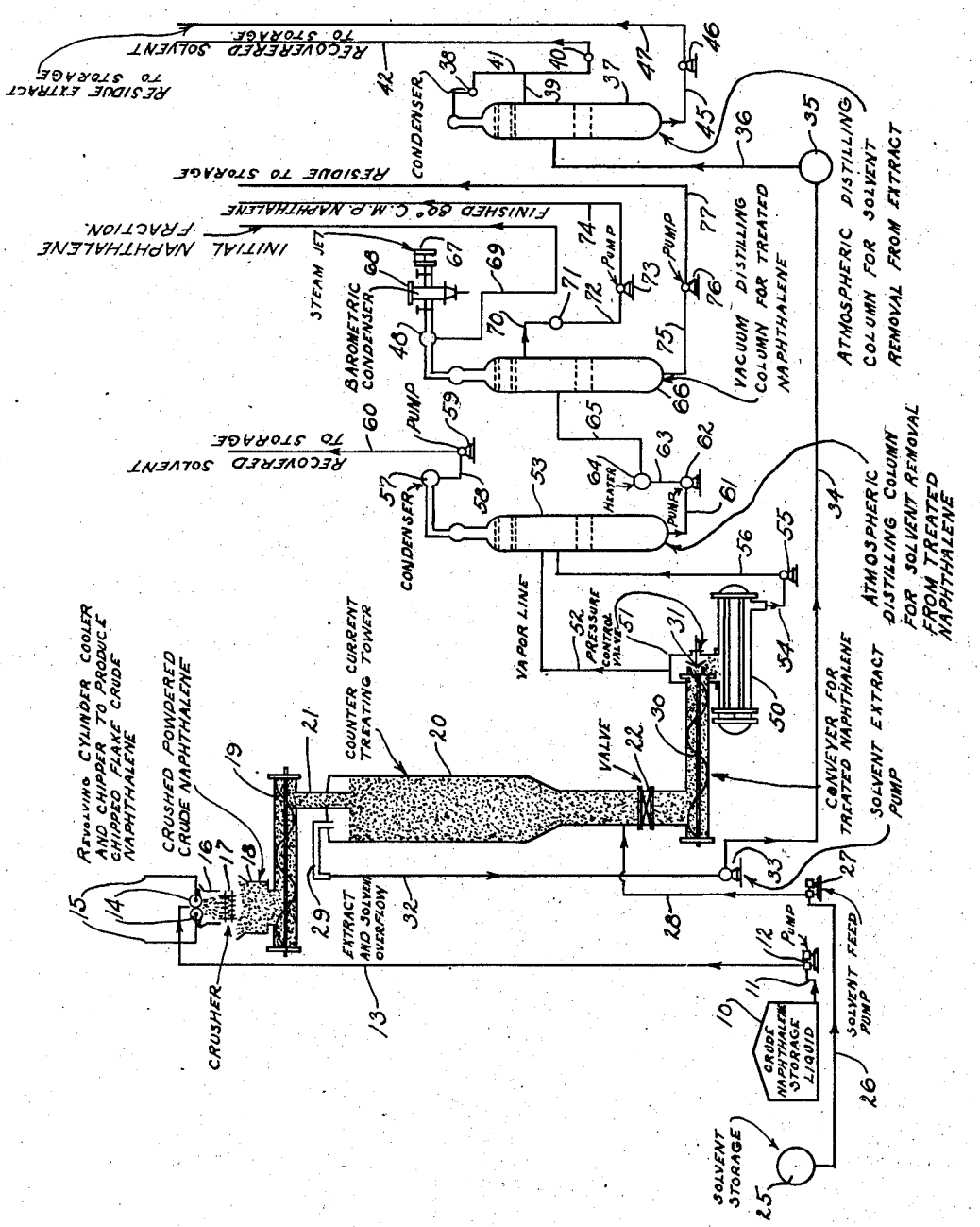
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PROCESS FOR THE MANUFACTURE OF POLYNUCLEAR AROMATIC HYDROCARBONS

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PROCESS FOR THE MANUFACTURE OF POLYNUCLEAR AROMATIC HYDROCARBONS

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6 Claims. (Cl. 260—674)

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This invention relates to processes for the purification of naphthalene, anthracene, phenanthrene, carbazol and other polynuclear aromatic hydrocarbons. The invention pertains particularly to the crystallizable hydrocarbon constituents of coal tar belonging to the above mentioned class.

