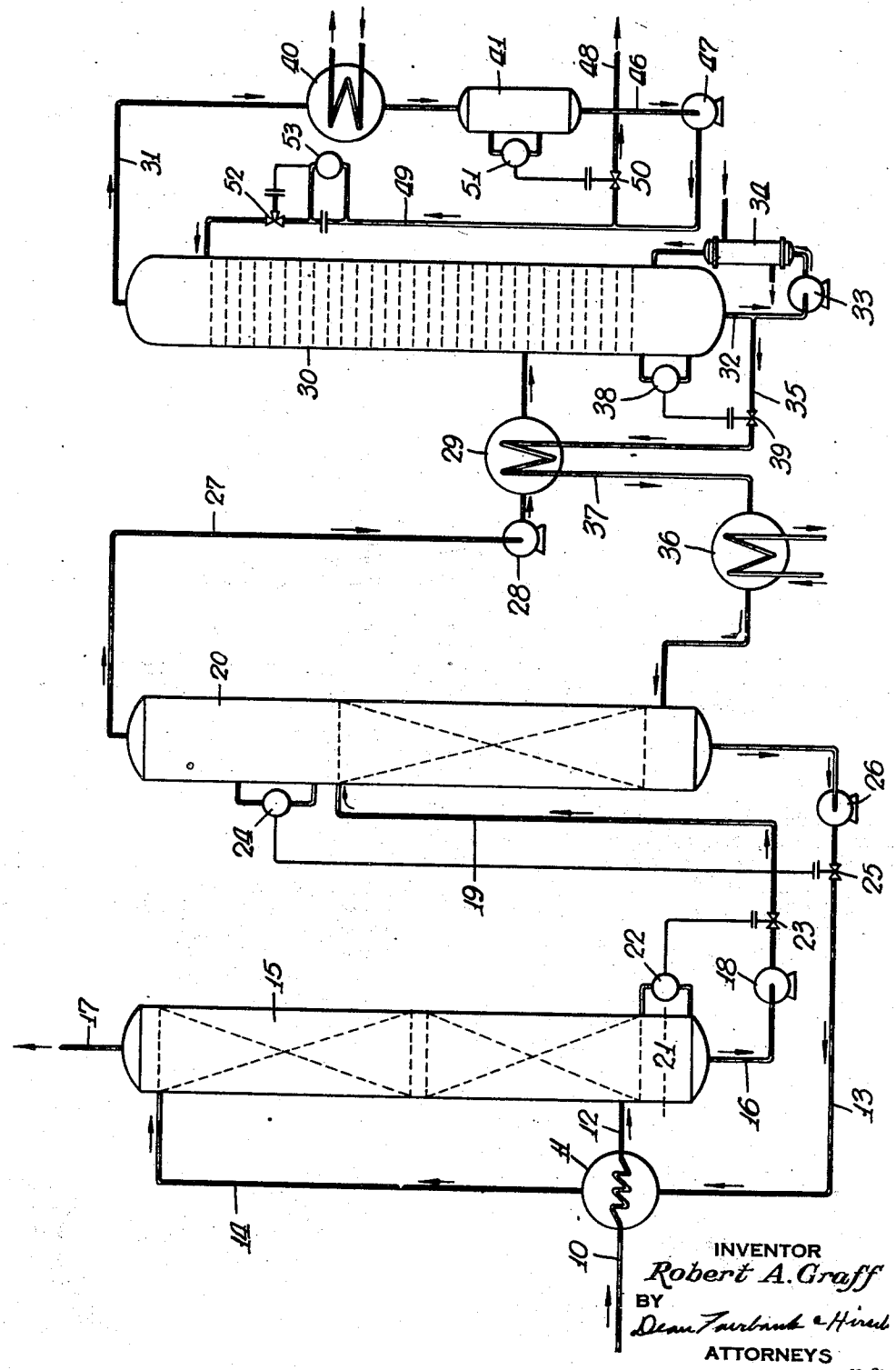
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SEPARATION AND RECOVERY OF UNSATURATED GASES

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SEPARATION AND RECOVERY OF UNSATURATED GASES

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This invention relates to the separation and recovery of unsaturated gases from the general type of aqueous copper-bearing ammoniacal solutions which have been heretofore proposed and used for the selective separation of unsaturated gases from gaseous mixtures.

