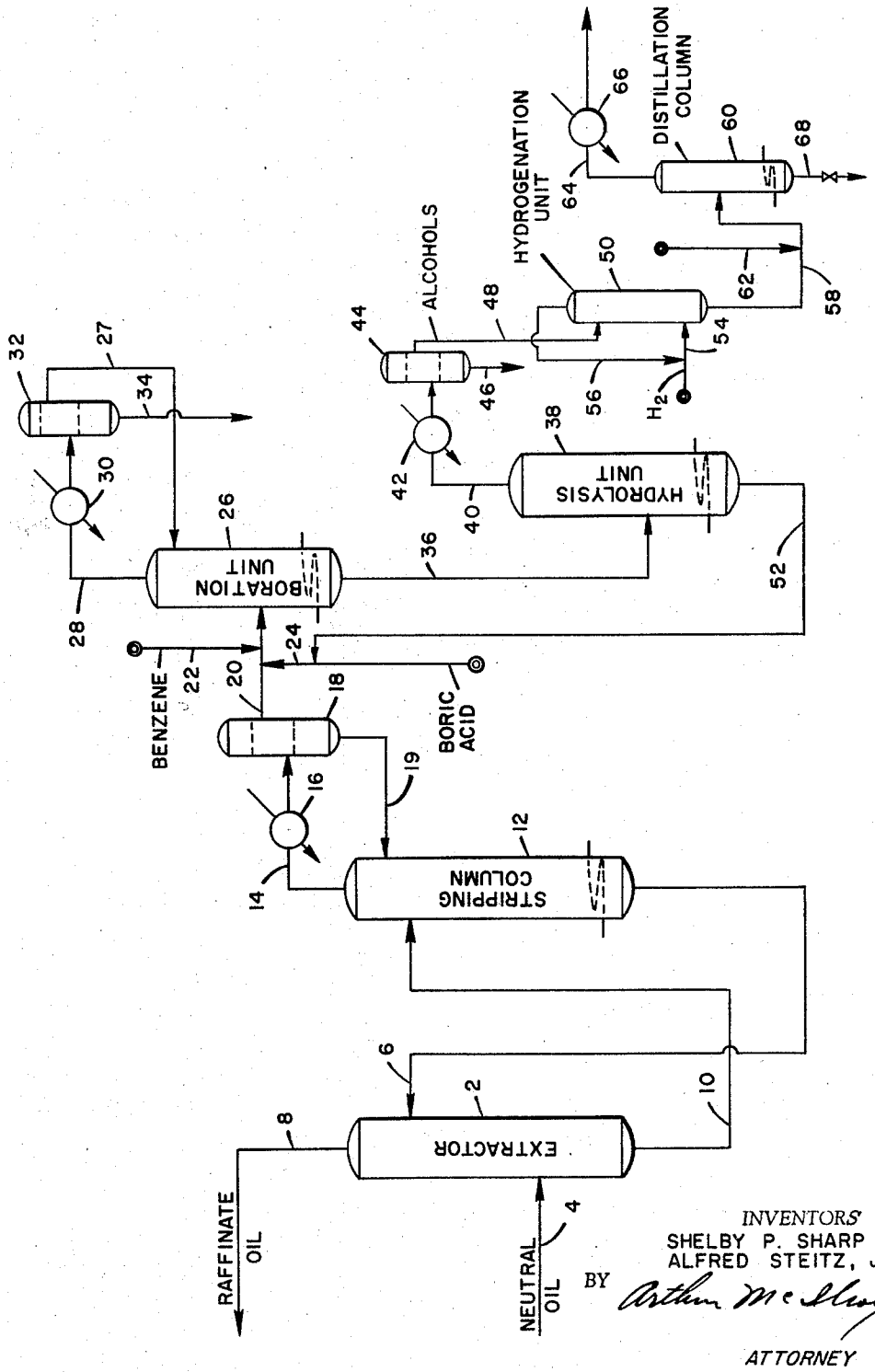
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PROCESS FOR IMPROVING COLOR OF OIL-SOLUBLE ALCOHOLS

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PROCESS FOR IMPROVING COLOR OF OIL-SOLUBLE ALCOHOLS

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The present invention relates to a process for the purification of alcohols. More particularly it is concerned with a method for removing objectionable color forming impurities present in small amounts in the alcohols found in the hydrocarbon fraction produced by the reduction of carbon monoxide with hydrogen using an iron or equivalent catalyst.

