

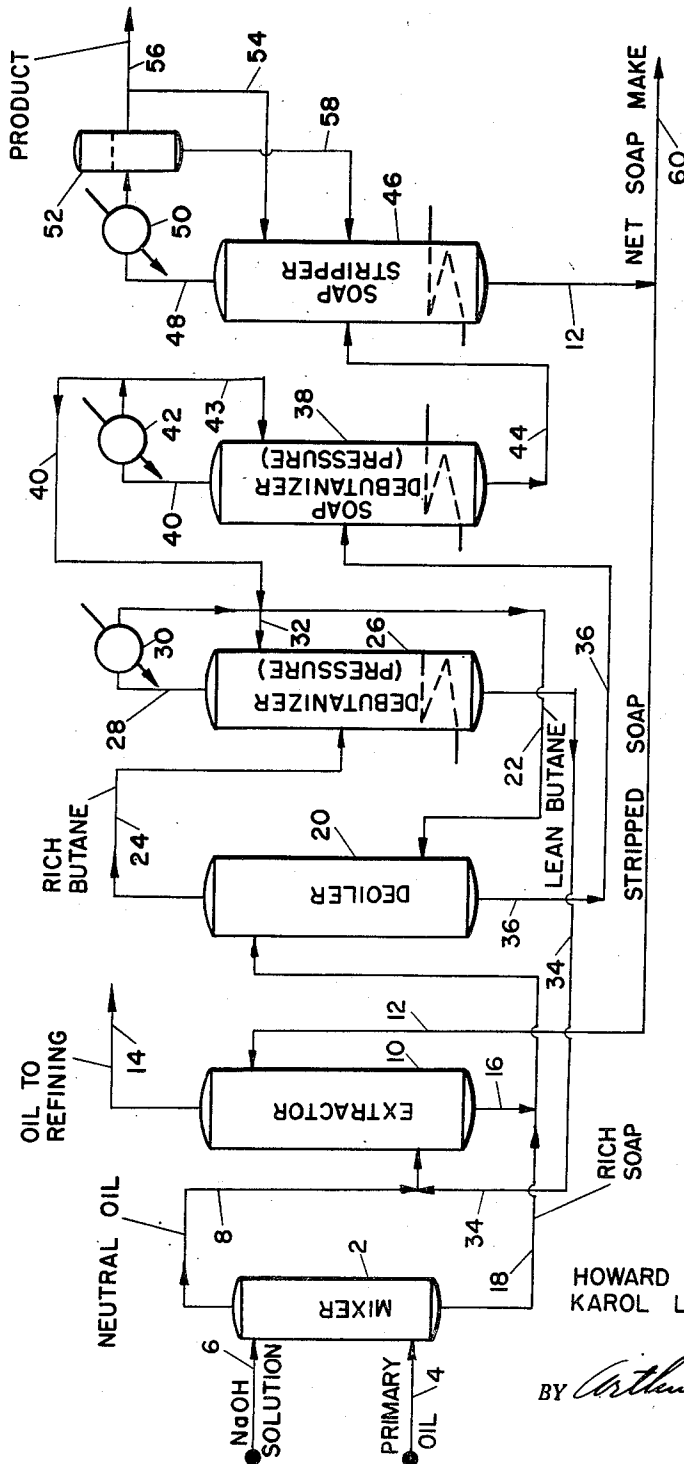
June 14, 1955

H. GREKEL ET AL
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CONTAINING OIL-SOLUBLE CHEMICALS

2,710,831

Filed May 29, 1952

2 Sheets-Sheet 1



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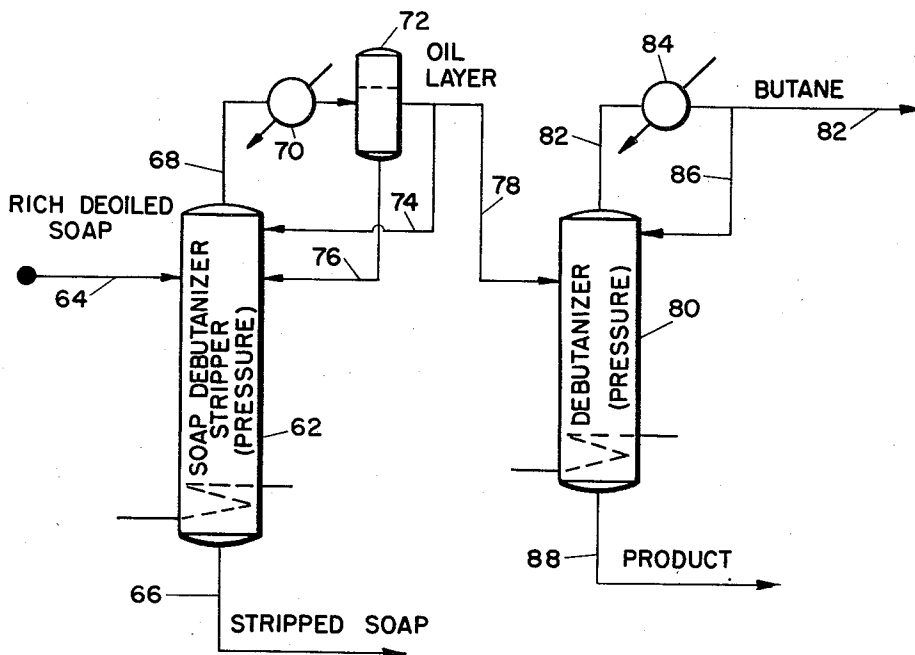


FIG. 2

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PROCESS FOR STRIPPING SOAP SOLUTIONS CONTAINING OIL-SOLUBLE CHEMICALS

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The present invention relates to the recovery of oxygenated organic chemicals from hydrocarbon-containing mixtures and the problems associated therewith. More particularly, it is concerned with the recovery of such chemicals present in hydrocarbon mixtures by soap extraction methods and to the problems encountered in recovering said chemicals from the resulting soap extract.

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 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 true sense, but are made up largely of substantially nonsurface-active salts of alkali metal, or their equivalent salts, derived from carboxylic acids having an average molecular weight ranging from about 115 to about 135. Salt or soap solutions of this type are most conveniently prepared by adding the required amount of caustic to the primary oil fraction produced in hydrocarbon synthesis, whereby the free acids present in said fraction are neutralized. By agitation of the resulting mixture, the oil-soluble chemicals tend to pass into the lower aqueous soap layer. The latter is then separated from the upper oil phase, and the dissolved chemicals recovered from the aforesaid soap solution by means of a stripping operation. In recovering the chemicals in this manner, however, severe foaming problems are encountered which reduce very substantially the capacity of the stripping column, as well as the over-all efficiency of the entire chemicals recovery operation. Numerous attempts have been made to overcome these foaming problems by the addition of known foam inhibitors to the stripping column; however, the performance of these materials was erratic. Also, it was attempted to solve the foaming problem by various physical means such as, for example, by varying the concentration of the soap solution employed, increasing the height of the disengaging space in the column, and by placing packing in the column above the feed point. While it was found that foaming could be reduced to some extent by such physical methods, these procedures all resulted in a substantially lower column capacity than that for which the particular column was designed.

Accordingly, it is an object of our invention to provide a method by which soap extracts of the type contemplated can be stripped without the occurrence of severe foaming problems and without reduction in capacity of the column. It is a further object of our invention to avoid the aforesaid foaming problems by refluxing to the stripping column a small portion of the system components. Our invention also contemplates operation of the stripping column under pressure for the purpose of reducing foaming, and refluxing of a portion of the system component to the column may be employed in combination therewith.