Such solutions usually contain dissolved salts of organic acids, such as formic, acetic, lactic, etc., and basic nitrogen compounds soluble in aqueous solutions, such as ammonia and amines. The amines may be alkanol amines or polyamines, and the copper compound may be cuprous chloride. Such compounds have a selective action on unsaturated hydrocarbons, and may therefore be used for the separation of the unsaturated from the saturated hydrocarbons, particularly those hydrocarbons which are in gaseous or vapor form. More specifically, the present process relates to the recovery of 1,3-butadiene, from the hydrocarbon products resulting from cracking or reforming operations.

It has been common practice to recover dissolved unsaturated hydrocarbons, and particularly 1,3-butadiene, from copper bearing ammoniacal solutions by boiling at atmospheric pressure, or at reduced pressures. This boiling entails heating the copper bearing solutions containing the dissolved unsaturated hydrocarbons to an elevated temperature. During this heating step, a considerable portion of the ammonia may be driven off, thereby weakening the solvent and requiring separation of the ammonia from the butadiene and the return of the ammonia to the solution. The heating also results in a certain amount of the butadiene being lost by polymerization, and it requires a large amount of heat exchange equipment for the heating and cooling of the liquids and vapors. The large amount of heat required for driving off the absorbed unsaturated hydrocarbons necessitates an equally large amount of cooling. In such a process, ammonia is the nitrogen compound commonly employed, and it is not practical to use amines, as they readily oxidize with heat.

In carrying out the present process the butadiene is removed from the copper bearing solution by the action of a stripping agent which is non-soluble or only slightly soluble in the solution, which is miscible with but does not react with the butadiene, which has low viscosity, which does not dissolve or react with ammonia, amines or other constituents of the copper bearing solution, and which may be easily separated from the hydrocarbons for reuse in the process. The medium is preferably one which has a boiling

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point quite different from that of butadiene, said medium being a liquid hydrocarbon which preferably has five or more carbon atoms.

The preferred examples of such a stripping agent are light hydrocarbon oils composed essentially of octane, heptane or hexane, or mixtures thereof, having a boiling point in the general vicinity of 100° F. Various other stripping agents may be used, such as suitable alcohols, ketones, aldehydes, phenols, or related compounds, or other liquids such as carbon tetrachloride.

The invention permits the regeneration of the unsaturated hydrocarbon bearing copper solution without the application of heat, and further permits the recovery of the dissolved hydrocarbon in the liquefied condition, whereas the vapor phase is the condition of the product when the conventional methods of reactivating copper bearing solvents are used.

By means of the present process a very much smaller amount of heat exchange equipment is required, polymerization of the unsaturated hydrocarbon is kept at a minimum, no extensive ammonia recovery equipment is required, and no compressors are required for the recovery of unsaturated hydrocarbon in liquefied condition if the hydrocarbon be of a type which is in gaseous form at atmospheric temperature and pressure.

The butadiene may be removed by blowing the enriched stripping agent containing the unsaturated hydrocarbon with a stripping gas such as steam or ammonia. If ammonia is used, it may be then separated from the unsaturated hydrocarbon gases by water washing, and if steam is used, it may be separated from the unsaturated hydrocarbon by fractional condensation.

The following is a specific example of applicant's process as employed for separating butadiene from gaseous hydrocarbon mixtures and removing the butadiene from the solvent by the use of hexane.

A gaseous hydrocarbon mixture containing n-butane, butene-1, butene-2, isobutylene and 25 mol. per cent 1:3 butadiene is contacted at 40° F. in a packed tower with a cuprous-cupric ammonium acetate solvent containing an excess of ammonia, and this solution, which will contain approximately 16 vols./vol. of substantially pure butadiene, is passed into a second contacting tower where the rich solvent is introduced at the top and flows down to the bottom of the tower countercurrently contacting hexane, which is introduced at the bottom of the tower and withdrawn at the top. The regenerated copper bear-

ing solvent is drawn off at the bottom of the tower and the hexane phase, which now contains substantially all of the 1:3 butadiene formerly held by the rich solvent, flows to a continuous fractionating still, operating under pressure, where the butadiene product is taken overhead and condensed, and the bottoms from the fractionating still are cooled through heat exchange and returned to the extraction process. The condensed butadiene now recovered as a liquid product may be used in any of the conventional processes for the production of elastomers.

In the accompanying drawing there is shown diagrammatically the apparatus units which may be used in a commercial process for separating butadiene from mixtures containing saturated hydrocarbons, and the flow lines of the various liquids and gases employed.

