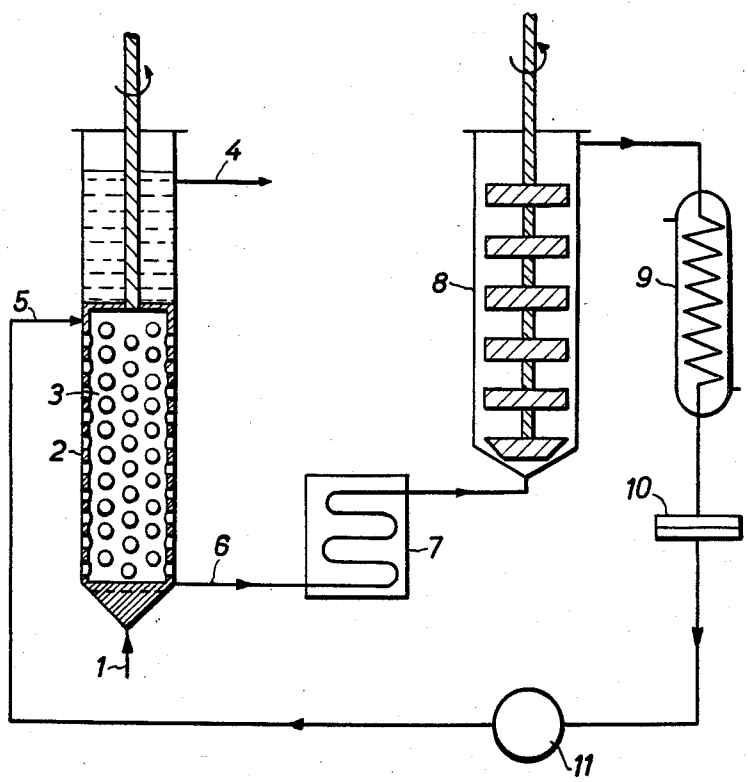
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PROCESS FOR REMOVING HIGHER ACETYLENES
FROM HYDROCARBON MIXTURES
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PROCESS FOR REMOVING HIGHER ACETYLENES FROM HYDROCARBON MIXTURES

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This invention relates to a process for removing higher acetylenes from hydrocarbon mixtures.

The cracking gases which are formed in the pyrolysis of mineral oils, mainly crude petroleums, their fractions and residues, are generally worked up by first of all compressing the cracking gases and thereafter distilling them under pressure. Butadiene can be recovered from the C_4 fraction thereby formed by washing this C_4 fraction under pressure with such a proportion of a cuprous salt solution of predetermined composition that all the butadiene contained in the fraction is dissolved therein. In the known processes, the higher acetylenes (for example vinyl acetylene and methyl acetylene) formed as by-products in the cracking process are taken up by the cuprous salt solution as well as the butadiene. The butadiene is recovered from the cuprous salt solution by the latter being relieved of pressure and heated to approximately 70° C. The butadiene obtained in this way still contains a proportion of higher acetylenes. In order to remove these acetylenes, the butadiene is washed in counter-current with small proportions of fresh cold cuprous salt solution (cf. United States patent specification No. 2,566,137). This counter-current washing is effective when the content of higher acetylenes in the crude butadiene is for example less than 4 parts by weight of higher acetylenes to 100 parts by weight of pure butadiene. During the desorption of the butadiene by heating the solution, some of the higher acetylenes are polymerised; the polymerisation is completed by heating for a relatively long time. After the solid polymers formed in this way have been filtered off and after the liquid polymers remaining in solution have been washed out, the solution is then used afresh for the extraction of the butadiene from the C_4-fraction.

If the pyrolysis of the mineral oils is carried out at temperatures higher than 750° C. relatively large amounts of higher acetylenes, for example 5–10% by weight or higher, based on butadiene, are formed as by-products, so that the C_{3+} fractions of the cracked gases, after condensation, can no longer be separated without danger into their separate fractions by pressure distillation, since the higher acetylenes are concentrated on certain trays, and thus there is the danger of explosive decomposition. On the other hand, difficulties are presented when attempts are made to recover butadiene from the C_{3+} condensate of and cracking gases in the presence of relatively large amounts of higher acetylenes in the conventional manner by extraction with the cuprous salt solution, since the butadiene obtained in this way is contaminated by large proportions of higher hydrocarbons (especially cyclopentadiene), and on account of the relatively high concentration of higher acetylenes, butadiene

cannot in practice be completely freed from the said acetylenes by the conventional process.

It has now been found that cracking gases which contain relatively large proportions of higher acetylenes and consequently cannot be worked up in the hitherto usual manner can be completely freed from the higher acetylenes before the butadiene is removed and without substantial loss of the butadiene by a process in which the condensed cracking gases are washed under pressure with aqueous solutions of cuprous salts, the washing solution is heated to polymerise the dissolved higher acetylenes, the solid polymers are filtered off and the filtrate recycled and used afresh for washing new fractions of condensed cracking gases without the cuprous salt solution being relieved of pressure during this recycling.

Cuprous salt solutions which are suitable for the process of the invention are such as have previously been used for working up C_4 fractions in order to recover butadiene.

In the novel process 0.5 to 5 parts by volume, and advantageously 1 to 3 parts by volume, of cuprous salt solutions are used to 1 part by volume of liquid hydrocarbon.