When crude coal tar (derived by destructive distillation of coal) is subjected to distillation, a number of condensates are obtained that contain various compounds of value as intermediates in the manufacture of dyestuffs, synthetic resins, medicinals and the like. While the specific treatment of any given coal tar may be governed by the nature of the tar being distilled, general results are probably satisfactorily summarized in the following table:

Fraction collected	Name of fraction	Percentage of coal tar
Up to 170° C.	Light oil	0.2
170°-230° C.	Carbolic oil (⅓ phenol+⅔ cresylic acid).	10.0
230°-270° C.	Creosote oil	10.0
270°-350° C.	Anthracene oil	25.0
Residue at 350° C.	Pitch	55.0

The carbolic and creosote oil fractions representing about 20% of the crude coal tar are conventionally treated with caustic soda or the like for the removal of tar acids. The remaining material contains minor proportions of neutral oils, aromatic hydrocarbons, tar acids, pyridine bases, unsaturated hydrocarbons, sulfur containing compounds and other compounds together with major proportions of naphthalene in crystal form. Heretofore it has been found very difficult and costly to separate the above mentioned compounds from the naphthalene so as to isolate pure naphthalene having a melting point of 80° C.

The residual material left after a caustic soda treatment of the carbolic and creosote oil fractions for the removal of tar acids is known to the trade as crude naphthalene. It has been a common practice to press or centrifuge such crude naphthalene in order to separate the oils and other contaminants. However, such methods fail to remove all the oil and other contaminants. For example, centrifuged crude naphthalene may have a melting point as low as 70° C. and may contain 20% or more of oil and other contaminants. This centrifuged material may be again centrifuged or even hot pressed to remove more oil and contaminants so as to raise its melting point to 74° or 78° C. but still contains impurities and is sold to the trade as crude naphthalene. This material having a melting point of from 74° to 78° C. is tan-colored and has a tar-like odor.

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Another known method of purification comprises mixing crude naphthalene in molten condition with an aqueous alkaline medium, cooling the mixture to crystallize the crude naphthalene in the presence of the aqueous alkaline medium, separating the liquid medium from the naphthalene crystals by centrifuging, remelting the naphthalene crystals, bringing the re-molten naphthalene into contact with an aqueous alkaline medium, effecting recrystallization of the naphthalene by contacting the same with a cold aqueous alkaline medium and separating the liquid medium from the recrystallized naphthalene by centrifuging. This method yields a naphthalene having a melting point of from 78° to 78.5° C., which still has a dark color. To produce pure naphthalene having a melting point of 80° C. from thus incompletely purified naphthalene it is necessary to subject the latter material to further purification by melting, treating the molten naphthalene first with sulfuric acid and then with a sodium hydroxide solution and finally distilling the treated material.

Still another conventional method of purifying crude naphthalene includes the steps of contacting crude naphthalene with organic solvents at elevated temperatures, heating the resulting mixture to a temperature sufficient for effecting complete solution of the naphthalene, cooling the solution to form a mass of naphthalene crystals and introducing into the mass a displacing liquid to displace the solvent from the mass together with whatever impurities are contained in the solvent. This method is carried out on the batch principle. The results obtained by this method are not satisfactory, for the purified naphthalene obtained has a melting point of only 78° to 78.5° C., which indicates that all the contaminants have not been removed from the naphthalene.

The above outlined and other conventional methods of manufacturing naphthalene by purification of coal tar fractions do not yield directly pure naphthalene having a melting point of 80° C. Even when the purifying procedures are repeated or combined so as finally to produce pure naphthalene, the final recovery or yield of pure naphthalene is in all cases too low due to excessive naphthalene losses incurred by emulsification, chemical attack, inclusion with residues and like factors. The purification of naphthalene by conventional methods is also expensive because

of the necessarily large investment in equipment, the consumption of large amounts of chemicals such as sulfuric acid or sodium hydroxide, the long time required for complete processing of crude naphthalene with consequent low capacity of the purifying equipment, and like circumstances.

It is therefore an important object of this invention to provide a method of purifying naphthalene that does not entail the disadvantages, loss of naphthalene and high costs of operating inherent in conventional methods of purifying crude naphthalene.

Another important object of the present invention is to provide an inexpensive and rapid method of producing directly from crude naphthalene pure, permanently colorless naphthalene having a melting point of 80° C.

A further object of the invention is to provide a method of purifying crude naphthalene including no chemical treatment, whether by sulfuric acid, sodium hydroxide, or other chemicals; including an extraction step requiring no heating and no refrigeration while extraction of impurities is effected; and involving losses of naphthalene reduced to the theoretical minimum.

Another object of the invention is to provide improved purifying procedures capable of continuous operation, whereby greater efficiency and economy of operation may be attained.

Still another object of the invention is to provide improved purifying methods of the nature indicated that are also applicable to other polynuclear aromatic hydrocarbons than naphthalene, in particular, anthracene, phenanthrene, carbazol and like materials present in high boiling coal tar fractions.

Other and further objects and features of the present invention will become apparent from the following description and appended claims.

