

[54] **RECOVERING CYCLOPENTADIENE  
VALUES FROM C<sub>5</sub> FRACTIONS**[72] Inventors: **Bernhard Schleppinghoff**, Dormagen; **Helmut Scherb**, Sinnersdorf; **Hans Puxbaumer**, Cologne-Zoolstock, all of Germany[73] Assignee: **Erdolchemie Gesellschaft mit beschränkter Haftung**, Cologne, Germany[22] Filed: **Aug. 11, 1970**[21] Appl. No.: **62,937**[30] **Foreign Application Priority Data**

Aug. 16, 1969 Germany.....D 19 41 704.0

[52] U.S. Cl. ....260/666 A, 208/255, 260/681.5

[51] Int. Cl. ....C07c 7/00

[58] Field of Search .....260/681.5, 666 A; 208/255

[56]

**References Cited****UNITED STATES PATENTS**

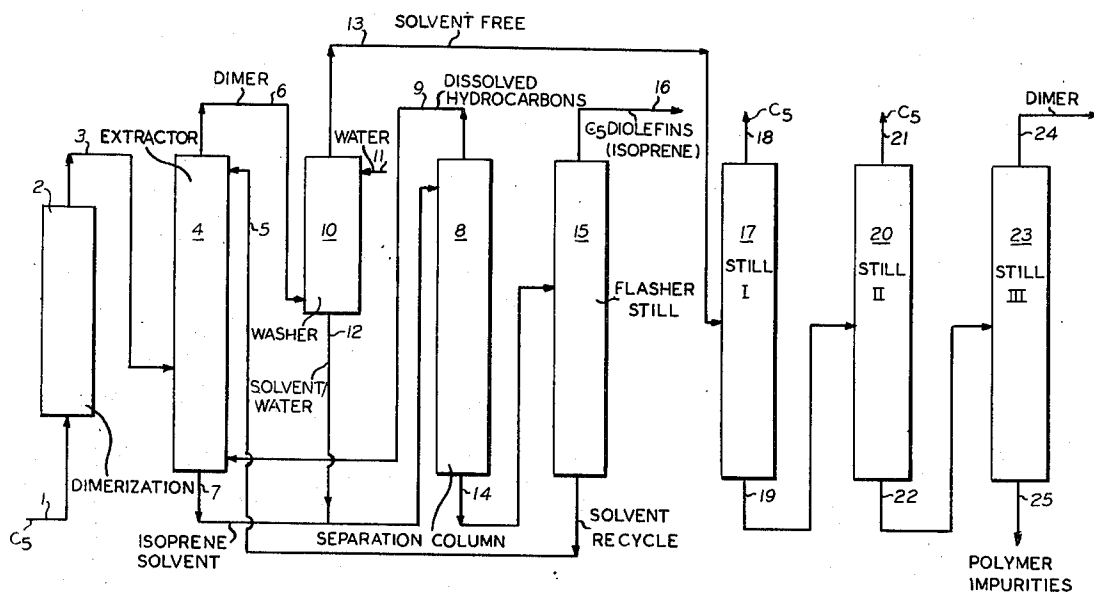
3,344,198 9/1967 Weitz et al.....260/666 A