In carrying out a preferred embodiment of our invention, primary oil from hydrocarbon synthesis is first mixed with sufficient caustic to neutralize the free acids in the oil, the resulting salts or soaps forming a lower aqueous phase which separates from the neutral oil. The neutral oil is next extracted with a lean soap solution, of the type hereinafter defined, and the resulting extract which contains oxygenated chemicals and some solubilized hydrocarbons is combined with the chemical-rich aqueous soap solution formed in the above-mentioned neutralization step. These combined streams are then subjected to extraction with a light hydrocarbon, hereinafter referred to as "deoiling" or "deoiling step," such as for example, liquid propane or liquid butane, for the purpose of removing from the soap solution any hydrocarbon dissolved by the soap in the neutralization step. The raffinate from this extraction, consisting chiefly of an oil-free soap solution containing oil-soluble oxygenated organic chemicals, is then fractionated under pressure to separate any light hydrocarbon solvent present, after which the soap solution is stripped free of chemicals in a conventional bubble-cap still. It is at this point that excessive foaming occurs. However, in accordance with our invention, such foaming is prevented by returning a relatively small portion of the resulting organic distillate layer to the top of the stripping tower. The quantity of the aforesaid distillate layer to be refluxed to the stripping column will, within limits, depend upon the means employed to distribute or dispense the distillate into the top of the tower. In general, a minimum of the organic distillate layer is required for a given soap solution to be stripped, if said distillate organic layer is returned to the top of the column in finely divided form by means of a spray device or other suitable means so as to improve the degree of contact of the soap solution with the active foam inhibiting components of the organic layer. Usually to prevent excessive foaming in such systems, the portion of the organic layer returned to the column should be in an amount sufficient to maintain a reflux ratio such as, for example, at least about 1.5 and preferably from about 2.0 to about 3.0.

In addition to preventing foaming in operations of this type, the efficiency of the over-all operation is substantially increased, owing to the fact that the distillate water layer produced in the stripping step may be returned to the column at the feed point, rather than having to add this stream to the column reboiler as formerly practiced. By the procedure of our invention, it is possible to insure substantially complete separation of water-soluble chemicals from the aqueous lower distillate layer returned to the column because of the multiple stage stripping which it is possible to effect under these conditions. When it is attempted to avoid foaming in the column and in the distillate by returning the aqueous distillate layer to the reboiler, said layer is subjected only to single-stage stripping which, of course, cannot provide as efficient separation of the chemicals as is done by returning the aqueous layer to the column at the feed plate. Consequently, when the lower aqueous layer is returned to the column reboiler, a certain amount of chemicals inevitably passes into the stripped soap bottoms, serving to contaminate any acids derived from acidification of the soap. If the stripped soap solution is to be recycled for use as an extractant, the presence of these chemicals obviously decreases the extraction efficiency of the soap.

We have also observed that foaming under the above-mentioned conditions can likewise be prevented merely by effecting the stripping step under pressure, or by a combination of pressure and refluxing a small portion of the organic or chemical distillate layer to the column. In such an embodiment, the rich soap extract from which the bulk of the dissolved higher molecular weight

hydrocarbons has been removed, but which contains a small amount of light hydrocarbon solvent from the deoiling step, is sent to a stripping column operating under a pressure of from about 40 to about 60 p. s. i. g. The light hydrocarbons and oil-soluble organic chemicals may be withdrawn substantially free from high molecular weight hydrocarbons and sent to a second fractionating column which is also operated under pressure, the light hydrocarbons taken overhead and the chemicals removed in the form of a substantially pure bottoms product. Also, if desired, in the operation of the first column, particularly where the system has a very strong tendency to foam, a portion of the organic distillate layer may be refluxed to the column. By the use of the combination of organic layer reflux and pressure distillation, it is possible to operate the system under such conditions at maximum capacity and efficiency.