The alcohols present in hydrocarbon synthesis oil range primarily from C_5 to C_{10} in molecular weight and constitute a relatively large source of such alcohols, approximately 85 to 90 percent of which have eight or less carbon atoms. For example, a synthesis plant capable of producing 6,000 barrels per day of petroleum hydrocarbons will also produce about 93,000 pounds per day of oil soluble alcohols in addition to about 225,000 pounds per day of other oil soluble chemicals such as esters, acids and carbonyl compounds.

In recovering oil-soluble chemicals from hydrocarbon solutions thereof such as, for example, hydrocarbon solutions of the type produced by the reaction of carbon monoxide with hydrogen at elevated temperatures and pressures in the presence of a fluidized alkali promoted iron catalyst, it has been proposed that aqueous soap solutions of various types be employed as selective solvents or extractants for such chemicals. Generally these "soap" solutions are not composed of soaps in the ordinary sense but are made up largely of relatively nonsurface-active salts of alkali metals or equivalent salts derived from carboxylic acid mixtures having an average molecular weight ranging from about 115 to about 155. Solutions of this type are most conveniently prepared by adding the required amount of an aqueous caustic solution, or other suitable base, to the primary oil fraction produced in hydrocarbon synthesis whereby the free acids present in said fraction are neutralized. A substantial proportion of the oil-soluble chemicals, containing about 5 to 10 weight percent of hydrocarbons, is solubilized in the aqueous soap layer formed as a result of the neutralization step. The soap solution used for extraction purpose is prepared by subjecting the aqueous layer, containing the neutralized acids, chemicals and minor amount of hydrocarbons, to a stripping operation in which substantially all of the chemicals and all of the hydrocarbons were taken overhead leaving a lean aqueous soap solution having a soap or salt content of the order of 20 to about 50 percent.

In practice, after the hydrocarbon synthesis oil had been extracted with a lean aqueous soap solution, the resulting rich soap extract, containing oxygenated chemicals and hydrocarbons, was combined with the rich soap formed in the above-mentioned neutralization step. These combined streams were then subjected to extraction under pressure with a low molecular weight liquid hydrocarbon such as, for example, liquid propane or liquid butane, for the purpose of removing from the soap solution any dissolved heavy hydrocarbons. The presence of heavy hydrocarbons, generally speaking, is undesirable since they lower the purity of the chemicals recovered from

such solutions. This step, involving extraction of the chemical-rich soap solutions, is ordinarily referred to as "de-oiling" or the "de-oiling step." The raffinate from the de-oiling step consisted chiefly of soap solution containing oxygenated organic chemicals free of heavy hydrocarbons. This solution was thereafter fractionated under pressure to separate the light hydrocarbon solvent present, after which the soap solution was stripped free of chemicals in a conventional bubble cap still. The chemical distillate was then topped under a pressure of about 150 mm. to remove light chemicals, i.e., boiling below about 115° F. and containing primarily methyl ethyl ketone, methyl propyl ketone, and propanol.

The alcohol mixtures obtained from the above-mentioned de-oiled soap extract are generally satsifactory in their initial color. However, we have found that they do not meet the required color specifications when used, for example, in the preparation of phthalate plasticizers. Such alcohols, which are initially of good color, tend to darken during esterification with phthalic anhydride and mineral acid catalyst. The exact nature of the color forming impurities in these alcohols is not known. Some of the materials causing this trouble are thought to be unsaturates of various types and carbonyl compounds having boiling points too close to those of the alcohols to effect a satisfactory separation by distillation. Numerous carbonyl complexing agents have been used without success in an effort to improve the phthalation color quality of these alcohols. In addition, the alcohol mixtures obtained by further careful fractionation of the distillate produced from fractionation of the aforesaid soap extract have been subjected to treatment with sulfuric and phosphoric acids and digested with caustic in an effort to improve the color quality of said alcohols. Such methods, however, have been entirely unsatisfactory. Also hydrogenation of the alcohols or treatment with reagents active to destroy carbonyl compounds such as, for example, N-hydroxylbenzenesulfonamide, sodium borohydride, hydroxylamine hydrochloride, and potassium permanganate, have likewise been unsuccessful.

Accordingly, it is an object of our invention to provide an effective and practical method for improving the color qualities of oil soluble alcohols produced during hydrocarbon synthesis. Another object of our invention is to provide a procedure particularly for the improvement in color of the C_8 and lower molecular weight alcohols found in hydrocarbon synthesis oil. It is another object of our invention to provide a method involving a specific sequence of steps comprising subjecting a crude mixture of the alcohol or alcohols to be purified to an esterification reaction with boric acid or an equivalent acid; separating the resulting borate ester or esters from the remaining components of the reaction mixture; hydrolyzing said ester or esters; subjecting the alcohol or alcohols thus liberated to hydrogenation; and thereafter fractionating the resulting hydrogenated product to obtain an alcohol or mixture of alcohols capable of forming esters of low color content.