To simplify a description of the process as carried out in this apparatus, reference will be made to butadiene as the unsaturated gas to be obtained, and butane the saturated gas with which it was mixed. It is to be understood that these are given as examples, and not to indicate specific limitations on the scope of the invention.

The mixture of butane and butadiene, together with other saturated and unsaturated hydrocarbons, in liquid form, under pressure, and at atmospheric temperature, is delivered through the line 10 to a heat exchanger 11, where the pressure is reduced, the liquid converted to gaseous form, and the amount of heat absorbed is only about equal to the heat of vaporization of the mixture. The mixture in gaseous form is then delivered through the line 12 at a low temperature, for instance about 30° F., and at about atmospheric pressure. The copper bearing solution, which may be a reagent containing cuprous copper, an organic acid, excess ammonia and water, is circulated in a closed cycle. It is delivered at a temperature of 50° F. or higher, is cooled by the vaporizing mixture of butane and butadiene in the heat exchanger 11, and is delivered from the heat exchanger through the line 14 at a lower temperature, for instance about 35° F.

A packed column or absorber 15 is provided, in which the packing may be of any common type permitting the downflow of liquid and the upflow of gases or vapors in intimate contact with each other. The copper containing solution is delivered through the line 14 to the upper part of the column 15, and the gaseous mixture containing the butadiene is delivered through the line 12 to the base of the column. During the upflow of the vapors and the downflow of the solvent, the butadiene is selectively absorbed by the copper solution. The rich solution is withdrawn from the bottom of the tower through the line 16, and the butane and other gases which are not absorbed pass off from the top of the column through the line 17. So far as concerns the general principles of operation of the packed column, this process step and the apparatus employed need not differ essentially from that heretofore commonly employed.

The rich solvent withdrawn through the line 16 is delivered by a pump 18 through the line 19, and the rate at which it is withdrawn may be so controlled as to maintain a liquid level at the bottom of the column at approximately the point 21. The control may be obtained by the use of conventional flow control apparatus diagrammatically illustrated as a liquid level controller 22 for applying pressure to the diaphragm of a valve 23 in the line 19.

The pump 18 and line 19 deliver the rich solution to a second column or desorber 20, in which the butadiene is washed out of the copper solution by the stripping agent in liquid form. This stripping agent will hereinafter be referred to as "hexane," but this term is here used only to simplify the description, and without limitation to the particular stripping agent employed.

As previously noted, the stripping agent and the copper containing solvent are immiscible, so that they tend to form separate layers. The liquid level between the two layers in the desorber column 20 is maintained near the upper part of the column, and this is likewise effected by a suitable form of liquid level controller 24 applying pressure on the diaphragm of a valve 25 in the line 13 which leads from the bottom of the desorber 20, and which line includes a suitable circulating pump 26. The rate of circulation may be varied through comparatively wide limits by regulation of the speed of either or both of the pumps 18 and 26. By circulating a large amount of the copper solution, very little refrigeration is required. Refrigerating the copper solution to about 25° F. before delivering to the top of the absorber column 15 would result in a somewhat more complete removal of the butadiene from the butane, but delivering the solution to the column at a temperature of about 35° F., or even up to 50° F., is more economical in many respects.

The liquid hexane or other stripping agent containing the dissolved butadiene is taken from the top of the column 20 through the line 27, and is delivered by a pump 28 through a heat exchanger 29 to the lower portion of a fractionating column 30. In this column the hexane is heated to such a temperature as will cause the butadiene to volatilize under about 75 pounds pressure, and the gaseous butadiene passes off from the top of the column 30 through the line 31.

In order to provide the required heat, the hexane may be continuously withdrawn from the bottom of the column 30 through a line 32 by a pump 33, heated in a heater 34, and returned to the column 30 at a point somewhat above the bottom, at the required temperature. Thus the heating is effected by circulating a portion of the hexane through the heater 34, and the amount of heat delivered to the column 30 may be controlled by the temperature or volume of the steam or other heating medium used in the heater 34, or by controlling the speed of the pump 33, or by both.

The heated hexane or other stripping agent, which is substantially free from butadiene, is withdrawn from the bottom of the column 30 through the line 35, and delivered through the heat exchanger 29 and a cooler 36. A portion of the heat of the stripped hexane is thus transferred to the enriched hexane delivered to the column 30 through the line 27, and the residual heat of the liquid hexane leaving the heat exchanger 29 through the line 37 is removed by the cooler 36, so that cold liquid hexane is delivered to the lower portion of the column 20. The rate of withdrawal from the column 30 may be such that a fairly constant liquid level is maintained in the column 30 near the lower end thereof, and this may be effected by a liquid level controller 38 acting on the diaphragm of a valve 39 in the line 35. No pump is required for the return of the stripping agent from the column 30

to the desorber 20, as the former is maintained at a higher pressure than the latter.