While the rich soap solutions that may be stripped in accordance with our invention are preferably those formed by the neutralization of primary hydrocarbon synthesis oil with caustic, other types of soap solutions, such as those disclosed in U. S. Patent No. 2,535,071, by S. W. Walker, likewise may be employed. Although such soap solutions normally tend to foam, when the dissolved chemicals are stripped therefrom, excessive foaming encountered in stripping operations of this type can be avoided by employing the process of our invention.

For a better understanding of our invention, reference is made to the accompanying flow diagram of Figure 1 in which the primary oil phase from hydrocarbon synthesis is introduced into mixer 2 through line 4. Sufficient sodium hydroxide in the form of an 8 to 25 per cent solution is thereafter added through line 6, with agitation, to neutralize the free acids in the aforesaid primary oil. The mixture is then allowed to stratify in two layers, after which the resulting neutral oil is withdrawn through line 8 and sent to extractor 10 where it is countercurrently contacted with a lean 25 to 50 weight per cent, preferably a 40 to 50 weight per cent, aqueous soap solution supplied by line 12 and derived from a subsequent operation to be discussed in detail below. Oil which is substantially free of chemicals is removed from the extractor through line 14 and sent to further refining. The resulting soap extract is taken from extractor 10 through line 16, combined with rich soap solution in line 18, and sent to deoiling unit 20 where it is washed with a light hydrocarbon such as butane introduced through line 22 under a pressure of from about 50 to about 60 p. s. i. By this operation, high molecular weight hydrocarbons dissolved in the soap formed in the neutralization step and in the soap used in the extraction step are removed therefrom and taken along with the butane out of the deoiler through line 24. This butane extract, containing high molecular weight hydrocarbons, and which also contains some high molecular weight chemicals, is sent to debutanizer 26 where the butane is recovered overhead through line 28 and condenser 30, a portion being returned through line 32 as reflux. The debutanizer in this step is usually operated at 50 p. s. i. g. and at a reboiler temperature of about 208° F. A portion of the butane in line 28 is returned to the deoiling step via line 22. The bottoms from debutanizer 26 which contains relatively high-boiling chemicals and hydrocarbons is returned to the extraction step by means of line 34. A rich soap solution containing chemicals together with a small quantity of butane, but substantially free from high molecular weight hydrocarbons, is taken from deoiler 20 through line 36 and introduced into soap debutanizer 38 which is also operated under a pressure of about 50 p. s. i. and at a temperature of about 275° F. A butane fraction is taken off through line 40 and condenser 42, a portion thereof refluxed to the column through line 43, and the remainder returned to deoiler 20 via lines 40

and 22. From the bottom of soap debutanizer 38 a rich soap solution free of hydrocarbons but containing oil-soluble oxygenated organic chemicals is withdrawn through line 44 and sent to stripper 46 which is preferably operated at a top tower temperature of about 200° to 205° F. An aqueous fraction of oil-soluble chemicals is taken overhead through line 48 and condenser 50 and introduced into separator 52 where the distillate is allowed to stratify into an organic and an aqueous phase. A portion of the organic layer is withdrawn and recycled through line 54 in order to prevent foaming within the column. Generally, for best results, it is desirable to introduce this stream into the top of the column in the form of a fine spray so that the contents of the column are thoroughly mixed with this reflux stream. The balance of the organic layer is taken off for further refining, if desired, through line 56. The lower water layer in separator 52, which contains water-soluble chemicals, is returned to the stripper, preferably at a point slightly above the feed plate through line 58, thus allowing more efficient stripping of the chemicals from the water. A lean soap stream is withdrawn through line 12, and a portion thereof recycled to extractor 10. Excess soap, over that required in the extraction step, is withdrawn from the system through line 60.