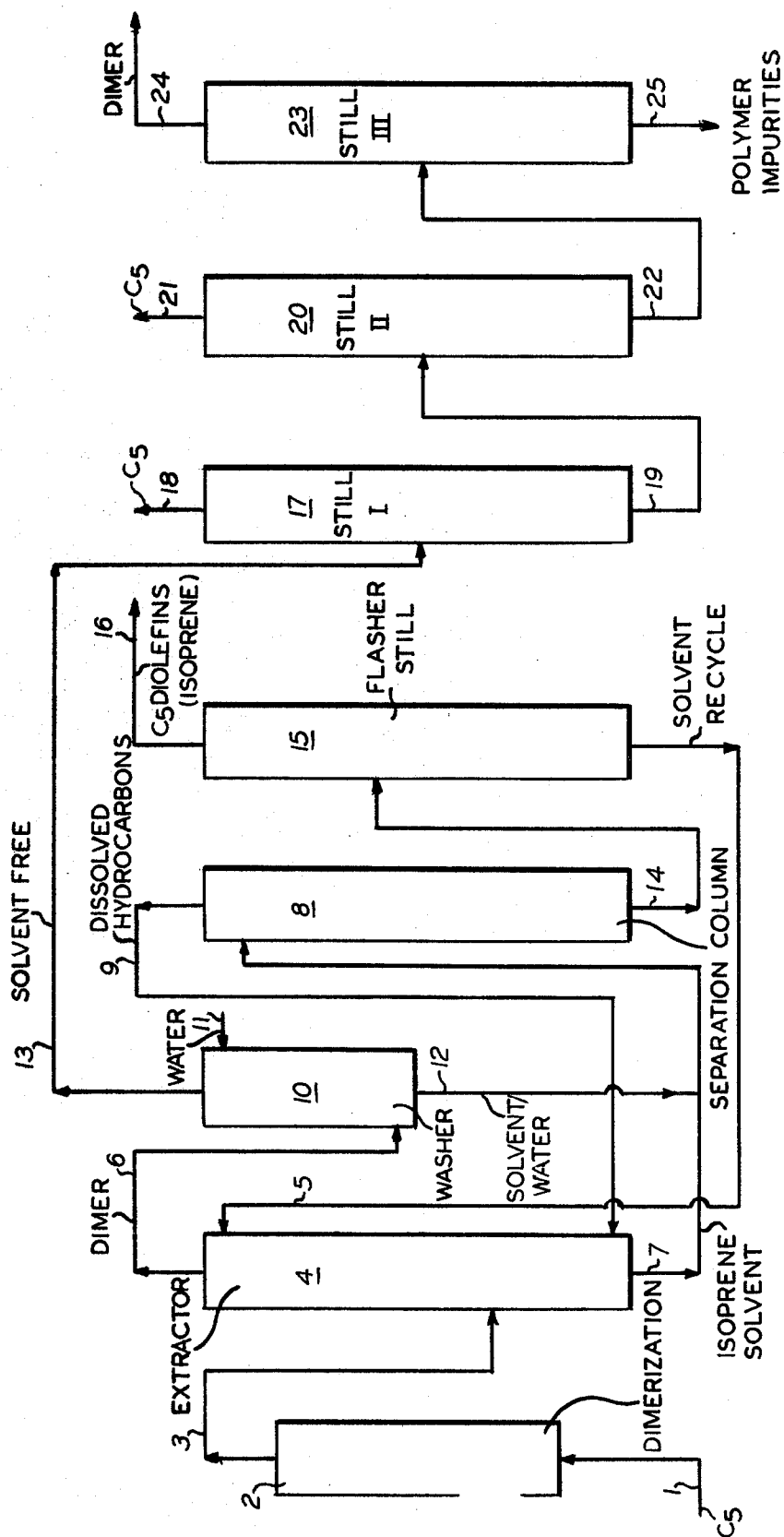
*Primary Examiner*—Delbert E. Gantz*Assistant Examiner*—Veronica O'Keefe*Attorney*—Burgess, Dinklage & Sprung

[57]

**ABSTRACT**

A process for recovering the cyclopentadiene values from a cyclopentadiene-containing C<sub>5</sub> fraction consisting of a mixture of paraffinic, olefinic and diolefinic hydrocarbons, which comprises subjecting the fraction to treatment to dimerize the cyclopentadiene to dicyclopentadiene; subjecting the fraction to a liquid-liquid extraction with a selective solvent whereby there is formed a solvent phase containing the diolefinic hydrocarbons and a paraffin-olefin phase containing the dicyclopentadiene, and recovering the dicyclopentadiene from said paraffin-olefin phase by distillation.

