

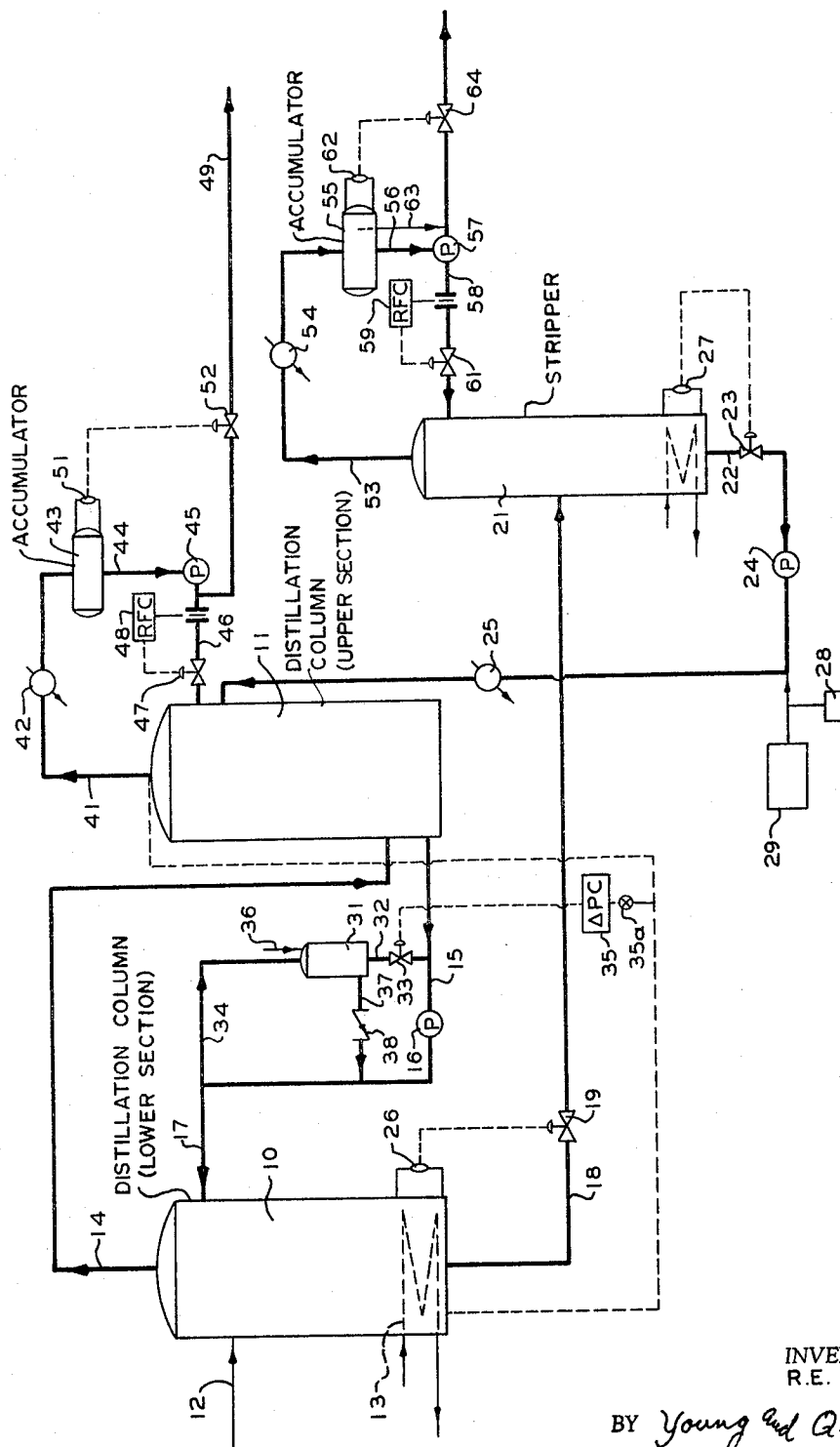
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3,264,365

FOAM CONTROL IN SEPARATION OF HYDROCARBONS

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ATTORNEYS

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3,264,365 FOAM CONTROL IN SEPARATION OF HYDROCARBONS

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This application is a continuation-in-part of my co-pending application Serial No. 160,068 filed December 18, 1961.

