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METHOD OF SEPARATING ACENAPHTHENE, DIPHENYLENE OXIDE AND FLUORENE FROM AROMATIC OILS

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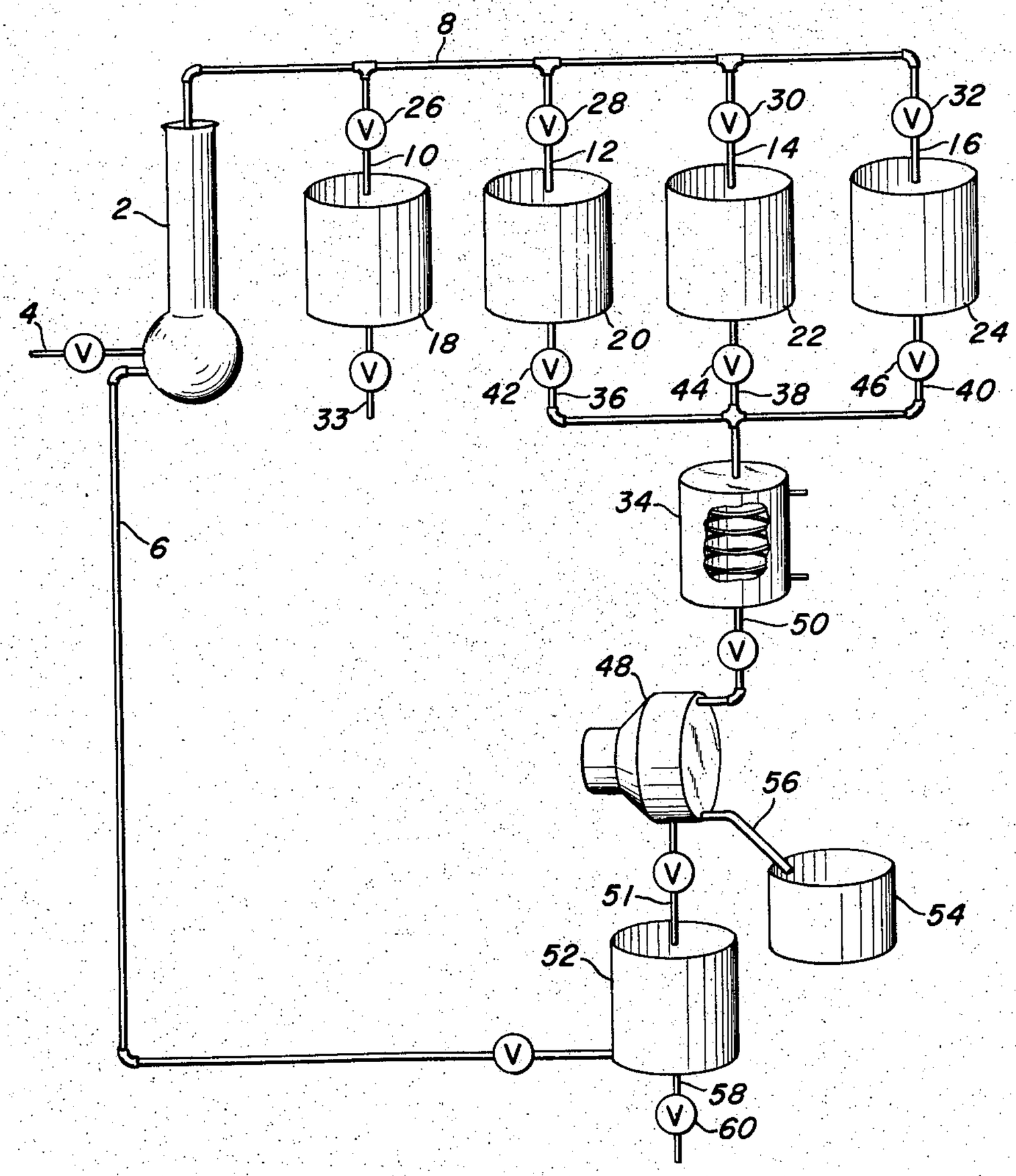

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METHOD OF SEPARATING ACENAPHTHENE, DIPHENYLENE OXIDE AND FLUORENE FROM AROMATIC OILS

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This invention relates to a method of separating acenaphthene, diphenylene oxide and fluorene from aromatic or partially aromatic oils boiling over the range of approximately 260 to 300° C. Such oils may be obtained from coal hydrogenation or petroleum reforming and the invention is particularly suitable for separating such components from coal-tar or other fractions such as creosote oil. To the best of our knowledge it has not been possible to recover all three of the above named compounds from such oils by any single process. Processes used to recover any one or two of the three compounds are based upon fractional distillation, crystallization and solvent washing. These processes have the disadvantages of being complex, costly and inefficient.

It is therefore an object of our invention to provide a simple, inexpensive and efficient process for the separation and recovery of acenaphthene, diphenylene oxide and fluorene from coal-tar or other fractions containing these three ingredients.

