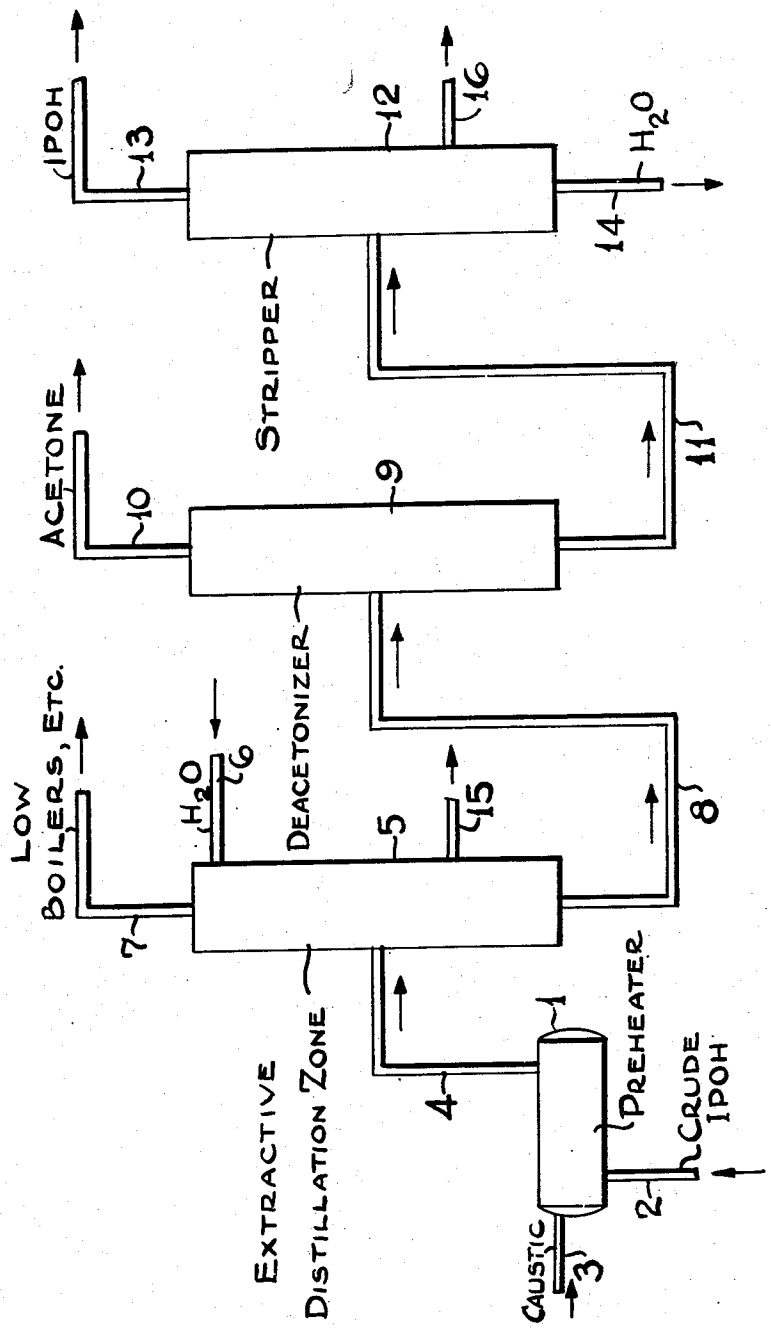
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PURIFICATION OF ISOPROPYL ALCOHOL

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PURIFICATION OF ISOPROPYL ALCOHOL

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This invention relates to the purification of isopropyl alcohol and particularly to the production of an isopropyl alcohol of improved odor quality. Specifically, the invention relates to a process whereby malodorous isopropyl alcohol is treated to remove the malodorous impurities therefrom.