The butadiene separated from the liquid hexane and leaving the column 30 through the line 31 is cooled to such a temperature that it will liquefy under the pressure employed in the column 30, which temperature might be in the neighborhood of 100° F., if the pressure in the column 30 is about 75 pounds. This cooling may be effected by any suitable form of condenser 40 in the line 31 which delivers to a small tank 41. From the bottom of this tank the liquid butadiene may be continuously withdrawn through a line 46, by a pump 47, and is preferably divided into two parts by the lines 48 and 49, the relative proportions of the parts being varied at will. Through the line 48 the butadiene product is delivered from the system in liquid form to any suitable point of storage or use. If it contains any traces of ammonia picked up in the column 15, such traces may be removed by water washing. The flow through the line 48 is controlled by a valve 50, the diaphragm of which is actuated by a liquid level controller 51, so as to maintain a substantially constant liquid level in the tank 41.

The butadiene delivered through the line 49 passes to the upper portion of the column 30 to act as a reflux, and its flow is controlled by a valve 52, the diaphragm of which is actuated by an orifice type flow controller 53 in the line 49.

It will be understood that various other types of apparatus parts and other details may be varied through a wide range for carrying out my improved process.

In the process as above described, the column 30 is operated under a superatmospheric pressure, for instance about 75 pounds gauge pressure. This is not essential, as the column 30 may be operated at atmospheric pressure, but in that event the butadiene, which leaves the top of the column as a vapor, must be compressed if it is to be delivered from the system in liquid form.

In the process as above described, the butadiene is removed from the hexane by the action of heat, but at a temperature below that at which the butadiene is liable to polymerize. It is not essential that heat be employed, as ammonia may be delivered to the bottom of the column 30 in place of heat, and the mixture of ammonia and butadiene delivered by line 31 may be readily separated by water washing, as ammonia is very soluble in water, whereas butadiene is substantially insoluble.

If the stripping agent be a hydrocarbon liquid of relatively high boiling point (345° F.), such for instance as a C_{10} hydrocarbon, the butadiene in solution may be driven off in vapor form by blowing steam through the column 30. In this case, upon cooling the outgoing vapors, the butadiene will readily separate from the condensed steam.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. The process for separating butadiene from a solution of cuprous-cupric ammonium acetate containing an excess of ammonia which includes extracting said butadiene from said solution in an absorber by the action of a liquid hydrocarbon stripping agent immiscible with said solution and having a boiling point substantially above that of butadiene, thereafter separating said stripping agent from the butadiene in a desorber by blowing therethrough a gaseous medium immiscible with the stripping agent and the butadiene, separating said medium from the butadiene and returning a part of the butadiene in liquid form to the top of the desorber to reflux vapors of said liquid hydrocarbon.

2. The process of separating butadiene from a solution containing a dissolved cuprous compound and a basic nitrogen compound soluble in aqueous solutions which includes extracting the butadiene from said solution by the action of a stripping agent which is immiscible with said solution, non-reactive with said butadiene and has a boiling point substantially higher than that of butadiene, thereafter driving off the butadiene from the stripping agent in a desorber, blowing a gaseous medium therethrough, cooling the butadiene vapors to condense them to liquid form under said pressure, and returning a part of the liquid butadiene to the top of the desorber to reflux vapors of said stripping agent.

3. The process of separating butadiene from a solution of cuprous-cupric ammonium acetate containing an excess of ammonia which includes extracting said butadiene from said solution in an absorber by the action of a liquid hydrocarbon stripping agent having a boiling point substantially above that of butadiene, thereafter driving off the butadiene from said stripping agent in a desorber by blowing ammonia up through said desorber, and water washing the ammonia from the butadiene leaving the top of the desorber.

4. The process of separating butadiene from a solution of cuprous-cupric ammonium acetate containing an excess of ammonia which includes extracting said butadiene from said solution in an absorber by the action of a liquid hydrocarbon stripping agent having a boiling point substantially above that of butadiene, thereafter driving off the butadiene from said stripping agent in a desorber by blowing ammonia up through said desorber, water washing the ammonia from the butadiene leaving the top of the desorber and returning a part of the separated liquid butadiene to the top of the desorber to reflux vapors of said stripping agent.

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