

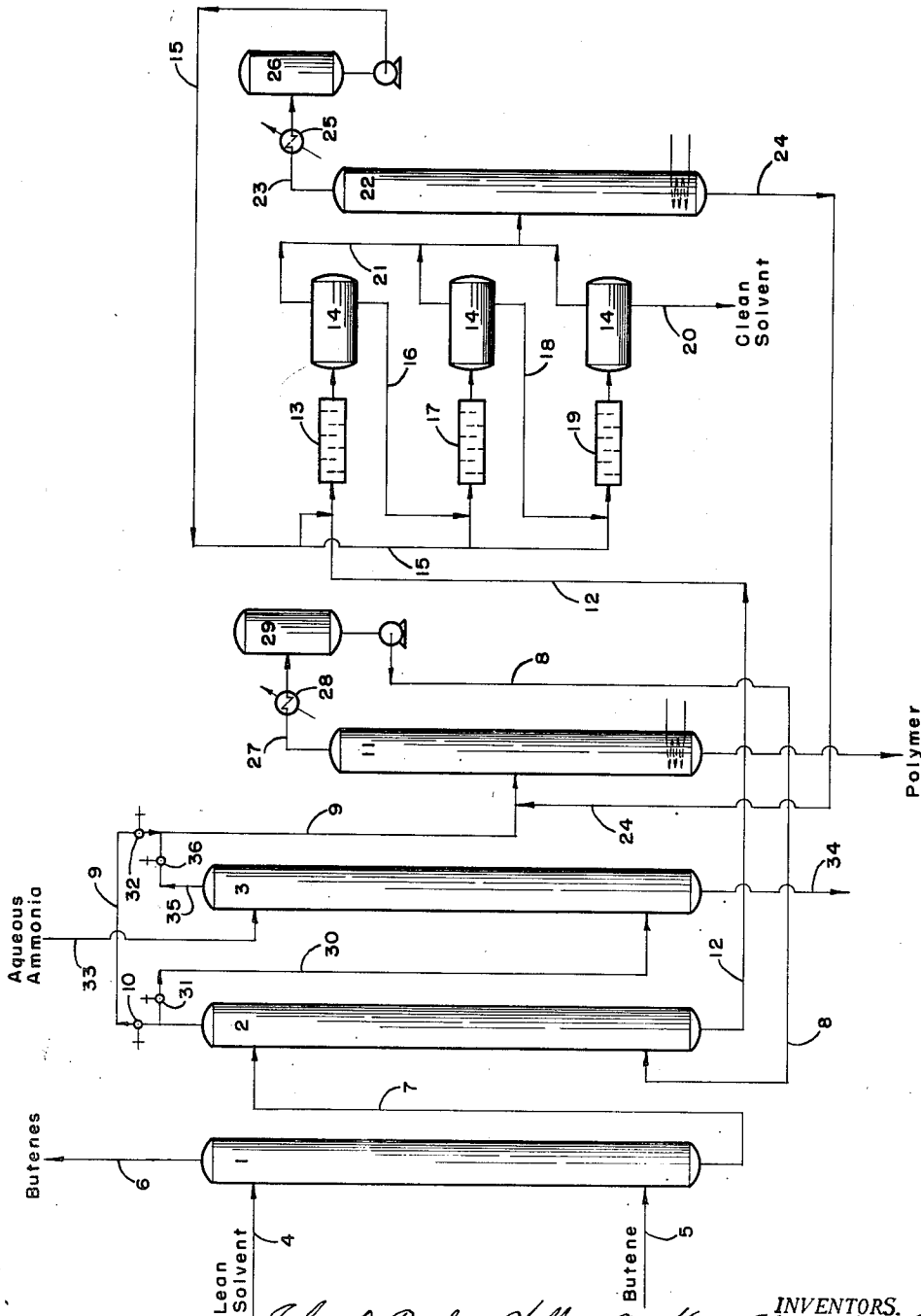
July 22, 1952

J. D. BOOKER ET AL

2,604,485

METHOD FOR PURIFYING CUPROUS AMMONIUM ACETATE SOLVENT

Filed Nov. 27, 1948



INVENTORS.
John D. Booker, William M. Karp, Edward F. Wadley.
 BY
R. G. Whelan
 ATTORNEY.