Briefly, our invention involves first forming the boric acid esters of the alcohols present in the distillate derived from the soap extract stripping operation referred to above. This reaction is simple and straightforward, the water formed in the reaction being removed azeotropically with a suitable hydrocarbon. No catalyst is required. After the esterification step, the reaction mixture is subjected to distillation, preferably under vacuum, to take off overhead impurities such as carbonyl compounds and low boiling esters leaving a residue consisting essentially of alcohol borates. This residue is next subjected to steam distillation causing the esters to hydrolyze and liberating the alcohols which are taken overhead. The recovered alcohols may then be fractionated into narrow boiling cuts. Alternatively, the recovered alcohols

may be split into a C_8 and lower fraction and a C_9 and higher cut. Separation of the C_8 and lower alcohols from the higher alcohols, we have found to be desirable since the required color specifications are difficult to obtain in the case of the C_9 and higher alcohols, even when employing the process of our invention. However, with a composite of C_8 and lower alcohols or with cuts of the individual alcohols having eight or less carbon atoms, good color quality can be secured by this process. Good color characteristics are not obtained, however, until the desired alcohol or alcohol composite, for example, the C_5 to C_7 alcohols, is subjected to hydrogenation. In this way any saturated materials present in the alcohols at this stage, and which might otherwise interfere with the color quality of said alcohols, are disposed of. Alcohols or alcohol mixtures having a color of 200 APHA (color standard of American Public Health Association) or less are required to produce phthalates or similar plasticizers of suitable color quality.

For a better understanding of the process of our invention, reference is made to the accompanying drawing wherein neutral oil containing alcohols, esters and carbonyl compounds is introduced into column 2 through line 4. Within column 2 the rising stream of oil is intimately mixed with a descending aqueous lean soap solution introduced through line 6. This solution contains between 30 and 40 weight percent of a soap solution prepared in the manner previously described. From the top of column 2 a raffinate oil stream, which may be sent to further refining, emerges through line 8 substantially depleted with respect to chemicals. From the base of the extractor a rich soap extract of chemicals is withdrawn through line 10. This extract may, if desired, be subjected to a de-oiling operation, not shown in the accompanying diagram, to remove dissolved hydrocarbons from said extract. Thereafter the de-oiled extract is sent to stripping column 12 where chemicals, together with azeotropic water are taken overhead through line 14, condenser 16 and sent to separator 18. The lower aqueous layer in separator 18 is returned to the column through line 19 as reflux while the upper organic layer in the separator is withdrawn through line 20, mixed with benzene added through line 22, and boric acid, preferably in the form of a saturated aqueous solution, added through line 24. The resulting mixture is then introduced into boration unit 26. The esterification of the alcohols by boric acid proceeds smoothly at a temperature of about 70° C. Water present in the reaction reaction medium is removed in the form of an azeotrope with benzene through line 28, condenser 30 and introduced into separator 32. The upper benzene layer formed in separater 32 is returned to column 26 through line 27 while the lower aqueous layer is discharged from the system through line 34. After the esterification step appears to be complete and substantially all volatile impurities have been driven overhead from unit 26 through line 28, the ester residue is transferred through line 36 to hydrolysis unit 38 where the esterified material is subjected to hydrolysis by the use of steam. Liberated alcohols are taken overhead via steam distillation, through line 40, condenser 42 and introduced into separator 44. The lower aqueous layer formed in the separator is withdrawn from the system through line 46 while the upper aqueous layer is taken from separator 44 through line 48 to hydrogenation unit 50. The bottoms material in hydrolysis unit 38 consists of an aqueous boric acid solution. This solution may be concentrated to the desired strength and recycled to the boration step via lines 52 and 24. Hydrogenation of the liberated alcohols is generally effected at temperatures in the neighborhood of 175° to about 200° C. in the presence of a hydrogenation catalyst such as nickel, for example, Raney nickel. Pressures of the order of 1,500 to 2,500 p.s.i. may be employed. Hydrogen is introduced into unit 50 via line 54 and contacts fresh alcohols added through line 48. Unreacted hydrogen may be recycled through line 56. Hydrogenated product is then withdrawn from hydrogenation unit 50 through line 58 and sent to distillation column 60. This column is preferably operated under reduced pressure to avoid decomposition of the treated alcohols. In order to secure substantially complete recovery of the hydrogenated alcohols, a higher boiling fraction, for example, a C_9–C_{10} alcohol fraction may be added to column 60 via lines 62 and 58 so that all of the desired alcohol fraction can be driven overhead through line 64 and condenser 66. High boiling residual material may be periodically withdrawn from column 60 through line 68.