It is well known that alcohols, particularly those produced by the acid-catalyzed hydration of olefin hydrocarbons, possess a distinct and apparently foreign odor, slightly penetrating and for the most part disagreeable. While no attempt will be made to definitely assign the disagreeable odor of alcohols prepared by olefin hydration to the presence of any one or combination of chemical compounds, it can be said with reasonable assurance that the odor of crude alcohol depends to a large extent on the quality of the olefin stream employed in the olefin hydration operation. Likewise, the odor of a refined alcohol depends to a large extent on the quality of the crude alcohol from which it is prepared.

Olefin hydrocarbons, such as those produced by the cracking of mineral oils, contain variable amounts of compounds having an obnoxious odor particularly sulfur compounds such as hydrogen sulfide, alkyl sulfides and mercaptans. These materials present, even in minute amounts, in the olefin stream to the acid catalyzed hydration process are believed to contribute to the obnoxious odor of the crude alcohol since, while sulfur alone has no smell, it is clear that in combination with other elements it is a powerful odoriferous agent. The bad odor of alcohols has also been attributed to the presence of so-called high-boiling polymer products formed in side reactions during the alcohol process. The odor of the polymer products is strengthened by the presence of any sulfur compounds dissolved therein, although the odor of some of the pure polymers themselves is by no means pleasing to the olfactory sense. A typical analysis of a sample of the so-called polymer product, in this case the so-called propyl oil, resulting from the production of isopropyl alcohol by the sulfuric acid catalyzed hydration of propylene, is as follows:

55 weight per cent sec.-heptanol (B. P. 137–140° C.)
21 weight per cent sec.-octanol (B. P. 160–165° C.)
2 weight per cent C_7 ketone (B. P. 131° C.)
13 weight per cent hydrocarbons (B. P. above 180° C.)
9 weight per cent ethers (B. P. above 160° C.)
Traces of sulfur compounds.

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The composition of the propyl oil or so-called high-boiling polymers obtained during the concentration of dilute crude isopropanol varies according to the point from which the alcohol containing it is withdrawn in the concentrating tower, and the odor likewise varies. Cuts can be identified with an odor of camphor, of menthol, etc. It has also been reported that the presence of nitrogen compounds also contributes to the odor of alcohols.

The odor imparted to isopropyl alcohol by the propyl oil impurities is a hydrocarbon type odor. This type of odor has been found to be effectively removed by a number of methods such as by careful and repeated conventional fractionations, but particularly by the water extractive distillation method as described and claimed in U. S. patent application Serial Number 24,626 filed May 1, 1948, and assigned to the present assignee. However, there is a second type of odor which is fugitive in nature and which may best be characterized as a mercaptan or thioaldehyde odor, and which is attributed to the presence of low-boiling sulfur compounds such as mercaptans or thioaldehydes which appear to be decomposition products of higher-boiling impurities which break up under alcohol purification distillation conditions. It has been found that this second type of odor is particularly noticeable when the alcohol production process is operated under upset regenerator conditions or when the purification process is operated under upset concentrator conditions. When the capacity of the regenerator or concentrator is exceeded some isopropyl alcohol creeps down into the reboiler associated with the regenerator or concentrator wherein a high temperature prevails and where a particular concentration of sulfuric acid exists. Under these conditions it is felt that the sulfuric acid present in the reboiler acts as a reducing agent on the isopropyl alcohol which decomposes into lower-boiling impurities, particularly mercaptan and/or thioaldehyde compounds which are volatile. These impurities go overhead with the alcohol from the regenerator. Subsequently in the concentrator they are not all removed with the low-boiling overhead, but remain in traces of parts per million in the isopropyl alcohol product which is removed as a top sidestream from the concentrator. Likewise if the concentrator conditions are upset the same decomposition occurs and the problem becomes aggravated. It has also been theorized that the second type of odor is due to the decomposition of sulfurized esters which are formed in minute amounts during the

propylene absorption in sulfuric acid. These esters are thought to decompose either thermally or by hydrolysis.