UNITED STATES PATENT OFFICE

2,604,485

METHOD FOR PURIFYING CUPROUS
AMMONIUM ACETATE SOLVENT

John D. Booker, William M. Harp, and Edward F. Wadley, Baytown, Tex., assignors, by mesne assignments, to Standard Oil Development Company, Elizabeth, N. J., a corporation of Delaware

Application November 27, 1948, Serial No. 62,342

9 Claims. (Cl. 260-438)

1

The present invention is directed to a process for increasing the efficiency of solvent extraction units in which aqueous type solvents, as for example, cuprous ammonium acetate, are utilized for the extraction of highly unsaturated hydrocarbons, such as butadiene, from their mixtures with other hydrocarbons having the same number of carbon atoms. More particularly, the invention is concerned with the removal of organic contaminants from aqueous cuprous ammonium acetate solutions which have been contacted with hydrocarbon fractions obtained by thermal or catalytic cracking of hydrocarbons or by dehydrogenation of butylenes and butanes.

This application is a continuation-in-part of U. S. Serial No. 619,646 filed October 1, 1945, and entitled "Solvent Extraction Process," now abandoned.

For ease of discussion, the present invention will be described with reference to the extraction of butadiene from its mixtures with other C₄ hydrocarbons such as butylenes, butanes, acetylenes, and the like, with aqueous cuprous ammonium acetate. This process may be performed by employing vapor-liquid or liquid-liquid operation. The aqueous copper solution is passed countercurrently to the C₄ hydrocarbons containing butadiene in an extraction tower where the solvent preferentially absorbs butadiene. The rich solution is denuded of butadiene by heating the solution in a separate tower to a temperature in the neighborhood of 150° to 180° F. The regenerated or lean copper solution is then cooled and recirculated through the absorption tower.

The hydrocarbon feeds from which butadiene is extracted as described above may be obtained by thermal or catalytic cracking of hydrocarbons to form a product from which a C₄ fraction containing butadiene, butylenes, butanes, acetylenes, and the like, may be obtained. The hydrocarbon fraction forming a feed stock from which butadiene is removed may also be obtained by dehydrogenation of butylenes and butanes by thermal and catalytic processes which are well known to the art. Such thermal and catalytic dehydrogenation processes produce, besides the desired butadiene, other compounds such as acetylenes, as exemplified by the substituted acetylenes. The cracked products mentioned above also contain varying quantities of acetylenes. C₄ hydrocarbon fractions containing butadiene obtained from either of the above mentioned types of processes also contain, besides the acetylenes, minor quantities of oxygenated organic compounds such as aldehydes, organic acids and possibly other

2

unidentified oxygenated organic compounds. These compounds, when present in the fraction from which butadiene is to be removed, result in the cuprous ammonium acetate solution becoming

contaminated with reaction products thereof and materials which may dissolve in it as will be described below. Thus, during continued recirculation of the solvent through the cycle it slowly becomes contaminated with small amounts of organic compounds which probably are reaction products of the contaminating hydrocarbons, such as acetylenes and the like, with the ammonia in the solvent. It is also believed that small quantities of aldehydes in the butadiene containing fraction contacting the solvent may also react with the solvent to form a compound which has a deleterious effect on the solvent as it is circulated in the system. Thus, it has been shown that the presence of contaminants of the type mentioned before in aqueous solutions increases the foaming tendency of the solvent which in turn decreases the efficiency of the operation. In addition, the presence of the contaminants decreases the ability of the copper solution to assimilate additional copper when the solution is contacted with metallic copper to restore its activity. The aqueous solution is also believed to contain polymers which may be present as a result of polymerization of substituted acetylenes under the conditions obtaining when the cuprous ammonium acetate solution is contacted with the butadiene-containing fraction for separation of the butadiene therefrom. These hydrocarbon polymers in combination with other contaminants present in the solution also contribute to the foaming tendency of the solvent and decrease in the efficiency of the overall operation.