The process of our invention will be further illustrated by the following specific example:

Example

Into a reaction vessel fited with a distillation column was added 174.4 grams of C_8 alcohol fraction derived from neutral hydrocarbon synthesis oil. Initially this fraction had a color of 2,000+ APHA (substantially black) by the phthalation color test. To this were also added 27.5 grams of boric acid and 521.0 grams of benzene. Reaction was carried out at about 70° C. until 22.1 grams of water had been brought overhead in the form of a benzene-water azeotrope. Thereafter the benzene was distilled off and the distillation temperature increased to 150° C. at 2 mm. to drive off any unborated materials. The ester residue thus obtained (153.3 grams) was next subjected to hydrolysis with steam. The mixture of alcohol and water taken overhead was allowed to settle and the upper (wet) alcohol layer amounting to 155.9 grams recovered. Thereafter 155 grams of the alcohol thus obtained was introduced into a suitable hydrogenation bomb and hydrogenated at 188° C. under a hydrogen pressure of 2,000 p.s.i. and in the presence of 0.43 weight percent Raney nickel catalyst. After four hours maintaining the pressure at 2,000 p.s.i.g., the contents of the bomb were emptied, filtered and the filtrate weighed. The filtered product amounted to 143.5 grams and had a color of 400 APHA.

The hydrogenated product was then subjected to fractionation at 60 mm. pressure over a temperature range of 35° to about 123° C. The charge to this fractionation step amounted to 138.5 grams. From this a total of 110.8 grams C_8 alcohol was recovered having a color averaging 200 APHA. Approximately 16 grams of distillate coming over between 35° and 115° C. was obtained.

The phthalate color of the C_8 alcohol secured was determined by an accepted method developed for isooctyl alcohol. This method is as follows: to a 5 ml. sample of the alcohol in a large open test tube is added 2.3 g. phthalic anhydride and 0.02 ml. of a mixture of 50 volume percent water and 50 volume percent concentrated sulfuric acid. The test tube is heated in an aluminum block at 125° C. for 90 minutes, stirring with a clean, dry stirring rod at the start to dissolve the anhydride and mix the solution. After 90 minutes the product is cooled, diluted with 5 ml. of acetone and the APHA color of the diluted product determined.

In another experiment under conditions identical to those given immediately above, a sample from the same batch of C_8 alcohol used in the preceding example was processed, the only difference in procedure being that the alcohol was hydrogenated prior to the boration step. The color of the recovered alcohol thus obtained was 2,500 APHA. After fractionation the minimum color obtained was 480 APHA. Heart cut alcohol averaged about 1,200 APHA.

C_5 to C_7 alcohol fractions derived from hydrocarbon synthesis neutral oil have been processed in the manner described in the foregoing example, with a highly satisfactory recovery of a purified material having a color of not more than 200 APHA.

We claim:

1. In a process for the removal of objectionable color forming impurities from C_8 and lower molecular weight oil soluble alcohols derived from hydrocarbon synthesis oil, said alcohols having a color substantially higher than 200 APHA, the improvement which comprises mixing an alcohol of the above indicated molecular weight range with boric acid, allowing said alcohol and boric acid to react in a reaction zone to form the corresponding alcohol borate, separating the latter from a boric acid solution and hydrolyzing said borate to liberate said alcohol, thereafter subjecting the latter to hydrogenation, and fractionating the resulting hydrogenated alcohol to recover an alcohol distillate fraction having a color of not more than about 200 APHA.

2. The process of claim 1 in which the alcohol being purified is a C_8 alcohol.

3. The process of claim 1 in which the alcohol component being purified constitutes a mixture of C_5 to C_7 alcohols.

4. The process of claim 1 in which said boric acid solution is evaporated to produce a concentrated solution

and thereafter returned to said reaction zone for further use in the form of additional quantities of said borate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,525,354	Hogg et al.	Oct. 10, 1950
2,569,671	Hughes et al.	Oct. 2, 1951
2,587,753	O'Connor et al.	Mar. 4, 1952
2,678,952	Krebs	May 18, 1954
2,746,984	Rottig	May 22, 1956
2,780,643	Buchner	Feb. 5, 1957

FOREIGN PATENTS

153,306	Australia	Feb. 5, 1957
278,777	Great Britain	Oct. 10, 1927

OTHER REFERENCES

Wender et al.: Report of Investigations (R. I. 4720, June 1948), U.S. Dept. of Int. Bureau of Mines; pp. 22, 23.

Anderson et al.: J. Applied Chem., vol. 2 (May 1952); pp. 241–4.