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PROCESS FOR THE RECOVERY OF INDENE

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2 Claims. (Cl. 260—168)

This invention relates to a process for the recovery of indene.

It has hitherto only been possible to recover indene from tar oils indirectly by converting the indene contained in the correspondingly fractionated tar oils into insoluble double compounds or into sodium indene. By separating the oils accompanying the indene, which have not taken part in the reaction, from the conversion products of the indene and decomposing these compounds, the indene can be obtained in a more or less pure condition. The indene can be caused to separate in this manner in the form of double compounds from an indene fraction obtained from coal tar oils, for example with the aid of picric acid or 1.3.5.tri-nitrobenzene. Another process is based on the conversion of the indene into a double compound with mercuric sulphate-mercuric oxide. It is also known to convert the indene by treatment with sodamide or metallic sodium and ammonia or sodium in the presence of organic bases into sodium indene and to separate the indene in this form from the accompanying tar oil. Not much is known concerning the purity of the qualities of indene obtainable in this way. Only Weger and Bilmann indicate in the Berichte der Deutschen Chem. Ges. Vol. 36, page 640 (1903) that the indene separated from tar oils by forming the picrate still contained about 10% to 17% of cumarones, about 5% of hydrindene-containing fractions and other oxygen-containing substances.

According to this invention it has been found that it is possible, notwithstanding the strong tendency of the indene to form liquid eutectics, to recover the indene in a pure form from tar oils merely by crystallizing and thereafter centrifuging. With this purpose in view the operation is effected by conducting the distillation in the production of the indene-containing tar oil fractions in such a way that the concentration of indene is increased up to about 80%. If an indene fraction prepared in this manner is subjected to cooling down to about —25° C. the indene crystallizes out, notwithstanding its extremely low melting point, notwithstanding the accompanying substances contained in the fraction such as cumarone, hydrindene, methyl cumarone and benzene hydrocarbons and notwithstanding its pronounced tendency to form liquid eutectics with the accompanying substances, in a form which enables it to be recovered in a chemically pure form without the aid of chemical processes. If, in addition, the crystallized material is centrifuged in a centrifuge cooled down to the same low temperature an indene can be recovered therefrom in a surprising manner which shows the theoretical melting point of —2° C. and accordingly is chemically pure.

According to an embodiment of the invention a so-called neutral oil, i. e. a tar oil freed from the phenols, which begins to boil at normal pressure at about 172° C. and shows the following boiling range serves as starting material: up to

175° C.	180° C.	185° C.	190° C.	194° C.	195° C.	197° C.
10%	43%	73%	86%	90%	93%	95%

This starting material is fractionally distilled, if desired repeatedly, in satisfactorily operating fractionating apparatus of any desired type and construction, so that as far as possible any benzene hydrocarbons present, having a lower boiling point than indene, pass over with a little indene in the first runnings and in the final fractions as far as possible benzene hydrocarbons, which have a higher boiling point than indene, also together with a little indene. A fractionating column with 40 bell bottoms and dephlegmator or a fractionating column filled with Raschig rings or a sieve column of suitable efficiency is, for example, employed for carrying out the distillation. The reflux proportion is, for example, selected as 1:5. The process of the distillation is controlled by testing the individual fractions for their boiling point, their specific gravity and freezing point. The control of the freezing point alone is in general sufficient as is shown in the following:

In the first fractional distillation of the aforementioned raw material approximately 50% of a fraction is obtained which shows the following boiling range: up to

175° C.	178° C.	179° C.	180° C.	181° C.	182° C.	183° C.	184° C.	187° C.
5%	23%	37%	57%	72%	83%	90%	93%	95%

Such a fraction has a freezing point of −30° C. If this fraction is subjected to renewed fractional distillation there is obtained therefrom about 16% of a fraction of −40° C. freezing point containing about 50% of indene, about 13% of an indene fraction having a freezing point of −26° C. and containing about 62% of indene, about 19% of an indene fraction having a freezing point of −19.5° C. and containing about 71% of indene, about 10% of an indene fraction having a freezing point of −17° C. and containing about 77% of indene, about 21% of an indene fraction having a freezing point of −14° C. and containing about 80% of indene, about 2% of an indene fraction having a freezing point of −20° C. and containing about 70% of indene, about 4% of an indene fraction having a freezing point of −30° C. and containing about 58% of indene, and 15% of residue and loss.

The indene fraction containing 80% of indene is subjected to crystallization at about −25° C. On centrifuging about 47% of a pure indene having a melting point of −2° C. is obtained. The remaining fractions can be again fractionated and be then utilized in the same manner for the recovery of pure indene.

According to this invention it has been further found that the remaining indene fractions, which have a lower freezing point than about −14° C. and contain less than about 80% of indene, can also be employed for the recovery of indene without renewed fractionation, by causing the same to freeze at correspondingly lower temperatures, separating them from the adhering liquid portion on a cooled suction filter or in a cooled centrifuge or in any other suitable apparatus and again subjecting the solid portion enriched in indene after first fusing the same, to crystallization and separation of the liquid particles.

An indene fraction is for example employed at the outset which shows a freezing point of −26° C. This indene fraction is caused to freeze at temperatures of about −27 to −35° C., the solidified portion separated from the liquid constituents and the solid portion, comprising raw indene containing about 75 to 85% of indene and having a melting point of about −18 to −11° C. subjected after first fusing the same to the process of this invention.

The mother liquors obtained in this process can be treated, if desired repeatedly, in a similar manner.

The determination of the indene content in the individual fractions may be effected by the known bromine titration method. The crystallization can also be carried out in two stages at different temperatures. The purity of the resulting indene can if necessary be increased by repeated fusion and freezing. The freezing, crystallization and separation of the individual constituents may be carried out in any suitable apparatus, for example in vessels provided with stirring means, filtering apparatus, centrifuges or the like capable of being cooled. The increase in the concentration of the indene content of the mother liquors as well as of the individual fractions in general can be carried out in the described manner either by fractional distillation or by repeated freezing out. These procedures may also be combined.

I claim:

1. A process for the recovery of indene from indene-containing tar oils, wherein the concentration of indene in the said tar oils is increased up to about 80% by fractional distillation, the fraction with this indene content cooled down to about −25° C. and the indene which crystallizes out separated in a centrifuge which is maintained at about the same low temperature.

2. A process according to claim 1, which comprises increasing the indene contents of fractions obtained by the fractional distillation and containing less than about 80% of indene by freezing the said fractions at low temperatures, separating the solid portions from the liquid portions, fusing the said solid portions, crystallizing the indene therefrom by cooling and mechanically separating the crystalline indene.

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