The principal object of the present invention is the provision of a process whereby contaminants of the aforesaid type can be removed from aqueous solutions, such as cuprous ammonium acetate, in a simple, inexpensive manner. Briefly, a contaminant or contaminants of the types mentioned before are removed by extraction of the contaminated solvent with a water-immiscible aliphatic alcohol, such as amyl alcohol. This operation in itself creates problems which are solved by the present invention. The first of these problems arises out of the fact that such alcohols are expensive and are to a very limited degree soluble in the copper solution. This means that the alcohol has to be recovered from the regenerated copper solution in order for the operation to be commercially feasible. The second of these problems is occasioned by the pres-

3

ence in the contaminated solvent of polymers of substances like acetylene or even butadiene which are soluble in the alcohols and are separated therefrom by distillation with great difficulty. Here again in order to make the operation economical this contamination of the alcohol should be avoided.

More specifically, according to the present invention, a contaminated aqueous solvent, of the type above described, is extracted with a water immiscible aliphatic alcohol such as amyl alcohol and is then extracted with a solvent immiscible with water but having strong solvent power for the alcohol and being of a character to permit easy separation therefrom of the alcohol. A convenient solvent for this purpose is a light hydrocarbon such as one of the butanes, butylenes, pentanes, amylenes and the like, or a mixture thereof. While a purified hydrocarbon may be employed, ordinarily a mixture will be used as a mixture of iso and normal butane or a mixture of the butylenes. The light hydrocarbon solvent may conveniently be described as being a low molecular weight aliphatic hydrocarbon having no triple bonds and not more than one double bond. The light hydrocarbon solvent thus may be selected from the group consisting of alkanes and mono-olefinic alkenes.

The alcohol employed in the practice of the present invention will be preferably amyl alcohol, although other alcohols of the same homologous series having a greater number of carbon atoms may be employed, for example the hexyl, heptyl, octyl, and nonyl alcohols may be used under some conditions; however, the amyl alcohols will be preferred. Thus the present invention contemplates employing a mono-hydroxy alkanol having from five to nine carbon atoms in the molecule.

In the preferred embodiment of the present invention, the contaminated aqueous solvent is first extracted with a water-immiscible solvent, other than an alcohol, for hydrocarbon polymers. Again a light hydrocarbon of the class heretofore mentioned may be utilized for this purpose. Thus, a specific preferred sequence of operations is an initial extraction of the aqueous solvent with liquid butylene, followed by an extraction of the aqueous solvent with amyl alcohol, followed by a second extraction of the aqueous solvent with liquid butylene. This alcohol extract may be given a treatment with an activated clay to increase the molecular weight of the polymers present whereby they may be readily separated from the alcohol by distillation.

In the extraction of an aqueous copper solvent of the aforesaid type with an alcohol such as amyl alcohol, there is frequently incurred a loss of copper into the alcohol. The present invention contemplates the additional step of extracting the alcohol extract of the aqueous copper-containing solvent with aqueous ammonia for the recovery from the alcohol of any copper salt it has taken up from the aqueous copper-containing solvent. The resulting aqueous ammonia extract can then be added to the copper-containing solvent as make-up.

Further objects and advantages of the present invention will appear from the following detailed description of the accompanying drawing in which the single figure is a front elevation in diagrammatic form of a plant suitable for the practice of the present invention.