The condensed cracking gases are washed under the pressure which is necessary for condensing cracking gases with 3 or more carbon atoms, that is to say, generally under a pressure of from 5 to 10 atm. The washing liquid is then recycled under the same pressure. The washing process itself is carried out at room temperature.

The operation of the process of the invention is explained by the single figure of the accompanying diagrammatic drawings. The hydrocarbons to be treated pass in liquid form through a pipe **1** into an extractor **2**, in which are disposed cuprous salt solution and a perforated screen stirrer **3**. The hydrocarbons freed from the higher acetylenes leave the extractor by way of a pipe **4** and pass to a fractional distillation column, which is not shown. Regenerated cuprous salt solution enters the extractor by way of a pipe **5**, the solution enriched with acetylene leaves the extractor by way of a pipe **6**, is brought to the prescribed temperature in a heater **7** and is kept at this temperature in a soaker **8**. The solution is cooled in a cooler **9**. The solid polymers are removed in a filter **10**, whereupon the solution is recycled to the extractor by means of a jump **11** and the pipe **5**.

When the cuprous salt solution is returned to the extractor, the liquid polymers contained in the solution are removed by the liquid hydrocarbons which are preferably propylene and butylene under treatment and are thus removed from the system. A separate washing process for removing the liquid polymers is therefore not necessary in this case.

By means of the process of the invention, it is possible to obtain the condensed cracking gases free from the higher acetylenes by washing with a comparatively small amount of cuprous salt solution, so that the gases can thereafter be split up into the separate fractions by pressure distillation without any danger. It was surprising that the butadiene simultaneously dissolved in the cuprous salt solution is not polymerised in the process carried out in accordance with the invention, so that the cuprous salt solution saturated with condensed cracking gases can be recycled in the novel process without any appreciable losses of cracking gases occurring.

The following example further illustrates the invention.

Example

A Middle East crude oil is cracked at 775° C. A C_{3+}

fraction is obtained from the cracked gas thus produced by compression, cooling and fractional distillation, the said fraction having the following composition:

Constituent	Percent by weight
Propane	2.9
Propylene	46.8
Allene	0.4
Butanes	0.8
n-Butenes	11.2
i-Butene	3.5
1,3-butadiene	15.2
Higher acetylenes (methyl and vinyl acetylenes	[1]1.1
C_{5+} hydrocarbons	18.1
	100.0

[1] 7.3% by weight, calculated on 1,3-butadiene.

1 part by volume of these liquid hydrocarbons is washed at 20° C. and a pressure of 7 atm. in the apparatus described above in counter-current with 2 parts by volume of an aqueous cuprous salt solution and discharged from the top of the extractor.

The solution contains per litre:

3 mols of Cu^{I} ions
0.2 mol of Cu^{II} ions
4 mols of acetic acid
11 mols of ammonia

The composition of the discharged hydrocarbons remains the same, except that the higher acetylenes are completely removed. This hydrocarbon mixture also contains approximately 0.7% by weight of liquid polymers. It is thereafter separated into the individual constituents or fractions by fractional pressure distillation. The enriched cuprous salt solution is brought in the heater to a temperature of 90° C. and is kept for one hour at this temperature in the soaker. The solution is then cooled to 20° C. and thereafter filtered, about 0.3–0.4% by weight of the originally introduced hydrocarbon mixture being removed as solid polymers. The filtered solution is recycled to the extractor, in which the liquid polymers contained in the solution are taken up by the hydrocarbons.

What we claim is:

1. Process for removing higher acetylenes from mixtures of hydrocarbons, having from 3 to 6 carbon atoms, containing the same which comprises contacting under pressure a mixture of such hydrocarbons with an aqueous cuprous salt solution, substantially saturated with said hydrocarbons other than said acetylenes, to thereby selectively extract the acetylene from the mixture, separating said cuprous salt solution containing the extracted acetylenes, polymerizing the acetylenes into liquid and solid polymers without substantial pressure relief, and thereafter removing said solid polymers thereby forming an extraction solution ready for reuse.

2. Process, according to claim 1, in which said contacting is effected at normal temperature with about one part by volume of said hydrocarbon mixture per 0.5–5.0 parts of said cuprous salt solution, and which includes agitating said cuprous salt solution during said contacting.

3. Process, according to claim 1, in which said polymerization is effected by heating the cuprous salt solution to a temperature between 80 and 100° C.

4. Process for recovering higher acetylenes from higher acetylene containing mixtures of hydrocarbons having from 3 to 6 carbon atoms, which comprises substantially continuously passing such a mixture through an extraction zone, substantially continuously passing an aqueous cuprous salt solution through said zone under pressure in contact with said mixture and out of said zone, polymerizing the extracted acetylene in said cuprous salt solution into liquid and solid polymers without substantial pressure relief, removing the solid polymers, and recycling the cuprous salt solution back to said extraction zone under pressure whereby the recycled cuprous salt solution will remain substantially saturated with said hydrocarbons other than the acetylenes and will selectively extract acetylenes from the hydrocarbon mixture.

5. Process according to claim 4 in which said cuprous salt solution is passed into contact with said mixture in amount of about 0.5–5.0 parts by volume per part by volume of said mixture at normal temperature, and which includes agitating the cuprous salt solution in said extraction zone.

6. Process according to claim 4 in which said polymerization is effected by heating the cuprous salt solution to a temperature between about 80 and 100° C.

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