**7 Claims, 1 Drawing Figure**



# RECOVERING CYCLOPENTADIENE VALUES FROM C<sub>5</sub> FRACTIONS

The present invention relates to the recovery of cyclopentadiene values from C<sub>5</sub> fractions consisting essentially of a mixture of paraffinic, olefinic and diolefinic hydrocarbons.

A petroleum fraction, known as cracked gasoline, containing relatively large quantities of diolefins, and particularly isoprene and cyclopentadiene, is formed during the high-temperature cracking of mineral oils and their fractions. A C<sub>5</sub> fraction, i.e. a hydrocarbon fraction essentially containing hydrocarbons with five carbon atoms, is obtained from this cracked gasoline during further processing by distillation. These C<sub>5</sub> hydrocarbons consist essentially of a mixture of paraffinic, olefinic and diolefinic hydrocarbons.

The cyclopentadiene which is also present in a cracked petroleum fraction of this kind causes considerable difficulties during the separation process due to its pronounced tendency towards dimerization and trimerization when the cracked petroleum fraction is subsequently processed, preferentially with a view to recovering isoprene which is generally achieved through a combination of distillation, extraction and extractive distillation. Furthermore, the purity requirements which a polymerizable grade isoprene has to satisfy permit a cyclopentadiene content of only a few ppm.

It is also of advantage to recover the cyclopentadiene, in addition to isoprene, in order thus to make the separation process more economical.

Accordingly, it is an object of the present invention to provide a process for removing most of the cyclopentadiene from the hydrocarbon mixture before the actual diolefin separation process.

This and other objects and advantages are realized in accordance with the present invention which provides a process wherein most of the cyclopentadiene present in a C<sub>5</sub> fraction consisting of a mixture of paraffinic, olefinic and diolefinic hydrocarbons can be removed by dimerizing most of the cyclopentadiene in a pre-treatment of the fraction at an elevated temperature, and subsequently carrying out a liquid-liquid extraction of the fraction with a selective solvent whereby the dicyclopentadiene passes into the paraffin-olefin phase from which it can be recovered in the form of dicyclopentadiene by straightforward distillation.

The process according to the invention can be carried out in any conventional extraction plant. For example, the liquid-liquid extraction can be carried out in pulsating sieve-plate columns, in centrifugal extractors or in a mixer-settler arrangement.

Suitable selective solvents include those of the kind which separate the diolefins on the one hand from the paraffins and olefins on the other hand with sufficient selectivity in a liquid-liquid extraction, for example N-methyl pyrrolidone, 1-oxo-1-methyl phospholine, phospholine, N-methyl oxazolidone, acetonitrile, dimethyl sulfoxide, furfural, dimethyl acetamide, sulfolane, dimethyl formamide, or mixtures thereof, in which case the dicyclopentadiene passes into the paraffin-olefin phase rather than into the diolefin phase. The quantity in which the selective solvent is employed should at least be sufficient to dissolve all the constituents to be extracted. In some cases, it is possible to use a considerable excess over and above this minimum quantity, especially in cases where stringent requirements are imposed upon the diolefin content of the raffinate. Suitable ratios by volume of the solvent to the starting material are in the range of from about 3:1 to 12:1.

The solvent may have a water content of from about 3 to 20 percent and preferably from about 5 to 10 percent by volume to improve the phase separation and to increase selectivity.

The extraction temperature can vary within a wide range, provided that, under the temperature and pressure conditions applied, it is lower than that temperature at which bubbles are formed in the mixture and provided that it is above the solidification temperature of the selective solvent. In most cases, a temperature of from about 10° to 40° C. is used. A slight positive pressure is usually maintained in the extraction column, in which case the optimum working temperature is substantially about 35° C.

It is of advantage to wash the paraffin-olefin phase (the raffinate) with water before the dicyclopentadiene is left behind as the residue in a distillation, so as to remove any last traces of the dissolved solvent. Otherwise, it has been found that with certain solvents dicyclopentadiene forms relatively low-boiling azeotropes which can lead to losses of the dimer to be obtained.