Referring to the drawing in detail, numerals 1, 2 and 3 represent scrubbing towers which may

4

be provided with suitable interior equipment or packing to insure thorough mixing of liquid materials introduced into the scrubbing towers. Lean aqueous solvent, such as a water solution of cuprous ammonium acetate which has become contaminated by use in the extraction of highly unsaturated hydrocarbons and from which such hydrocarbons have been removed, is introduced into the top of tower 1 through line 4. A suitable hydrocarbon solvent, such as liquid butylenes, is introduced into the bottom of tower 1 by line 5 and passes upwardly through the tower countercurrently to the aqueous solvent. The butylenes, containing such hydrocarbon polymeric material as it has washed out of the aqueous solvent, leaves the top of the tower 1 by line 6, while the scrubbed aqueous solvent leaves the bottom of the tower through line 7 which discharges into the top of tower 2. In the bottom of tower 2, through line 8, is introduced a suitable alcohol, such as amyl alcohol, which passes upwardly through the tower countercurrently to the aqueous solvent. The alcohol, containing extracted constituents, leaves the top of the tower through line 9 provided with a valve 10. Line 9 conducts the contaminated alcohol to an intermediate point in a distillation tower 11.

The scrubbed aqueous solvent leaves the bottom of tower 2 by way of line 12 which conducts it through a mixer 13 into the uppermost of three settlers 14. Before entering the mixer 13, the aqueous solvent is mixed with butene supplied by line 15. The aqueous solvent separates from the butene in the uppermost settler 14 and passes by way of line 16 to the next lower settler again passing first through a scrubber 17 after being mixed with further amounts of butylenes. In like manner, the aqueous solvent leaves the bottom of the middle settler 14 through line 18, is mixed with further amounts of butylenes, passes through another mixer 19 into the bottom settler from the bottom of which the purified aqueous solvent is drawn off through line 20. The butylenes containing any alcohol recovered from the aqueous solvent is drawn off from the top of each of settlers 14 and passes by way of manifold line 21 to an intermediate point in a distillation tower 22 from the top of which the butylenes are drawn off through line 23 while recovered alcohol is drawn off from the bottom by way of line 24. The butylenes are liquefied in a condenser 25 and passed to an accumulator 26 to which line 15 is connected. Line 24 conducts the recovered alcohol to line 9 and thence to distillation tower 11. Purified alcohol is taken off the top of tower 11 through line 27, condensed in condenser 28 and passed to an accumulator 29 to which line 8 is connected and is recycled to scrubbing tower 2.

Line 9 is provided with a branch line 30 ahead of valve 10, this branch line being provided with a valve 31. If desired, valve 10 and a second valve 32 in line 9 are closed, valve 31 is opened and the effluent from the upper part of tower 2 is passed through line 30 to the bottom of tower 3 into the upper part of which aqueous ammonia is introduced by way of line 33. This step is used in case the aqueous solvent is one containing copper, some of which has been taken up by the alcohol. The aqueous ammonia, containing the recovered copper, leaves the bottom of tower 3 through line 34 while the purified alcohol leaves the top of tower 3 through line 35 provided with valve 36 which empties into line 9. This operation prevents excessive loss of copper and also

prevents harmful quantities of copper from depositing in the lower portion of tower 11.

The aforesaid operations may be carried out at atmospheric temperature except, of course, for the distillation steps. In the various scrubbing steps sufficient pressure is utilized to maintain the scrubbing mediums in the liquid phase at the operating temperature. It may be mentioned that it is important that the alcohol be removed as completely as possible from the aqueous solvent not only for economic reasons but because its presence in the aqueous solvent would impair the selectivity of the latter.

The nature and objects of the present invention having been fully described, what we desire to claim is:

1. In a continuous process in which aqueous cuprous ammonium acetate solution is contacted with a hydrocarbon fraction containing diolefins, acetylenes and oxygenated organic compounds to absorb diolefin from the hydrocarbon fraction and in which an aqueous cuprous ammonium acetate solution contaminated by such contact with foam-inducing organic impurities soluble in mono-hydroxy alkanols is separated from contact with said hydrocarbon fraction, the steps of scrubbing the contaminated aqueous solution with a mono-hydroxy alkanol having from five to nine carbon atoms in the molecule, washing the scrubbed aqueous solution with a low molecular weight hydrocarbon selected from the group consisting of alkanes and mono-olefinic alkenes to remove traces of the alkanol from the scrubbed solution, and then employing the scrubbed and washed solution to contact additional amounts of said hydrocarbon fraction to absorb diolefin therefrom.