This invention relates to the separation of hydrocarbons by means of a solvent. In one aspect this invention relates to control of foam in an extractive distillation of hydrocarbons wherein a solvent is utilized. In a more specific aspect this invention relates to the detection of incipient flooding conditions in an extractive distillation operation and to the prevention of such flooding.

In a commercial process for the manufacture of butadiene, including the steps of butane dehydrogenation to butenes, butene recovery or purification, butene dehydrogenation to butadiene, and butadiene recovery or purification, the use of furfural as a selective solvent in the extractive distillation of butenes and butadiene has made the process practical and economical. The use of furfural permits separations of C_4 hydrocarbons which were heretofore considered either impractical or impossible on a commercial scale. Such separations are necessary for the production of high purity butadiene.

One of the major problems encountered in the extractive distillation of C_4 hydrocarbons for the recovery of butenes and butadiene and for the separation of butadiene from butenes has been that of flooding or stacking in the extractive distillation column as a result of furfural foaming. It has heretofore been discovered that certain polymeric organo-silicon compounds are useful for reducing the foaming of furfural in an extractive distillation operation and a method for reducing furfural foaming has been disclosed and claimed in U. S. Patent 2,750,435 issued June 12, 1956, to John Fetchin. The use of organo-silicon polymers such as liquid polydimethyl siloxane has been found to be extremely beneficial in providing a measure of control of furfural foaming and hence column stacking in the extractive distillation of C_4 hydrocarbons. Since these siloxanes are expensive materials and are not recoverable in the operation, it is desirable to use the minimum amount of material which will provide satisfactory operation of the extractive distillation columns. Experience has indicated that about 1 or 2 parts per million of a polymeric organo-silicon compound such as polydimethyl siloxane will provide satisfactory operation when the extractive distillation column is operating at normal conditions. Although the practice of maintaining 1 or 2 parts per million of the siloxane in the furfural solvent employed in the extractive distillation process provides, under normal conditions, satisfactory operation, there still occur periods of unbalance in the extractive distillation operation which result in column stacking and necessitate reduction of feed to the column as well as reduction of heat input to the column until normal operation can be resumed. The cause or causes of such periods of unbalance have not been determined. The operation of an extractive distillation column is a delicate operation which requires a proper balance of a great number of variables including temperature, pressure, feed rates and withdrawal rates. Any change in operating conditions which tends to upset this delicate balance can result in stacking in the column.

It is an object of this invention to provide a method for preventing the occurrence of flooding or stacking in an extractive distillation operation. It is also an object of this invention to provide a means for detecting incipient

stacking conditions and for effecting prevention of such stacking. A still further object of this invention is to provide a means for sensing conditions leading to stacking in a column and to introduce into the column a material to prevent such stacking. Other objects and advantages will be apparent to one skilled in the art upon study of this disclosure including the detailed description of the invention and the appended drawing wherein:

The sole figure is a schematic flow sheet illustrating the operation of the invention.

Broadly, the invention contemplates the prevention of stacking in an extractive distillation column by dumping into the column, preferably at a lower portion thereof, an amount of a polydimethyl siloxane equal to about the amount which is normally added over an 8-hour period when the differential pressure from the bottom of the column to the top of the column exceeds a value indicating incipient stacking. Stacking or flooding of the column is preceded by an increase in the differential pressure across the column resulting from the increased quantity of liquid on the trays of the column. Attempts to alleviate this condition by increasing the quantity of siloxane in the furfural added to the column have been unsuccessful and in each instance it has been necessary to reduce the feed of hydrocarbon and solvent to the column and to reduce the input of heat to the column until the excess liquid has been vaporized and removed. The column can then be brought back to normal operation gradually. I have discovered that stacking of the column can be avoided by the introduction of a large slug of siloxane into the lower portion of the column when the pressure drop across the column indicates that the column is in a state of unbalance which, experience has shown, results in stacking of the column.

