the C_3 acetylenes in liquid phase, passing the distilled propylene with said distilled impurities into a higher pressure fractional distillation zone, maintaining a substantial portion of the propylene in liquid phase with said impurities in said higher pressure fractional distillation zone, withdrawing overhead from said higher pressure fractional distillation zone a propylene-rich fraction substantially free of said impurities for hydration to the alcohol, withdrawing from said higher pressure fractional distillation zone a liquid residue containing liquid propylene with said impurities, passing said liquid residue from said higher pressure to said relatively lower pressure fractional distillation zone, and withdrawing said impurities in liquid phase from said relatively lower pressure fractional distillation zone.

5. In the production of high quality isopropyl alcohol by hydration of propylene in the presence of sulfuric acid, the steps of separating by distillation a propylene-rich fraction containing between 0.1 and 1% by weight of C_4 hydrocarbons and from 0.05 to 0.15% C_3 acetylenes from a commercial propylene fraction, partially condensing under increased pressure from said propylene-rich fraction a condensate containing 10 to 60 weight per cent of C_3 hydrocarbons with a portion of the C_4 hydrocarbons and C_3 acetylenes so as to leave the remaining propylene-rich vapor fraction with a C_4 hydrocarbon content of less than 0.1 weight per cent and a C_3 acetylene content of less than 0.05 weight per cent.

ALBERT P. GIRAITIS.
MACK C. FUQUA.

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