2. In a continuous process in which aqueous cuprous ammonium acetate solution is contacted with a hydrocarbon fraction containing diolefins, acetylenes and oxygenated compounds to absorb diolefin from the hydrocarbon fraction and in which an aqueous cuprous ammonium acetate solution contaminated by such contact with foam-inducing organic impurities soluble in mono-hydroxy alkanols is separated from contact with said fraction, the steps of scrubbing the contaminated aqueous solution with a low molecular weight hydrocarbon selected from the group consisting of alkanes and mono-olefinic alkenes, washing the scrubbed solution with a mono-hydroxy alkanol having from five to nine carbon atoms in the molecule, scrubbing the scrubbed and washed solution with a low molecular weight hydrocarbon selected from the group consisting of alkanes and mono-olefinic alkenes to remove traces of the alkanol from the scrubbed and washed solution, and then employing the last scrubbed solution to contact additional amounts of said hydrocarbon fraction to absorb diolefin therefrom.

3. In a continuous process in which aqueous cuprous ammonium acetate solution is contacted with a hydrocarbon fraction containing butadiene, acetylenes and oxygenated organic compounds to absorb butadiene from the hydrocarbon fraction and in which an aqueous cuprous ammonium acetate solution contaminated by such contact with foam-inducing organic impuri-

ties soluble in mono-hydroxy alkanols is separated from contact with said fraction, the steps of scrubbing the contaminated aqueous solution with a mono-hydroxy alkanol having from five to nine carbon atoms in the molecule, washing the scrubbed aqueous solution with a low molecular weight hydrocarbon selected from the group consisting of alkanes and mono-olefinic alkenes to remove traces of the alkanol from the scrubbed solution, and then employing the scrubbed and washed solution to contact additional amounts of said hydrocarbon fraction to absorb butadiene therefrom.

4. In a continuous process in which aqueous cuprous ammonium acetate solution is contacted with a hydrocarbon fraction containing butadiene, acetylenes and oxygenated organic compounds to absorb butadiene from the hydrocarbon fraction and in which an aqueous cuprous ammonium acetate solution contaminated by such contact with foam-inducing organic impurities soluble in mono-hydroxy alkanols is separated from contact with said hydrocarbon fraction, the steps of scrubbing the contaminated aqueous solution with liquefied butylene under conditions to cause removal of hydrocarbon polymer from said aqueous solution, separating butylene from said scrubbed solution, scrubbing the separated solution with amyl alcohol, separating amyl alcohol from said last scrubbed aqueous solution, washing the last separated solution with liquid butylenes to remove amyl alcohol therefrom, separating the liquid butylenes from said washed solution and then employing the solution last separated from butylenes to contact additional amounts of said hydrocarbon fraction to absorb butadiene therefrom.

5. A method according to claim 3 in which the alkanol scrubbing step is preceded by a scrubbing of the contaminated aqueous solution with a low molecular weight hydrocarbon selected from the group consisting of alkanes and mono olefinic alkenes.

6. A method according to claim 3 in which the alkanol is amyl alcohol.

7. A method according to claim 3 in which the hydrocarbon is butylene.

8. A method according to claim 3 in which the alkanol is amyl alcohol and the hydrocarbon is butylene.

9. A method according to claim 3 in which the hydrocarbon is butylene and the alkanol scrubbing step is preceded by the scrubbing of the aqueous solution with butylene.

JOHN D. BOOKER.

WILLIAM M. HARP.

EDWARD F. WADLEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,383,784	Fleer	Aug. 28, 1945
2,397,996	Wilson	Apr. 9, 1946
2,399,882	Morrell et al.	May 7, 1946
2,444,945	Morrell	July 13, 1948
2,463,846	Bain et al.	Mar. 8, 1949