Since the invention herein described is directed to the concept of preventing stacking in a distillation column during the extractive distillation of a hydrocarbon, and since the extractive distillation technique can be employed for separating a variety of hydrocarbons, it is apparent that the invention can be applied to any extraction wherein a less saturated hydrocarbon is separated from a more saturated hydrocarbon by means of a solvent. For example, the invention can be practiced in connection with the separation of hydrocarbons wherein the individual molecules contain from three to seven or more carbon atoms each. Thus, the invention can be used to prevent stacking in an extractive distillation zone which is used to separate a less saturated C_3 hydrocarbon from a more saturated C_3 hydrocarbon, such as propylene from propane, or a less saturated C_4 hydrocarbon from a more saturated C_4 hydrocarbon, such as butene from butane. The invention can also be used to prevent stacking in an extractive distillation zone wherein a solvent is used to separate a less saturated C_5 hydrocarbon from a more saturated C_5 hydrocarbon, such as pentene from pentane or pentadiene from pentene. Further uses for the invention include processes of separating heptene from heptane, normal hexane from cis-2 hexene, and cyclohexane from isoheptenes.

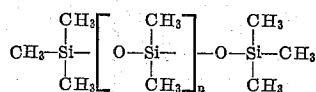
The invention may be more readily understood by reference to the drawing wherein an extractive distillation column comprising two sections is represented by the lower section 10 and the upper section 11, each of which contains 50 conventional bubble cap trays. Hydrocarbon feed is introduced into the lower section 10 at about the 41st tray via conduit 12. Heat is supplied to the kettle of the column by a heater indicated at 13 which can be a steam coil or other conventional heating element. The overhead vapors from the lower section 10 are passed via conduit 14 to the lower portion of the upper section 11. Liquid from the bottom of the upper section 11 is passed via conduit 15, pump 16 and conduit 17 to the

top of the upper section 10. The kettle product from the lower section 10, comprising rich furfural solvent, is passed via conduit 18 containing motor valve 19 to the stripper 21 for regeneration of the solvent and lean solvent is removed from the bottom of stripper 21 via conduit 22 containing motor valve 23 and passed through pump 24 and cooler 25 and introduced into the upper portion of upper section 11. Valve 19 is actuated by liquid level controller 26 and valve 23 is actuated by liquid level controller 27. A proportioning pump 28 adds siloxane from a reservoir 29 to conduit 22. Reservoir 31 contains a quantity of polydimethyl siloxane equivalent to that added over a period of about 8 hours by proportioning pump 28. Siloxane is introduced into conduit 15 as a single dump via conduit 32 and motor valve 33. An equalizing line 34 connects the top of reservoir 31 with conduit 15 downstream from pump 16. Motor valve 33 is actuated by differential pressure controller 35 which senses the pressure at the top of section 11 and the bottom of section 10 of the extractive distillation column and opens valve 33 when the differential of these two pressure values exceeds a predetermined value. The differential pressure controller closes valve 33 when the differential pressure returns to normal and reservoir 31 is then ready to be recharged with siloxane for the next occasion of unbalance of the extractive distillation column. Charging of the reservoir 31 with the siloxane is accomplished by forcing a measured quantity of siloxane into reservoir 31 via conduit 36. The siloxane displaces the heavier furfural downwardly through conduit 37 containing check valve 38 and into conduit 15.

The overhead vapors from the extractive distillation step are removed via conduit 41, cooled and condensed in cooler 42, and passed to accumulator 43 from whence the condensate is removed via conduit 44 by pump 45, a measured portion of the condensate being returned to section 11 as reflux via conduit 46 containing motor valve 47 which is operated by rate of flow controller 48. The remainder of the condensate is removed as product via conduit 49, the quantity being governed by liquid level controller 51 actuating motor valve 52 in conduit 49. The overhead vapors from stripper 21 are removed via conduit 53, cooled and condensed in cooler 54 and passed to accumulator 55. A portion of the condensate is removed from accumulator 55 via conduit 56 and passed via pump 57 and conduit 58 to the top of stripper 21 as reflux as controlled by rate of flow controller 59 which controls valve 61 in conduit 58. Excess condensate as determined by liquid level controller 62 is removed from accumulator 55 via conduit 63 containing motor valve 64 which is actuated by liquid level controller 62.