Furthermore, there are indications that some of the malodorous compounds are rather strongly bound in the aqueous alcohol product in such a manner that they tend to concentrate along with the alcohol during such operations as heads removal, water extractive distillation and even regular distillation for alcohols finishing. However, the nature of the chemical reactions tending to bind these malodorous compounds is such that unstable addition compounds result and the malodorous compounds are liberated and volatilized to some extent during all alcohol finishing operations of the types described. For instance, in typical alcohol finishing operations the following problems are encountered. Crude alcohol, after passing through the heads operation to remove ether and other low boilers, is fed to a finishing column in which certain low-boiling materials are taken overhead with a purified alcohol taken as a sidestream. Materials contributing to recycle odor appear to be lower boiling than the alcohol proper but are nevertheless not completely removed from the alcohol sidestream. This result is believed to be due in large part to the fact that decomposition reactions liberating low boiling malodorous compounds occur during the distillation, allowing these malodorous compounds to pass overhead. Similar difficulties are encountered when applying water extractive distillation to the same crude alcohol. In fact, water extractive distillation appears to concentrate the compounds giving rise to mercaptan odor along with the alcohol so that, in the final alcohol finishing operation, an alcohol product high in mercaptan odor is obtained. This seems to be particularly true of isopropyl alcohol prepared by the so-called weak acid method as described below.

It has been found that an isopropyl alcohol of improved odor characteristics can be obtained from crude isopropyl alcohol by adjusting the pH of the crude to 8.0 to 10.0 and preheating the crude alcohol prior to purification by distillation, to a temperature and pressure above that normally existing in the distillation tower proper and for a sufficient time to permit decomposition reactions liberating low boiling malodorous compounds to occur. Thereafter the alcohol is subjected to a series of distillation operations including a water extractive distillation step, a deacetonizing step and a stripping step.

Crude isopropyl alcohol may be produced by the sulfuric acid catalyzed hydration of propylene by the weak acid method or the strong acid method. In the former process a relatively rich propylene stream containing about 50–80 volume percent propylene is absorbed in sulfuric acid of approximately 60 to 80 weight percent concentrations, preferably 70 weight percent at about 170° F. and approximately 250 p. s. i. g. pressure to form an extract comprising isopropyl sulfate which is partially hydrolyzed to alcohol during the absorption. The hydrolysis is completed by dilution of the extract with water to approximately 45 weight percent acid strength and maintaining the extract at a temperature of about 190° F. for a period of about 10 minutes residence time. The hydrolysis products are then distilled in an alcohol regenerator wherein crude alcohol vapors are removed overhead and condensed, and wherein spent sulfuric acid is recovered as bottoms for reconcentration and subsequent re-use in the absorption process. The crude isopropyl alcohol contains approximately 30–60 percent by volume of isopropyl alcohol, some impurities including hydrocarbons, isopropyl ether, acetone and unknown impurities, and the balance water. The crude alcohol is condensed and cooled and is ready for the purification stage of the process.

In the strong acid process a propylene stream of relatively lower propylene content, i. e., about 30–60 volume percent propylene is contacted under similar conditions with a stronger sulfuric acid, e. g., acid of 80–95 weight percent concentration preferably 85–88 weight percent, whereby an extract is formed as above. The extract goes through a similar hydrolysis and stripping treatment to produce a crude isopropyl alcohol as described for the weak acid process.

When the isopropyl alcohol is purified by conventional fractionation it is led to a heads column the purpose of which is to remove ether and other low-boiling water-insoluble impurities, such as hydrocarbons, hydrocarbon polymers, oxygenated compounds, and unknown impurities. This is accomplished by a steam stripping operation whereby the lighter materials are withdrawn overhead while weak aqueous alcohol is recovered as bottoms. The weak aqueous alcohol is then distilled in a concentrating column where the alcohol is concentrated to a composition approaching its water azeotrope, viz., 91 volume percent isopropyl alcohol—9 volume percent water. The alcohol of azeotropic composition may be further distilled for removal of acetone if present, or concentrated further to 95 volume percent or 99 volume percent isopropyl alcohol if desired.