The flow diagram shown in Figure 2 is a modification of the system illustrated in Figure 1, wherein rich deoiled soap from the deoiling unit enters combination soap debutanizer and stripping column 62 through line 64. This column, which is operated under essentially the same conditions as are employed in column 38 of Figure 1, serves to fractionate the butane and oil-soluble chemicals from the soap removed from column 62 through line 66 in the form of a lean solution, a portion of which may be recycled to the extraction step as described above. The overhead from column 62 is taken off through line 68, condenser 70, and introduced into separator 72. The resulting distillate forms a water and an oil layer, a portion of the latter being returned to the column through line 74 for the purpose of preventing foaming within the stripper. The water layer containing water-soluble chemicals is returned to the column through line 76. A portion of the oil layer in separator 72 is withdrawn therefrom through line 78 and sent to column 80 which is operated at a reboiler temperature of about 280° F. and at a pressure of 50 p. s. i. g. A stream of substantially pure butane is taken off overhead through line 82 and condenser 84. A portion of this distillate is refluxed to the column through line 86, while the remainder may be returned through line 82 to the deoiling unit for further use as previously described. A bottoms product consisting essentially of oil-soluble oxygenated organic chemicals is withdrawn through line 88. The system shown in Figure 2 may be slightly modified, if desired, by taking the entire oil layer from separator 72, fractionating it in column 80 and returning a portion of the butane-free bottoms product from line 88 as reflux to column 62. Our invention may be further illustrated by the following specific example.

Example I

Into the bottom of a suitable extraction tower, a 40 weight per cent aqueous soap solution, derived by neutralizing the free carboxylic acids in hydrocarbon synthesis oil with caustic, is introduced at the rate of 17 pounds per hour. At the top of the extractor, neutral hydrocarbon synthesis oil is added at the rate of 12 pounds per hour. During the extraction operation the temperature of the liquids within the extractor is maintained between about 60° and 70° F. Raffinate is withdrawn at rate of about 11 pounds per hour and the extract layer removed at 18 pounds per hour. Rich soap from the extractor is introduced into the deoiling unit at 16 pounds

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per hour, while soap from the neutralization step is added at the rate of 2 pounds per hour. Butane is introduced at the rate of 1 pound per hour. The deoiling operation is carried out at a pressure of about 51 p. s. i. g. and at a temperature of 65° F. Butane rich in high molecular weight hydrocarbons is withdrawn at the rate of about 1 pound per hour. This deoiled soap stream is subjected to fractionation in a column having a reboiler temperature of 279° F. and at a pressure of about 50 p. s. i. g. whereby butane present in the soap solution is removed overhead. The resulting butane-free, rich, oil-soluble chemicals are next introduced into a suitable stripping column operated at atmospheric pressure and at a top tower temperature of about 207° F. Under these conditions, the organic distillate layer is withdrawn from the system at a rate of about 1 pound per hour. This organic layer is refluxed to the column at a ratio of about 3:1 through an open pipe, and under these conditions foaming does not occur in the column to an objectionable extent and the distillate obtained is free from soap contamination. On discontinuing reflux of the organic layer, excessive foaming occurs within about five minutes after the refluxing step has been stopped. The bottoms fraction is withdrawn from the stripper at the rate of 18 pounds per hour and consists essentially of lean soap suitable for use in further extraction operations. The aqueous distillate layer containing water-soluble chemicals is returned to the column with the feed at a rate of 15 pounds per hour.

Example II

In a similar run, without the use of organic layer reflux to the stripper, the process shown in Figure 2 is employed. The soap debutanizer-stripper column is operated at the same rates as described in the above example but at 51 p. s. i. g. Water layer reflux to the distillation zone is 2 pounds per hour, and the distillate organic layer is withdrawn at a rate of about 1 pound per hour. Under these conditions of operation, objectionable foaming is avoided.

It will be obvious to those skilled in the art to which the present invention relates that numerous modifications in manipulative steps may be made in the procedures described above without departing from the scope thereof. In general it may be said that our invention contemplates the prevention of foaming in soap stripping columns, employing as feed soap solutions of the class herein defined and containing oil-soluble organic chemicals of the type produced in hydrocarbon synthesis, by refluxing to said columns a portion of the distillate organic layer produced by the stripping operation.