I accomplish the objects outlined hereinabove by washing crude naphthalene crystals with a liquid aliphatic hydrocarbon having a boiling point below the boiling point of naphthalene and with which preferably is admixed some liquid having a higher solvent power for naphthalene. Such washing is suitably carried out at normal working temperatures which may vary, say, from 40° to 100° F., depending on atmospheric temperatures.

The solvent or solvent mixture used should be relatively low boiling to make the same easily and completely recoverable. Further, since in order to operate at normal atmospheric pressure the solvent must boil above the temperature of operation, the boiling range of suitable solvents or solvent mixtures is limited in both directions, ranging preferably between an initial boiling point of from 100° to 150° F. and a final end point of between 225° and 275° F. The necessity of excluding high boiling solvents can be traced to the fact that in dilute solutions the partial pressure of a substance decreases directly with the decreasing concentration. Hence in the case of solvents which possess high boiling points it becomes very difficult to remove the last traces of such solvents by distillation, for temperatures that approach or reach the boiling point of naphthalene must be employed. In the case, however, of a solvent or solvent mixture having an end point between 225° and 275° F., all the solvent can be recovered at low operating temperatures without entrainment of pure naphthalene, which has a boiling range of approximately 410° to 420° F. In other words, I am able to recover the

solvent in its entirety below the boiling point of the naphthalene.

Solvents such as benzene, acetone, methyl acetate, ethyl acetate, toluene and the like, if used separately or in combination with each other to wash crude naphthalene would remove in their entirety all the impurities contained in the crude naphthalene. However, such solvents, when employed at normal working temperatures ranging from 40° to 100° F., would also have a high solvent power for naphthalene and if used at these temperatures would carry from 10 to 30% or more of the naphthalene into the extract. If, on the other hand, petroleum naphtha is used by itself without any admixture of the above mentioned type of solvent, then, in most cases, some small amounts or traces of impurities are left in the naphthalene. Whether or not petroleum naphtha per se is operative for complete purification depends, as I have found, on the type of crude naphthalene being purified. Now I have found that petroleum naphtha has a relatively low degree of solvent power for naphthalene, the solubility of naphthalene in a petroleum fraction having the hereinabove specified boiling range being less than 2.5% at 70 to 80° F. By blending or mixing any of the hereinabove mentioned solvents or their equivalents in the ratio of from 5 to 20% with from 80 to 95% of the petroleum fraction I have obtained a combination solvent that will remove entirely all contaminants contained in crude naphthalene with a minimum percentage of lost naphthalene in the resulting extract. Such combined solvents are also operative in the purification of such crude naphthalene as can be satisfactorily purified with plain petroleum naphtha.

More particularly, I may blend from 80 to 95% of a petroleum fraction having a boiling range falling between an initial boiling point of 100° F. and a final boiling point of 275° F. with from 5 to 20% acetone; or 80 to 95% of the same petroleum fraction with from 5 to 20% benzene; or any other solvent mentioned hereinabove or any equivalent solvent may be blended in the desired ratio with a petroleum naphtha having a boiling range as set forth, to form solvent blends having the specified boiling range that can be utilized in the purification of crude naphthalene. Certain additional advantages can be obtained by interblending several of the above mentioned solvents and blending in from 80 to 95% petroleum naphtha with from 5 to 20% of the resulting mixture.

It is important that the solvent or solvent mixture used should have great selectivity, i. e. ability to remove contaminants and deleterious compounds from crude naphthalene, and this regardless of whether the crude naphthalene be that having a melting point of 55° C. or that having a melting point of 78° C. It should be understood, in this connection, that the lower the melting point of crude naphthalene, the greater the percentage of contaminating products contained therein. At the same time, the solvent or solvent mixture should be distinguished by low solvent power for naphthalene to render the percentage of recovery of this material high.

In the case of a few types of crude naphthalene, petroleum naphtha is sufficiently selective for complete purification with good yield. In most cases, however, it is necessary, as indicated hereinabove, to admix with the petroleum naphtha or the like, minor proportions of organic liquids that are better solvents than petroleum naphtha

for naphthalene and, incidentally, the contaminants present in crude naphthalene. Such liquids include aromatic hydrocarbons, for instance, benzene; ketones such as acetone; esters such as methyl and ethyl acetates; alcohols such as methanol and ethanol; and other like solvents miscible with petroleum naphtha.

The solvents and solvent mixtures used are such as are chemically inert toward the material treated. No naphthalene is lost or chemically modified by the solvents or solvent mixtures. Nor is there any corrosion of the equipment used, which therefore may be made of ordinary construction materials. The solvents or solvent mixtures are completely recoverable without the use of any special fractionating means for the separation of solvent from extract and naphthalene by distillation. The solvents or solvent mixtures can be used at ordinary temperatures and are readily available commercially at a low cost.

