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PROCESS FOR RECOVERING POLYMERIZED DIENES

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The light oil which is recovered from the gaseous products of coke ovens or other coal carbonizing operations consists principally of benzol and its homologues. It contains, in addition, a few per cent of hydrocarbons boiling up to approximately 79° C.

Among the lower-boiling compounds are conjugated dienes which have commercial value if recovered in a substantially pure form.

The principal member of this diene group of compounds is cyclopentadiene, which boils close to 41.5° C. at atmospheric pressures. This compound is finding commercial use in the production of certain plastics and is of potential value for the production of synthetic rubber.

Owing to the fact that other materials present in the light oil boil at temperatures close to the boiling point of cyclopentadiene, separate recovery of this compound by distillation is impractical on an industrial scale; and these dienes are only available in the complex mixture of oils which boil at atmospheric pressures from atmospheric temperatures up to the boiling point of benzene. This mixture is known as benzol forerunnings, since it constitutes the first distillate from the stills for fractionating the light oil.

The present invention has for its object the recovery of the dienes originally present in said light oil, and carried over from the said light oil, substantially completely in the said first distillate from the stills employed for fractionating the light oil, that is, these dienes now are present in the forerunnings.

The process of the present invention involves a conversion under controlled conditions of the cyclopentadiene in the said forerunnings into dicyclopentadiene, which is a relatively stable polymer of cyclopentadiene, and boils at a relatively high temperature, that is, at 172° C. at atmospheric pressures.

It is known in the art that cyclopentadiene polymerizes, in the pure state, spontaneously to dicyclopentadiene. Likewise, it is known in the art that cyclopentadiene will polymerize to dicyclopentadiene, when present in materials containing benzene and its homologues, such materials including carburetted water gas and coal gas or coke oven gas. But in such materials, it is found that the polymerization of cyclopentadiene proceeds at a practicable rate only upon application of considerable amounts of both heat and pressure. (See for example, the United States Letters Patent to Ward, No. 2,211,038, dated April 13, 1940). In fact, in order to operate the process of this Ward patent, the use of an autoclave is recommended.

While the procedure outlined in the Ward patent can be applied to forerunnings, the present process offers certain advantages thereover, because of the discovery by the present applicants that the presence of benzene and its homologues inhibits the polymerization of the dienes, and that, in the case of the forerunnings obtained from coke oven light oil, if the forerunnings be cut at a temperature sufficiently below the boiling point of benzene, which is approximately 80° C., so that the forerunnings are substantially free from benzene and its homologues, the polymerization proceeds at an entirely commercial rate at atmospheric temperatures and pressures, thereby obviating the special equipment required to operate at elevated temperatures and pressures, with attendant substantial economic advantages; and this is true notwithstanding the diluting effect on the dienes of the remaining compounds present with the dienes in the forerunnings, the dienes being actually present in an environment which is far from a pure condition for the said dienes.

The present invention comprises the steps of separating the forerunnings from coke oven light oil under conditions so that the forerunnings are condensed and collected substantially entirely free from benzene and its homologues, the resulting collected forerunnings containing the dienes originally present in the light oil. The recovered forerunnings, thus substantially free from benzene and its homologues, are stored in closed containers to prevent loss by evaporation, at atmospheric temperatures, but not substantially below 15° C. Summer atmospheric temperatures will run higher, obviously, but nowhere will such be encountered much, if any, above 40° C.

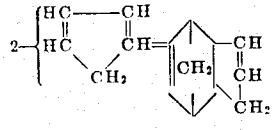
The polymerization of cyclopentadiene to dicyclopentadiene proceeds spontaneously and rapidly to completion in the stored forerunnings. To separate the formed dicyclopentadiene, the forerunnings from storage are distilled at temperatures not exceeding 120° C. and at atmospheric pressure in order to remove the components which boil up to 80° C. The still residue contains the dicyclopentadiene, which boils, when pure, at a relatively high temperature, that is 172° C. at atmospheric pressures.

The still residue is fractionated under vacuum in order to obtain the polymerized dienes of the desired quality as distillate.

During the storage period the conjugated di-

enes polymerize. Thus, cyclopentadiene polymerizes principally to dicyclopentadiene, and only to a smaller extent to the tricyclopentadiene and higher polymers. The change to the trimer is promoted by higher temperatures, and this change is to be avoided, since the trimer is very stable and is substantially impossible to depolymerize back to the cyclopentadiene; whereas, the dimer is stable enough for handling, while it is depolymerized readily. Consequently, there must be a control of temperature in order to polymerize the cyclopentadiene into its favorable dimer.