Differential pressure controller is composed of the controller-recorder 35 which can be, for example, a Foxboro Model 58P2 controller, Model 56 Recorder; and the differential pressure transmitter 35a which can be a Foxboro Type 13A d/p cell, differential pressure transmitter. Such instruments are well known and are commercially available. The controller is set at the value at which action is to be taken. For example, the controller can be set at 10 p.s.i. differential so that valve 33 is opened wide when the differential pressure is above about 10.1 p.s.i. and will be completely closed at 9.9 p.s.i.

The siloxanes which have been found effective in the process of the invention are the organo-silicon polymers represented by the empirical formula



wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes, and preferably at least 100 centistokes at 25° C. and may be classed as polydimethyl siloxanes. Polydimethyl siloxanes suitable for use in the process of the invention are marketed by Dow

Corning Corporation as "DC 200 Fluids" and "DC Anti-foam A."

The continuous addition of siloxanes to reduce foaming of furfural in the extractive distillation of C_4 hydrocarbons is described in the above-referred to Patent 2,750,435.

The drawing illustrates a typical operation wherein the process and apparatus of the claims has been successful in preventing or decreasing the severity of flooding in the extractive distillation step in the separation of n-butane and butene-2. The extractive distillation column or absorber is 13½ feet in diameter and is divided into two 50-tray sections. The hydrocarbon feed is introduced onto the 41st tray and the furfural solvent is introduced onto the 96th tray. The ratio of solvent to hydrocarbon is about 6½ to 1 on a volume basis. The column pressure is about 60 p.s.i. at the top and about 65 p.s.i. at the bottom. The kettle temperature is about 310° F. and the top temperature is about 120° F.

During the run now being considered siloxane (DC 200 Fluid) was added continuously to the furfural feed to the absorber at a rate of about 1 p.p.m. (volume) per pass of furfural through the absorber. The siloxane was added as a solution of siloxane in deoiler bottoms (C_5 and heavier hydrocarbons including those containing 10 carbon atoms or more per molecule obtained as kettle product in the distillation of C_4 hydrocarbons in the process of dehydrogenation of C_4 hydrocarbons to form butadiene) as described in Patent 2,750,435.

The pressure drop across the absorber was relatively steady at 4 to 5 p.s.i. for about 20 hours of the day's run under consideration and then began to increase rapidly to about 11 p.s.i. so that the reservoir 31, containing two gallons of a 50-50 mixture of siloxane in deoiler bottoms, was dumped into the lower portion of the absorber. This amount of siloxane is equivalent to about 5 p.p.m. (volume) based on the per pass of furfural through the absorber. The pressure drop across the absorber returned to normal within about 30 minutes and continued to operate at normal for the rest of the day. The next day the pressure drop was normal for the first 14 hours of operation, then began to fluctuate between 2 and 6 p.s.i. After about 4 hours of rough operation, as indicated by the fluctuating pressure drop, the pressure drop began to increase rapidly indicating that flooding or stacking was beginning to occur and at 10 p.s.i. differential pressure the reservoir containing two gallons of a 50-50 mixture of siloxane and deoiler bottoms was dumped into the lower portion of the absorber. The pressure differential from bottom to top of the absorber dropped to normal in about one hour and the absorber continued to operate normally.

The cause or causes for these two conditions of unbalance in the absorber on two successive days is not known but the rapid return to normal operation indicates that the slug of siloxane acts as a defoaming agent as distinguished from the antifoaming agent characteristics of the siloxane which is added continuously.

Practice of the invention achieves a savings in siloxane by allowing the use of the minimum amount necessary during normal operation. Prevention of the occurrence of flooded conditions in the absorber also prevents unbalance in operations downstream from the absorber; for example, a flood in the absorber means that there is an excess of liquid in the absorber so that the feed to the furfural stripper is thereby reduced. A reduction in the feed to the stripper can cause furfural to be passed out of the stripper with the overhead vapors, necessitating reprocessing of the stripper overhead vapors to recover the furfural.