When the crude isopropyl alcohol is being purified by extractive distillation such as is described in S. N. 24,626 referred to above, the crude alcohol is distilled countercurrent to an internal water reflux containing 70–99 mol percent water, preferably 80–95 mol percent, whereby the low-boiling impurities both water-soluble and water-insoluble and some of the high-boiling impurities are removed overhead, while a dilute aqueous solution of the alcohol is recovered as bottoms and sent to a concentrating column where azeotropic alcohol is separated as a top sidestream from the balance of the high-boiling impurities and water.

According to this invention the malodorous crude alcohol is treated with caustic or other basic material to adjust the pH to 8.0 to 10.0 and is subjected to heating under pressure for a sufficient period of time to permit the substantially complete decomposition or polymerization of the total malodorous bodies in the alcohol. The pressure employed in the soaking of the crude alcohol ranges from 15 to 300 p. s. i. g., preferably about 40 to 150 p. s. i. g. Sufficient pressure is employed to keep the alcohol in the liquid phase during the preheating, although partial vaporization may occur. Temperatures in the range of 65° C. to 150° C., preferably about 100–125° C. are required. Temperatures below 65° C. have been found insufficient to induce complete removal of the malodorous bodies. The residence time of the preheater-soaking may vary widely depending upon the nature of the crude alcohol. Preferably the residence time should be kept as low as possible but at the same time obtaining good removal of malodorous compounds in the overall operation. In general, residence times of 1 to 3 hours, preferably about 2 hours, suffice but the time, of

course, varies also with the pressure and temperature employed.

The pH of the alcohol during the preheating step is of importance from the standpoint of catalyzing the decomposition or polymerization reactions desired. The pH of the alcohol is adjusted within the range of 8.0 to 10.0 preferably about 9.0.

The operation of the process consists in heating the crude alcohol at a pH of 8.0 to 10.0 in a suitable vessel to the temperature and under the pressure required. The heating is continued for the required time to produce the decomposition and/or polymerization reactions which are desired. The crude alcohol is then led through a pressure reducing valve, preferably immediately into an extractive distillation zone wherein the low-boiling volatile decomposition products are removed overhead by extractive distillation employing water as the aqueous refluxing medium. In the water extractive distillation step the crude alcohol is distilled and the vapors thereof pass upwardly countercurrent to a descending solution of the vapor condensate in water. The bulk of the low-boiling impurities are substantially completely removed as distillate together with some of the high-boiling impurities. The resulting dilute aqueous solution of isopropanol is then deacetonized in a separate distillation zone and thereafter pure alcohol is recovered by stripping from the aqueous solution.

The accompanying drawing illustrates one form of apparatus for carrying out the process of the invention.

Referring to the drawing crude isopropanol is pumped to preheater 1 via pipe 2. Caustic soda or other suitable reagents such as caustic potash, ammonia, the amines, etc. is introduced to the preheater via line 3 to adjust the pH of the alcohol to point of about 8.0 to 10.0. The preheater is heated by any suitable means such as by a heating coil. The crude alcohol containing impurities giving rise to mercaptan odor is maintained in the preheater at a temperature between 65° C. and 150° C. for a residence time of 1 to 3 hours under pressure sufficient to keep the alcohol in liquid phase. When the alcohol has been soaked for the required period of time it is removed from the preheater via line 4, preferably through a pressure reducing valve and introduced at a point near the midsection of the extractive distillation zone 5. In zone 5 the crude alcohol is subjected to a water extractive distillation in which considerable quantities of water are introduced into the distillation zone at a point near the top thereof via line 6. Sufficient water is introduced to maintain a concentration of 70 to 99 mol percent, preferably 80 to 95 mol percent, in the liquid concentrate on each plate in the tower. During the distillation in zone 5 vapors of isopropanol and impurities pass upwardly countercurrent to a solution of condensate in water. During the distillation the relative volatilities of the impurities with respect to isopropanol are enhanced to such an extent that the low-boiling materials including ethers, hydrocarbons, part of the acetone, decomposition products normally giving rise to mercaptan odor, etc. are removed overhead via line 7. Some of the high-boiling impurities are also removed. In some instances high-boiling impurities not removed overhead tend to form a separate layer in zone 5 at a point below the feed point thereof. These high-boiling impurities which are chiefly hydrocarbon impurities may be removed as a sidestream via line 15.