This and other objects will be more apparent after referring to the following specification and attached drawing, in which the single figure is a schematic view of apparatus suitable for carrying out our method.

Referring more particularly to the drawing, reference numeral **2** indicates a distillation unit to which coal-tar fractions or the like containing acenaphthene, diphenylene oxide and fluorene are fed through a conduit **4**. Recycle oil boiling over the range of approximately 260 to 300° C. is also delivered to the distillation unit **2** through a conduit **6**. The distillation unit **2** is connected to a header **8** having four branch conduits **10**, **12**, **14** and **16** connected thereto. The conduits **10**, **12**, **14** and **16** are connected to tanks **18**, **20**, **22** and **24**, respectively. Flow of material to the tanks **18**, **20**, **22** and **24** is controlled by means of valves **26**, **28**, **30** and **32** located in the conduits **10**, **12**, **14** and **16**, respectively. Suitable means such as a valve outlet **33** may be provided to drain off material from tank **18**. Tanks **20**, **22** and **24** are connected to a heat exchanger **34** by means of conduits **36**, **38** and **40**, respectively. Valves **42**, **44** and **46** are located in the conduits **36**, **38** and **40**, respectively, to control the flow therethrough. Heat exchanger **34** is connected to a centrifuge **48** by means of a conduit **50**. Centrifuge **48** is connected by means of conduit **51** to a recycle oil storage tank **52** and to a product container **54** by means of a conduit **56**. The tank **52** is connected by means of the conduit **6** to the distillation unit **2**. The tank **52** is also provided with conduit **58** having a valve **60** therein.

The operation of our method is as follows:

The oil to be processed and recycle oil boiling over the range of approximately 260 to 303° C. are fed to the still **2** through the conduits **4** and **6** and are distilled therein, the distillate being removed through the header **8**. We have found that by adding such recycle oil until the total weight thereof in the mixture is at least three times the combined weight of the acenaphthene, diphenylene oxide and fluorene, each of these last named

compounds will distill in a relatively narrow range below and at the boiling point of the pure compound as compared to the broad range in the original mixture. For economic operation the ratio should not exceed twenty to one and for best operation the ratio is approximately five to one. It is preferred to have the ratio greater when one of the compounds is present in greater amounts than the other two. Initially valve **26** is open and valves **28**, **30** and **32** closed. When a vapor temperature of approximately 265° C. (264°–268°) is reached, valve **26** is closed and valve **28** opened. When a temperature of approximately 279° C. (278°–280°) is reached, valve **28** is closed and valve **30** opened and when a temperature of approximately 288° C. (287°–289°) is reached, valve **30** is closed and valve **32** opened. When a vapor temperature reaches approximately 299° C. (298°–300°) the distillation is discontinued. Thus the fraction distilling in the range of approxiamtely 265 to 279° C. is collected in tank **20**, the fraction distilling in the range of approximately 279 to 288° C. is collected in tank **22** and the fraction distilling in a range of approximately 288 to 299° C. is collected in tank **24**. These distillation fractions are then processed individually to recover the crystalline solids in the following manner. Valve **42** is first opened and the distillate in tank **20** passes through the heat exchanger **34** where it is cooled to a temperature where the solids will crystallize, this temperature being approximately between zero and 45° C. and preferably about 20° C. The cooled distillate then passes into the centrifuge **48** where it is separated into oil and the crystal solids. The oil will pass through conduit **51** to tank **52** and the solids into the container **54**. This solid is acenaphthene substantially free of diphenylene oxide and fluorene. The distillate fractions from tanks **22** and **24** are processed in a similar manner and yield commercially pure diphenylene oxide and fluorene, respectively.

The original recycle oil may be obtained as follows. A coal-tar fraction of the type described is distilled in the still **2** and the three fractions distilling in the ranges of approximately 265 to 284° C., approximately 284 to 291° C. and approximately 291 to 303° C. are collected separately in tanks **20**, **22** and **24**. These distillation fractions are then processed individually in substantially the same manner as described above, that is, they are individually cooled in the heat exchanger **34** and the crystals separated from the oil in the centrifuge **48**. The crystalline fraction from tank **20** consists mainly of acenaphthene with appreciable amounts of diphenylene oxide and fluorene. The crystalline fraction from tank **22** consists principally of diphenylene oxide but also contains appreciable amounts of acenaphthene and fluorene. The crystalline fraction from tank **24** is mostly fluorene with an appreciable amount of diphenylene oxide present. The oil fractions from all of these fractions are collected in the tank **52** as the recycle oil. Such oil will contain the quantities of acenaphthene, diphenylene oxide and fluorene which are soluble in the oil at the temperature of crystallization. While the method described above is preferred because of its efficiency, the oil fractions originally obtained can be mixed and the mixture distilled with the fractions distilling in the ranges of approximately 265 to 279° C., approximately 279 to 288° C. and approximately 288 to 299° C. being collected separately in the tanks **20**, **22** and **24**.