It is to be understood that a greater amount of siloxane than about 5 p.p.m., based on a per pass of furfural through the absorber, can be added to the absorber to stop a flooding condition which has started. It is also possible that in some situations a smaller amount of siloxane will be sufficient; however, since the cause of

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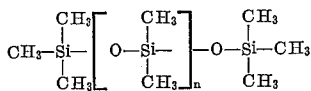
the flooding is not known in each instance, I prefer to add an amount at least equivalent to about 5 p.p.m. (volume) based on the per pass of furfural through the absorber.

Although the invention has been described in connection with the extractive distillation step in the separation of n-butane from butene-2, it is obviously within the scope of this invention to employ the inventive concept in connection with the separation of various other hydrocarbons including propylene from propane, pentene from pentane, and the like. In these other applications of the invention, the polydimethyl siloxane can be employed in the same concentrations and in the same manner as described in connection with the separation of n-butane from butene-2. Thus, the siloxane can be added in substantially pure form or it can be added in solution in a liquid hydrocarbon containing from about 5 to about 10 carbon atoms per molecule as described in U.S. Patent 2,750,435.

Variations and modifications are possible within the scope of the disclosure of the invention without departing from the spirit and scope of the invention.

That which is claimed is:

1. In a process for separating butene-2 from n-butane in an extractive distillation zone in the presence of a solvent comprising furfural to which is added at least about 1 p.p.m., per pass of furfural through said distillation zone, of liquid polydimethyl siloxane of the formula

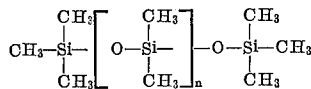


wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C., the improvement comprising adding to the lower portion of said distillation zone a single increment of said siloxane equivalent to about 5 to 10 p.p.m. by volume based on the per pass of furfural through said distillation zone when the pressure drop across the distillation zone exceeds a value indicating incipient flooding of the distillation zone.

2. The process of claim 1 wherein the siloxane is added in substantially pure form.

3. The process of claim 1 wherein the siloxane is added as a solution in a liquid hydrocarbon containing from about 5 to 10 carbon atoms per molecule.

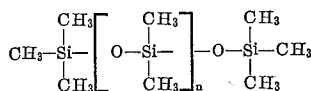
4. In a process for the manufacture of olefins from normal butane which comprises, catalytically dehydrogenating normal butane to said olefins, subjecting the C_4 hydrocarbon content of the reaction effluent to fractional distillation so as to remove the butene-1 content thereof as an overhead product and produce a bottoms product containing principally the n-butane and butene-2 content thereof, subjecting the resulting mixture of n-butane and butene-2 to extractive distillation with a solvent comprising essentially a mixture of furfural, 1 to 60 weight percent of C_5 - C_{10} hydrocarbons formed in said process and comprising principally butadiene dimer, and liquid polydimethyl siloxane of the formula



wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C. in a concentration of about 1 to 2 p.p.m. by volume per pass of furfural so as to selectively dissolve butene-2, and stripping the dissolved butene-2 from the rich solvent, the improvement comprising continuously determining the pressure drop across the distillation, and adding to the lower part of the distillation a single increment of said polydimethyl siloxane equivalent to about 5 to 10 p.p.m. by volume based on the per pass of furfural through said distillation when the pressure drop across the distillation indicates a state of unbalance which will result in flooding in the distillation.

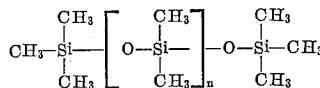
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5. In a process for separating a less saturated C_4 hydrocarbon from a more saturated C_4 hydrocarbon wherein a mixture of said hydrocarbons is subjected to an extractive distillation step in the presence of furfural solvent and at least about 1 p.p.m., based on the furfural passing through the distillation step, of liquid polydimethyl siloxane which is added to said furfural substantially continuously, said polydimethyl siloxane being of the formula



15 wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C., the improvement which comprises continuously determining the pressure drop across the distillation step; adding to the lower region of said distillation zone a single increment of said siloxane equivalent to the incremental addition of a period of about 8 hours when the pressure drop across the distillation step exceeds a value indicating incipient flooding.