One embodiment of the process according to the invention is illustrated in the drawing which is a flow sheet of the process wherein, in the interests of simplicity and clarity, not all the pumps, heat exchangers and intermediate containers required for practical operation have been shown.

A C<sub>5</sub> fraction, obtained by distillation from crude cracked gasoline or a cracked gasoline cut, is supplied via pipe 1 to a residence vessel 2 maintained at an elevated temperature, whereby in known manner the cyclopentadiene is preferentially reacted to form dicyclopentadiene, while the remaining diolefins such as isoprene and the piperylenes remain substantially unchanged. The dimerization is effected as described by V. N. Timkin et al. in *Petroleum Chemistry* (Russ.) No. 3 (1964) pages 435-440, i.e. heating in a closed vessel under autogenous pressure for about 1 to 4 hours at about 80° to 130° C. The hydrocarbon stream 3 leaving vessel 2, enriched in dicyclopentadiene at the expense of cyclopentadiene, is delivered to a liquid-liquid extractor 4 which in the present case consists of a complex of mixing and settling chambers. A water-containing stream of the selective solvent 5 from which most of the C<sub>5</sub> hydrocarbons have been removed by degasification in column 17, is introduced into the upper part of the extraction apparatus. The selective solvent flows countercurrent to the starting material in the extraction column and dissolves the diolefins out of it, while dicyclopentadiene together with the paraffins and monoolefins is run off from the head of the extraction column as the raffinate 6. The solvent 7 containing the diolefins is run off at the lower end of the extractor and, by boiling in a separation column 8, is freed from the dissolved hydrocarbons which leave at 9 and are recycled to the extractor 4. The residue from still 8 leaves through line 14 and is boiled in column 15, driving off residual C<sub>5</sub> diolefins and some water at 16 with the now purified selective solvent being recycled through line 5 to extractor 4.

The raffinate 6 from extractor 4, still containing a little solvent which is run off from the head of the extractor, is delivered to a raffinate washer 10 which consists optionally of a mixer-settler complex or a trickle column filled with a packing. The washing liquid 11, in the present case water, is delivered to the head of the washing column, the solvent-containing wash water 12 is run off from the lower end of the column and delivered to the diolefin-containing solvent stream 7.

The solvent-free raffinate 13 run off from the head of the washer 10 is distilled without depolymerization of the dicyclopentadiene by initially distilling off most of the C<sub>5</sub> hydrocarbons in a column 17 at normal pressure and at sump or pot temperatures below 100° C., the C<sub>5</sub> hydrocarbons leaving at 18. The residue from still 17 passes through pipe 19 to still 20 operating at the same sump temperature but at an absolute pressure of about 30 mm Hg, additional C<sub>5</sub> hydrocarbons being boiled off at 21, the residue comprising more concentrated dicyclopentadiene. This residue leaves through pipe 22 and in still 23 operating at about 30 mm Hg and 100° C. is boiled off at 24 in the form of dicyclopentadiene of very high purity. The residue, leaving at 25, comprises polymeric impurities. The process is further illustrated in the following example wherein all parts are by weight unless otherwise stated.

## EXAMPLE

The C<sub>5</sub> cut of a crude cracked gasoline 1 containing 8.0 percent of cyclopentadiene and 0.2 percent of dicyclopentadiene is pre-treated at elevated temperature in residence vessel 2, as a result of which approximately 85 percent of the cyclopentadiene is converted into the dimer. The C<sub>5</sub> fraction thus pre-treated then contains 7.0 percent by weight of dicyclopentadiene and 1.2 percent of cyclopentadiene.