What we claim is:

1. In a process for the recovery of oil-soluble oxygenated organic chemicals from aqueous solutions containing from about 25 to about 50 weight per cent of a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid which solutions tend to foam when subjected to distillation, the steps which comprise introducing a mixture containing said chemicals and salt solution into a distillation zone, taking overhead a mixture comprising essentially said oil-soluble chemicals and water, allowing said mixture to stratify into an upper organic layer and a lower aqueous phase, and returning said organic layer to said distillation zone in a minor amount but sufficient to maintain a reflux ratio of at least 1.5

2. A method for preventing the occurrence of foaming during the distillation of an aqueous solution containing from about 25 to about 50 weight per cent of a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid and oil-soluble oxygenated organic chemicals produced by the hydrogenation of carbon monoxide in the presence of an alkali-promoted fluidized iron catalyst which comprises introducing said solution into a distillation zone, taking overhead a mixture comprising essentially said oil-soluble chemicals and water, allowing said mixture to stratify into an upper or-

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ganic layer and a lower aqueous phase, and returning said organic layer to said distillation zone in an amount sufficient to maintain a reflux ratio of from about 2.0 to about 3.0.

3. A method for preventing the occurrence of foaming during the distillation of an aqueous solution containing from about 25 to about 50 weight per cent of a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid which comprises introducing said solution into a distillation zone, taking overhead a mixture comprising essentially said oil-soluble chemicals and water, allowing said mixture to stratify into an upper organic layer and a lower aqueous phase, and returning said organic layer to said distillation zone in the form of a spray and in an amount sufficient to maintain a reflux ratio of from about 2.0 to about 3.0.

4. The process of claim 3 in which the aqueous solution contains a mixture of salts derived from carboxylic acids varying in an average molecular weight from about 115 to about 135.

5. A method for preventing the occurrence of foaming during the distillation of an aqueous solution containing from about 25 to about 50 weight per cent of a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid and oil-soluble organic chemicals produced by the reaction of carbon monoxide with hydrogen which comprises introducing said solution into a distillation zone, taking overhead a mixture comprising essentially said oil-soluble chemicals and water, allowing said mixture to stratify into an upper organic layer and a lower aqueous phase, and returning said organic layer to said distillation zone in the form of a spray and in an amount sufficient to maintain a reflux ratio of from about 2.0 to about 3.0.

6. A method for inhibiting foaming during distillation of an aqueous solution containing from about 25 to about 50 weight per cent of a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid, a light hydrocarbon and oil-soluble oxygenated organic chemicals produced by the hydrogenation of carbon monoxide in the presence of an alkali-promoted fluidized iron catalyst, which comprises introducing said solution into a distillation zone, taking overhead a mixture consisting essentially of said chemicals, water and light hydrocarbon, allowing said mixture to stratify into an upper organic layer and a lower aqueous layer, separating said organic layer and removing said light hydrocarbon therefrom, and returning said organic layer to said distillation zone in an amount sufficient to maintain a reflux ratio of from about 2.0 to about 3.0.

7. A method for inhibiting foaming during distillation of an aqueous solution containing from about 25 to about 50 weight per cent of a substantially nonsurface-active salt of a preferentially oil-soluble carboxylic acid, a light hydrocarbon and oil-soluble oxygenated organic chemicals produced by the hydrogenation of carbon monoxide in the presence of an alkali-promoted fluidized iron catalyst, which comprises introducing said solution into a distillation zone, taking overhead a mixture consisting essentially of said chemicals, water and light hydrocarbon, allowing said mixture to stratify into an upper organic layer and a lower aqueous layer, and returning said organic layer to said distillation zone in the form of a spray and in a minor amount but sufficient to maintain a reflux ratio of at least about 1.5.

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