6. In a system for the extractive distillation of C_4 hydrocarbons to separate a less saturated C_4 hydrocarbon from a more saturated hydrocarbon comprising an extractive distillation column, a stripping column to strip absorbed hydrocarbon from rich solvent, means to pass rich solvent from said distillation column to said stripping column, conduit means containing a pump to return lean solvent from said stripping column to said distillation column, conduit means containing a pump to introduce C_4 hydrocarbons to said distillation column, means to recover less saturated C_4 hydrocarbons from said stripping column, and means to recover more saturated C_4 hydrocarbons from said distillation column, apparatus comprising dumping means to introduce a single dump substantially instantaneously into said distillation column a measured quantity of a liquid polydimethyl siloxane of the formula



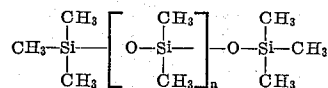
45 wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C.; pressure sensing means to sense the difference in pressure between the bottom and the top of said distillation column; pressure control means operatively connected to said sensing means and to said dumping means to dump said measured amount of said siloxane into said distillation column when the difference in pressure between the bottom and the top of said distillation column exceeds a value indicating incipient flooding of said distillation column.

7. The apparatus of claim 6 wherein said dumping means comprises a closed vessel of sufficient volume to contain the measured quantity of said siloxane; a dumping conduit connecting the bottom portion of said vessel to a conduit to introduce fluid to said distillation column at a point upstream from said pump; a motor valve in said dumping conduit operatively connected to said pressure control means; a relief conduit connecting the upper portion of said vessel to the conduit to introduce fluid to said distillation column at a point downstream from said pump; a displacement conduit connecting the lower portion of said vessel to said conduit to introduce fluid to said distillation column; a check valve in said displacement conduit to prevent flow of fluid into said vessel; and means to force a measured amount of said siloxane into the top of said vessel against the pressure in said conduit to introduce fluid to said distillation column.

8. In a process including an extractive distillation step in a distillation zone in the utilization of a solvent com-

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prising furfural in which foaming is prevented by the addition of liquid polydimethyl siloxane of the formula

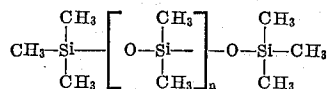


wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C., the improvement comprising adding to the lower portion of said distillation zone a single increment of said siloxane equivalent to about 5 to 10 p.p.m. by volume based on the per pass of furfural through said distillation zone when the pressure drop across the distillation zone exceeds a value indicating incipient flooding of the distillation zone.

9. The process of claim 8 wherein the siloxane is added in substantially pure form.

10. The process of claim 8 wherein the siloxane is added as a solution in a liquid hydrocarbon containing from about 5 to 10 carbon atoms per molecule.

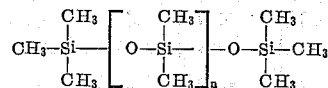
11. In a process for separating a less saturated hydrocarbon from a more saturated hydrocarbon wherein a mixture of said hydrocarbons is subjected to an extractive distillation step in the presence of furfural solvent in which foaming is prevented by the addition of liquid polydimethyl siloxane of the formula



wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C., the improvement comprising adding to the lower portion of said distillation zone a single increment of said siloxane equivalent to about 5 to 10 p.p.m. by volume based on the per pass of furfural through said distillation zone when the pressure drop across the distillation zone exceeds a value indicating incipient flooding of the distillation zone.

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12. In a system for extractive distillation comprising an extractive distillation column, a stripping column to strip rich solvent; means to pass rich solvent from said distillation column to said stripping column, means to return lean solvent from said stripping column to said distillation column, means to introduce hydrocarbons to said distillation column, means to remove less saturated hydrocarbons from said stripping column, and means to remove more saturated hydrocarbons from said distillation column, apparatus comprising dumping means to introduce a single dump substantially instantaneously into said distillation column a measured quantity of a liquid polydimethyl siloxane of the formula



wherein n is an integer resulting in a compound having a viscosity of at least 40 centistokes at 25° C.; pressure sensing means to sense the difference in pressure between the bottom and the top of said distillation column; pressure control means operatively connected to said sensing means and to said dumping means to dump said measured amount of said siloxane into said distillation column when the difference in pressure between the bottom and the top of said distillation column exceeds a value indicating incipient flooding of said distillation column.

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