The dilute aqueous solution of isopropanol containing some acetone is removed from the bottom of zone 5 via line 8 and introduced into deacetonization column 9 where heat is applied to the mixture to remove overhead the acetone plus any remaining traces of low-boiling materials. The aqueous isopropanol solution, free of acetone, is removed from column 9 via line 11 and stripped in stripper 12 whereby pure isopropanol in the form of its aqueous azeotrope and free of mercaptan odor is recovered as a vapor stream overhead via line 13. Any remaining traces of polymer oils may be removed as a lower sidestream from the stripping column via line 16. Water is removed from the system via line 14.

Data confirming the necessity of (1) soaking the crude alcohol at the proper pH, (2) submitting the soaked or preheated alcohol to water extractive distillation followed by (3) deacetonizing, and (4) stripping to recover purified isopropanol is shown in the following tables.

In the runs listed below the crude isopropanol possessed an ether odor indicated as greater than 5.0 and possessed an optical density of 2.0+ at 2250 Å.

TABLE I

Run No.	Heads removal	Deacetonizing column	pH of crude adjusted to —	Crude preheat temp. (2 hrs.), ° C.	Odor	U. V. at 2,250 Å.
26-2	WXD*	Yes	9-10	125	2	0.198
26-3	WXD	Yes	9-10	67	2	.517

TABLE II

28-1	WXD	No	9-10	125	[a] 3	0.365
28-2	WXD	No	9-10	68	[a] 5	.582

TABLE III

28-3	WXD	Yes	***3-5	125	[a] 2	0.500
30-1	WXD	Yes	3-5	67	[a, b] 5	.480

TABLE IV

40-1	Conv.**	Yes	9-10	125	[a, b] 3	0.745
24-2	Conv.	Yes	9-10	67	[a] 5	.820
30-2	Conv.	No	9-10	125	[a] > 5	.650
30-3	Conv.	No	<7.0	70	[a] > 5	.900
159	Conv.	No	<7.0	70	[a] > 5	.520

[a] The odor present was characterized as mercaptan type.
[b] The odor present was characterized as hydrocarbon type.
*WXD—Water extractive distillation.
**Conv.—Conventional fractionation.
***pH of water employed in WXD adjusted with caustic to 9.0-10.0.

The data in Table I indicate that a prime grade alcohol free of mercaptan odor was obtained when all 4 conditions were observed. The data in Table II demonstrate that the deacetonizing column cannot be dispensed with even though the other conditions were present. In the runs described in Table III the crude was maintained for two hours at the temperature indicated but in the absence of pH adjustment, that is, the crude was left in its acid state, namely at a pH of 3-5. In the subsequent water extractive distillation, however, the pH of the water employed was adjusted to 9-10 by the addition of caustic. Although in run 28-3 an alcohol with an odor rating of 2(*a*) was obtained, the data demonstrate that the preheating must take place while the alcohol has a pH of 9-10, and that preheating at 125° C. even in the absence of pH adjustment is better than preheating at 67° C.

The data in Table IV demonstrate that con-

ventional distillation even in the presence of other conditions does not produce an alcohol of proper odor quality.

Although the invention has been described and illustrated with the de-acetonizing step preceding the stripping step, the order of these two steps may be reversed since the order of the steps is not at all critical. Thus, the stripping operation may occur first and the de-acetonizing operation then performed on the stripped alcohol. In this case the isopropyl alcohol and acetone are removed overhead from the stripper together with any other remaining low-boiling materials. Water is removed from the bottom of the stripper. The total overhead is then submitted to a de-acetonizing step in the final column wherein all the acetone and any low-boiling materials are removed overhead leaving a purified isopropanol to be recovered from the de-acetonizer.