The reaction for the polymerization of cyclopentadiene to dicyclopentadiene may be expressed as follows:



The resulting dicyclopentadiene boils at 172° C. under normal atmospheric pressure, and at its boiling point at atmospheric pressure, it depolymerizes to form cyclopentadiene.

The storage period required for the polymerization of the cyclopentadiene depends to a large extent on the temperature. At higher temperatures, such as those prevailing during the summer months, only a few days may be necessary to effect the conversion, although a longer period, such as perhaps from two to four weeks or longer, may be required, depending upon conditions.

Since dicyclopentadiene depolymerizes at temperatures approaching its boiling point, a temperature not in excess of 120° C. is to be recommended during the distillation of the lower-boiling components of the forerunnings away from the dicyclopentadiene. The residue remaining from this distillation may be further purified by vacuum distillation to give a relatively pure dicyclopentadiene melting at about 25° C. The melting point may be increased by filtration in the absence of air at temperatures of 20° C. to 25° C. The still residue from the vacuum distillation contains the trimers and higher polymers.

The process of the present invention must be carried on in an inert atmosphere which is maintained in the system throughout the entire process. If the reactants in the system should come in contact with the air, there is formed the compound, dicyclopentadiene di-peroxide. Since many di-peroxides are explosive, it is possible that the formation of this compound would create an explosive hazard, and it would reduce the yield of the desired dicyclopentadiene and its depolymerized product.

The present process is based upon the fact that no separation of cyclopentadiene is possible from the forerunnings, owing to the closeness of its boiling point to the boiling points of other materials in the forerunnings. Advantage is taken of the property of cyclopentadiene to polymerize readily to the more stable dicyclopentadiene, the boiling point of which enables the other components present in the forerunnings to be boiled away for the recovery thereof, leaving the dicyclopentadiene as a still residue, which may be purified by vacuum distillation, as has been pointed out above. The minimum temperatures possible for the polymerization of the cyclopentadiene and for the boiling off of associated materials from the less volatile dimer are maintained during the entire process in order to control the conversion of substantially all of the cyclopentadiene into its dimer, with, at most, only relatively slight amounts of still higher polymerization products; and also minimum temperatures are maintained during the separation of the dicyclopentadiene from the associated materials in the forerunnings, for preventing conversion of any substantial parts thereof into higher polymerization products; and, as has been said before, an inert atmosphere, such as nitrogen or gaseous hydrocarbons is maintained throughout the system during the entire process.

The process is illustrated by the following specific example, which illustrates, typically, the procedure and results obtained.

In a suitable closed container, 1,000 gallons of the forerunnings substantially entirely free from benzene and its homologues and having a distillation range of 31 to 46° C., and containing 49.7% of dienes, were allowed to stand at temperatures between 22° C. and 25.5° C. At the end of ten days, the forerunnings contained 39.3% by weight of polymerized material, in twenty-two days, 43.3%, and in thirty-four days, 45.5%.

The forerunnings after storing for the thirty-four days were placed in a still and heated by steam to a liquid temperature of 120° C. The volume of still residue was 433 gallons. It was light yellow in color, and had a melting point of 7.0° C. This residue was distilled under vacuum of 15 cm. of mercury, absolute pressure, into the following fractions:

Vapor temperature °C.	Gallons	Distillate	
		Per cent by volume of charge	Melting point, °C.
Up to 103	43.3	10.0	Below 3
103–110	39.0	9.0	24.5
110–114	311.8	72.0	29.5
Residue	21.7	5.0	5.5
Loss	17.2	4.0	

The crude dicyclopentadiene having a freezing point of 24.5° was filtered by suction in an atmosphere of natural gas. The filtrate had a freezing point of 27° C., due to the evaporation of low-boiling constituents held in the crude material. The filter cake had a freezing point of 32°, with an index of refraction of 1.5058. The filtrate was subjected to further filtrations.

Dicyclopentadiene in the form of a white solid, with a freezing point of 29° C. or better, was recovered to 85% of the crude material.

The total yield of dicyclopentadiene, with a melting point of 29° C. or better, from 1,000 gallons of the original forerunnings, was 319.5 gallons, or 64.3% of the cyclopentadiene found by analysis.

The resulting dicyclopentadiene is stable and can be shipped without danger of deterioration under ordinary atmospheric conditions and in an atmosphere of natural gas, nitrogen, or other atmosphere inert to the material, to any location of use. Whereupon, it may be depolymerized to cyclopentadiene (1 mol. of dicyclopentadiene yields 2 mols. of cyclopentadiene), which material is of potential use in the production of synthetic rubber, as has been noted above, or is used in combination with maleic anhydride to make alkyd resins, or for whatever other utilization is to be made of the cyclopentadiene. The dimer makes a very satisfactory transition product which enables the transfer or shipment of

unstable cyclopentadiene to its location of use, the unstable compound being converted into a stable form for the purpose of transfer, the stable product being capable of being transformed readily into the original compound at such time as this original compound is desired for use.