Also, if desired, proportionate parts of the crystal fractions originally collected from tanks **20**, **22** and **24** may be added to the oil fractions in tank **52** with the total amount of such additions not exceeding one-fifth the weight of the oil fractions. This mixture can then be distilled, cooled and filtered in the manner described above to obtain acenaphthene, diphenylene oxide and fluorene in commercially pure form.

Another modification of our process is as follows. Creosote oil or coal-tar fractions containing acenaphthene, diphenylene oxide and fluorene is distilled into four fractions. With creosote oil containing approximately 1.5% acenaphthene, 1.7% diphenylene oxide and 3.4% fluorene, the boiling ranges of these four fractions are approximately 265 to 279° C., approximately 279 to 288° C., approximately 288 to 295° C. and approximately 295 to 300° C. The first fraction will be crude acenaphthene, the second crude diphenylene oxide, the third crude fluorene and the fourth commercially pure fluorene amounting to about 60% of the total fluorene present in the raw material. These fractions are separately cooled to between 0 and 45° C., preferably to 20° C., and filtered to separate the crystalline solids. The combined oils from the filtration of the four fractions are added to the mixture of the crystalline solids from the first three fractions in an amount of about one part solids to four parts of oil by weight. This mixture is then distilled into the three fractions distilling in the ranges of approximately 265 to 279° C., 279 to 288° C. and 288 to 299° C. and the fractions separately collected and filtered in the manner described above.

It will be understood that the crystals may be separated from the oil by other methods such as by filtration. The methods employed may be either of the batch or continuous type.

In each of the methods described above, it will be seen that the product finally distilled is a mixture of the solids acenaphthene, diphenylene oxide and fluorene with aromatic or partially aromatic oils boiling over the temperature range of 260 to 303° C. with the amount of oil being at least three times the combined weight of the solids.

While several embodiments of our invention have been shown and described, it will be apparent that other adaptations and modifications may be made without departing from the scope of the following claims.

We claim:

1. The method of separating acenaphthene, diphenylene oxide and fluorene from a coal-tar fraction or the like containing the same which comprises adding a coal-tar recycle oil distilled over the range of 260 to 303° C. to the said coal-tar fraction in the ratio of between three and twenty times the total weight of acenaphthene, diphenylene oxide and fluorene in the said coal-tar fraction, fractionally distilling the mixture of coal-tar fraction and oil, separately collecting the fractions distilled in the ranges of approximately 265 to 279° C., approximately 279 to 288° C. and approximately 288 to 299° C., cooling said last named fractions until crystals of the solids form, separating the crystals formed upon cooling from the oil of the fractions to obtain acenaphthene, diphenylene oxide and fluorene each substantially free of the other two compounds.

2. The method of obtaining acenaphthene, diphenylene oxide and fluorene from a coal-tar fraction or the like containing the same which comprises fractionally distilling a portion of said coal-tar fraction, separately collecting the fractions distilled in the ranges of approximately 265 to 284° C., approximately 284 to 291° C. and approximately 291 to 303° C., cooling said fractions to a temperature of between 0 and 45° C., separating the crystals formed upon cooling from the oil of the fractions, adding the said oil fractions to a portion of said coal-tar fraction in the ratio of between three and twenty times the total weight of acenaphthene, diphenylene oxide and fluorene in the last named portion of said coal-tar fraction, fractionally distilling the mixture of coal-tar fraction and oil, separately collecting the fractions distilled in the ranges of approximately 265 to 279° C., approximately 279 to 288° C. and approximately 288 to 299° C., cooling said last named fractions to a temperature of between 0 and 45° C., and separating the crystals formed upon cooling from the oil of the fractions to obtain acenaphthene, diphenylene oxide and fluorene each substantially free of the other two compounds.

3. The method of obtaining acenaphthene, diphenylene oxide and fluorene from a coal-tar fraction or the like containing the same which comprises fractionally distilling said coal-tar fraction, separately collecting the fractions distilled in the ranges of approximately 265 to 279° C., approximately 279 to 288° C., approximately 288 to 295° C. and approximately 295 to 300° C., cooling said last named fractions until crystals of the solids form, separating the crystals formed upon cooling from the oil of the fractions, mixing the oils from all the fractions to the solids from the first three fractions in such amounts that the weight of said oil is at least three times the combined weight of the acenaphthene, diphenylene oxide and fluorene, fractionally distilling the last named mixture, separately collecting the fractions distilled in the ranges of approximately 265 to 279° C., approximately 279 to 288° C. and approximately 288 to 299° C., cooling said last named fractions until crystals of the solids form, and separating the crystals formed upon cooling from the oil of the fractions to obtain acenaphthene, diphenylene oxide and fluorene each substantially free of the other two compounds.

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