Other modifications of the process may be employed without departing from the spirit of this invention.

What is claimed is:

1. A process for the purification of crude isopropanol prepared by an acid catalyzed olefin hydration process and containing low-boiling impurities including acetone and minute amounts of malodorous bodies introduced by the olefin utilized and giving rise to "mercaptan odor" which consists of, adjusting the pH of the crude isopropanol to 8.0 to 10.0, preheating the crude alcohol in the liquid phase under pressure of 15 to 300 p. s. i. g. to a temperature of 65° C. to 150° C. for a period of 1 to 3 hours, introducing the preheated crude alcohol into an extractive distillation zone wherein vapors of the crude alcohol are distilled countercurrent to an internal aqueous reflux containing 70–99 mol per cent water for removal of low-boiling materials including part of the acetone overhead and to obtain an aqueous solution of isopropanol containing some acetone as bottoms, distilling the remaining acetone from the aqueous alcohol bottoms, and stripping purified isopropanol-water azeotrope free of malodorous bodies from the deacetonized aqueous isopropanol.

2. A process according to claim 1 in which the pH of the crude isopropanol is adjusted to 9.0 with sodium hydroxide.

3. A process according to claim 2 in which the crude isopropanol is preheated for 2 hours at a temperature of 125° C.

4. A process according to claim 2 in which the internal aqueous reflux contains 80–95 mol percent water.

5. A process according to claim 1 in which the crude isopropanol is prepared by the sulfuric acid-catalyzed hydration of propylene.

6. A process according to claim 1 in which the crude isopropanol is prepared by the absorption of propylene by 60–80 weight percent sulfuric acid to form a propylene-sulfuric acid extract which is hydrolyzed and from which crude isopropanol is recovered by stripping.

7. A process for the purification of crude isopropanol prepared by an acid catalyzed olefin hydration process and containing low-boiling impurities including acetone and minute amounts of malodorous bodies introduced by the olefin utilized and giving rise to "mercaptan odor" which consists of adjusting the pH of the crude isopropanol to 8.0 to 10.0, preheating the crude alcohol in the liquid phase under pressure of 15 to 300 p. s. i. g. to a temperature of 65° C. to 150° C. for a period of 1 to 3 hours, introducing the preheated crude alcohol into an extractive distillation zone wherein vapors of the crude alcohol are distilled countercurrent to an internal aqueous reflux containing 70–99 mol percent water for removal of low-boiling materials including part of the acetone overhead and to obtain an aqueous solution of isopropanol containing some acetone as bottoms, stripping the isopropanol water azeotrope and acetone by distillation from the aqueous solution, and thereafter separating the acetone from the stripped isopropanol-water azeotrope by distillation leaving purified isopropanol-water azeotrope free of malodorous bodies.

8. A process according to claim 1 in which the pressure employed is 40 to 150 p. s. i. g.

9. A process for the purification of crude isopropanol prepared by an acid catalyzed olefin hydration process and containing low boiling impurities including acetone and minute amounts of malodorous bodies introduced by the olefin utilized and giving rise to "mercaptan odor" which consists of adjusting the pH of the crude isopropanol to 8.0 to 10.0, preheating the crude alcohol in the liquid phase under a pressure of 15 to 300 p. s. i. g. to a temperature of 65° C. to 150° C. for a period of one to three hours, introducing the preheated crude alcohol into an extractive distillation zone wherein vapors of the crude alcohol are distilled countercurrently to an internal aqueous reflux containing 70 to 99 mol. percent water for removal of low boiling impurities including part of the acetone overhead and to obtain an aqueous solution of isopropanol containing some acetone as bottoms, and thereafter removing the remaining acetone from the aqueous isopropanol solution.

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