The present application is a continuation-in-part of the pending application Serial No. 402,866, filed July 17, 1941, entitled "Process for recovering polymerized dienes."

We claim:

1. Process of recovering cyclopentadiene contained in benzol forerunnings substantially free from benzene, which comprises causing the cyclopentadiene to polymerize at atmospheric temperatures and pressures to dicyclopentadiene, with at most only relatively minor amounts of higher polymers, removing from the resulting dicyclopentadiene substantially all other materials originally present in the said forerunnings, and purifying the said dicyclopentadiene.

2. Process of recovering cyclopentadiene contained in benzol forerunnings substantially free from benzene, which comprises causing the cyclopentadiene to polymerize, at atmospheric temperatures and pressures and in a closed container, to principally dicyclopentadiene, with at most only relatively minor amounts of higher polymers, distilling from the resulting dicyclopentadiene substantially all of the lower-boiling components present therewith in the forerunnings, leaving the dicyclopentadiene as a still residue, subjecting the dicyclopentadiene to vacuum distillation, thereby further purifying the discyclopentadiene, filtering the said dicyclopentadiene, and maintaining a neutral atmosphere in contact with the diene materials throughout the entire process.

3. Process of recovering cyclopentadiene contained in benzol forerunnings substantially free from benzene, which comprises polymerizing cyclopentadiene to dicyclopentadiene in the presence of a halide catalyst and at atmospheric temperatures and pressures, and separating the resulting dicyclopentadiene from associated compounds.

4. Process as claimed in claim 3, wherein the catalyst employed is stannic chloride.

5. Process as claimed in claim 3, wherein the catalyst employed is boron fluoride.

6. Process of recovering cyclopentadiene originally contained in benzene-containing light oil recovered from by-product coke ovens, which comprises distilling the light oil at a temperature below the boiling point of benzene to concentrate the cyclopentadiene in forerunnings that are substantially free from benzene and its homologues, condensing the said benzene-free forerunnings having the cyclopentadiene concentrated therein, storing the forerunnings at atmospheric temperatures and pressures until the cyclopentadiene has polymerized substantially to dicyclopentadiene, with at most only relatively minor amounts of higher polymers, distilling from the resulting dicyclopentadiene substantially all of the lower boiling components present therewith in the forerunnigs, leaving the said dicyclopentadiene as a still residue, subjecting the dicyclopentadiene to vacuum distillation, thereby further purifying the said dicyclopentadiene, filtering the dicyclopentadiene, and maintaining a neutral atmosphere in contact with the diene materials throughout the entire process.

7. Process of recovering cyclopentadiene originally contained in benzene-containing light oil recovered from by-product coke ovens, which comprises distilling the light oil at a temperature below the boiling point of benzene to concentrate the cyclopentadiene in forerunnings that are substantially entirely free from benzene and its homologues, condensing the said benzene-free forerunnings having the cyclopentadiene concentrated therein, storing the forerunnings at atmospheric temperature and pressure until the cyclopentadiene has polymerized substantially to dicyclopentadiene, with at most only minor amounts of tricyclopentadiene, distilling off, at a temperature not exceeding 120° C. and at atmospheric pressure, the lower boiling components in the forerunnings, leaving the dicyclopentadiene as a still residue, and subjecting the still residue to fractional distillation in vacuum to purify the dicyclopentadiene.

8. Process of recovering cyclopentadiene originally contained in benzene-containing light oil recovered from by-product coking of coal, which comprises distilling the light oil at a temperature below the boiling point of benzene to concentrate the cyclopentadiene in forerunnings that are substantially entirely free from benzene and its homologues, condensing the benzene-free forerunnings having the cyclopentadiene concentrated therein, storing the forerunnings at atmospheric temperature and pressure, but not substantially below 15° C. until the cyclopentadiene has polymerized substantially to dicyclopentadiene, with at most only minor amounts of tricyclopentadiene, distilling off lower boiling components in the forerunnings, leaving crude dicyclopentadiene as a still residue, controlling distillation temperatures to avoid formation of substantial amounts of tricyclopentadiene, fractionating the still residue under controlled temperatures to purify the dicyclopentadiene and maintaining a neutral atmosphere in contact with the diene materials throughout the entire process.

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