100 kg/hour of the dicyclopentadiene-containing material are continuously delivered via 3 into the sixth chamber from the bottom of an extraction apparatus 4 consisting of an arrangement of 18 superimposed mixing and settling chambers. 530 kg per hour of N-methyl pyrrolidone containing 8 percent of water are delivered into the uppermost chamber via line 5. The extract is run off from the bottom of the extraction apparatus at 7 in a quantity of 646 kg/hour ( $C_5$  hydrocarbon content 18 percent by weight). This extract is heated in a following column 8, the so-called extract recycle column, until the dissolved paraffins and olefins and also some of the dienes have been distilled off as the head product and, upon condensation, are delivered into the lowermost chamber of the extractor via line 9. The extract with a residual  $C_5$  hydrocarbon content of approximately 5.4 percent is run off at 14 from the sump of the extract recycle column. In the following column 15 the solvent is completely freed of hydrocarbons by heating and, after intermediate cooling, is recirculated via 5 to the top of the extractor 4. A substantially cyclopentadiene-free  $C_5$  diolefin fraction is removed from the head of the column 15 in a quantity of 30 kg per hour along with 3 kg per hour of water. 73 kg per hour of the raffinate containing 11.0 percent by weight of dicyclopentadiene accumulate at the head of the extractor 4. As shown by the mass balance, more dicyclopentadiene has been formed from the residual monomers during extraction, also passing into the raffinate. The raffinate contains 4 percent by weight of N-methyl pyrrolidone in solution. It is passed via line 6 through a wash column 10 filled with Raschig rings to which 3 kg per hour of fresh water are continuously delivered at 11. Wash water is continuously run off from the lower end of the washing column 10 via line 12 in a quantity of approximately 6 kg per hour. The raffinate is removed from the head of the washing tower at 13 with an N-methyl pyrrolidone content of 200 ppm. The raffinate is distilled at atmospheric pressure in a first distillation stage 17 and the dicyclopentadiene concentrated to 85 percent in the sump at a temperature of 90° C. The remaining  $C_5$  is then distilled in column 20 at a pressure of 30 mm Hg at the same sump temperature, as a result of which the dicyclopentadiene is concentrated to 95 percent in the sump. In the next distillation stage 23, dicyclopentadiene is distilled off from the polymeric impurities at 30 mm Hg and 100° C. and obtained

as the head product 24 in a purity of 97 percent by weight.

It will be appreciated that the instant specification and example are set forth by way of illustration and not limitation and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. A process for recovering the cyclopentadiene values from a cyclopentadiene-containing  $C_5$  fraction consisting of a mixture of paraffinic, olefinic and diolefinic hydrocarbons, which comprises subjecting the fraction to treatment to dimerize the cyclopentadiene to dicyclopentadiene, subjecting the fraction to a liquid-liquid extraction with a selective solvent whereby there is formed a solvent phase containing the diolefinic hydrocarbons and a paraffin-olefin phase containing the dicyclopentadiene, and recovering the dicyclopentadiene from said paraffin-olefin phase by distillation.

2. A process according to claim 1, wherein said solvent comprises N-methyl pyrrolidone, 1-oxo-1-methyl phospholine, phospholine, N-methyl oxazolidone, acetonitrile, dimethyl sulfoxide, furfural, dimethyl acetamide, sulfolane, dimethyl formamide, or mixtures thereof.

3. A process according to claim 2, wherein said solvent contains about 3 to 20 percent of water by weight.

4. A process according to claim 1, wherein dimerization of the cyclopentadiene is effected by heating.

5. A process according to claim 1, wherein the paraffin-olefin phase is washed with water prior to its distillation to remove therefrom dissolved solvent.

6. A process according to claim 1, wherein the distillation of said paraffin-olefin phase is carried out at a temperature below about 100° C., whereby the paraffins and olefins are for the most part distilled off leaving a residue which is predominantly dicyclopentadiene, and said residue is distilled under vacuum at a temperature below about 100° C. to distill over dicyclopentadiene in excess of 90 percent purity.

7. A process according to claim 6, wherein dimerization of the cyclopentadiene is effected by heating, wherein the solvent comprises N-methyl pyrrolidone and contains about 3 to 20 percent of water by weight, and wherein the paraffin-olefin phase is washed with water prior to its distillation to remove therefrom dissolved N-methyl pyrrolidone solvent.

\* \* \* \* \*