The purifying process according to the present invention involves essentially a washing or extraction treatment of crude naphthalene or the like by means of the solvents or solvent mixtures disclosed hereinabove. It should be clearly understood that these liquid media, although referred to as "solvents" do not dissolve anything except the impurities to be removed and that very small amount of naphthalene which is carried away by the "solvents" along with the contaminants. That naphthalene which is finally obtained in pure form remains in solid state during the whole washing or extracting process.

The working of the present invention is illustrated by the typical example of a specific method of purifying naphthalene according to the present invention described in some detail hereinbelow with special reference to the appended drawing showing diagrammatically a plant wherein the process of the invention can be effectively carried out and including a flow sheet showing the progress of the various materials involved through the plant.

The drawing shows the principal apparatus or equipment parts in side elevation, with parts shown in longitudinal vertical section. The plant shown is adapted and arranged for the continuous processing of crude naphthalene stock having a melting point ranging all the way from 55° C. to 78° C., to remove completely the contaminating more or less complex impurities varying inversely in amount according to the melting point of the material.

Liquid crude naphthalene having a melting point of 78° C. is drawn from a storage tank **10** through a supply line **11** by a pump **12** and discharged through a line **13** at the rate of 2.8 gallons or 23¼ pounds per minute. The liquid crude naphthalene is discharged into the nip of a pair of opposed revolving cylinders **14** internally cooled by water supplied by pipes **15**. As soon as the liquid naphthalene contacts the cool surface of the rotating cylinders the liquid naphthalene crystallizes in the form of a thin sheet. The thickness of this sheet is governed by the spacing of the cylinders, which are set to give sheets so thin as to be readily permeable by the washing medium after having been broken up. The crystallized naphthalene in the rotating cylinders is shaped off by a knife edge (not shown), falling into a hopper or container **16** whence it falls into crusher **17** where it is pulverized and crushed to a fineness such as to be readily permeable by the washing medium. The crushed crude naphthalene leaving the crusher **17** falls into a hopper **18** and thereafter enters a conveyor **19**. The speed of the conveyor **19** is controlled to deliver 23¼ pounds per minute to the counter-current extraction tower **20** through the line **21** which extends down into the tower **20** to a point distant from the top of the tower by about one foot. The extraction tower **20** may be 18 inches in diameter and 10 feet high, being constricted to a 12 inch diameter for a distance of about 5 feet from the base of the tower. A valve **22** located one foot from the bottom of the tower **20** is closed and remains closed until the tower **20** has been filled with crude naphthalene.

When crushed crude naphthalene has reached the outlet level of the discharge line **21** in the tower, the conveyor **19** is stopped. The tower **20** has sight glasses (not shown) located at suitable points permitting visual inspection of the interior of the tower so that the level of naphthalene as well as the liquid level in the tower can be ascertained. When thus filled, the tower **20** will contain about 1250 pounds of crushed crude naphthalene. At the charging rate of 23¼ pounds per minute from the conveyor **19** it will take approximately 54 minutes to charge the tower **20**.

The washing or extracting medium used may be a mixture of 5% acetone with 95% (by volume) of a petroleum naphtha fraction having an initial boiling point of 130° F. and a final boiling point of 250° F. This solvent mixture is now drawn from a storage tank **25** through a line **26** by a pump **27** and discharged through a line **28** to the tower **20** at a controlled rate of 2.5 gallons per minute. This specific washing medium has a specific gravity of 0.737 or 6.15 pounds per gallon, so that the total weight of solvent fed to the tower per minute amounts to 15.37 pounds. The outlet of the discharge line **28** into the tower **20** is located about 6 inches above the valve **22**. At the above mentioned controlled rate of solvent feed into the tower **20** approximately 60 minutes will elapse before the liquid level in the tower **20** will reach an overflow line **29**. The crude naphthalene at the bottom will then have been washed by all the solvent entering the tower and will be in substantially pure condition, the extracted impurities having been carried toward the top of the tower. At this time the solvent pump **27** is shut down and the valve **22** is opened. The purified naphthalene, compressed by the weight of overlying naphthalene and solvent so as to have all but 30% of its weight of solvent squeezed out of the purified naphthalene, will leave the constricted base of the tower **20** and will enter a conveyor **30** which operates against a pressure control valve or cone **31**. The conveyor **30** is now started, and will discharge at a controlled rate of about 22 pounds per minute plus 30% by weight of clean extracting medium. At this time the conveyor **19** is again started, as is also the solvent feed pump **27**, and the process is now ready for continuous operation.

The extract together with the 70% (by weight of naphthalene) of spent solvent displacing the same overflow through the outlet line **29** located at the top of the tower **20** through a line **32** to a pump **33** and are thence discharged through a line **34** to a heater **35**. The last mentioned element may be a tubular type heater. The heating medium can be either steam or hot circulating oil. The heater **35** serves to preheat the solvent extract to the proper temperature prior to discharging the preheated solvent extract through a line **36** into a distilling column **37** where the

solvent is recovered from the extract by atmospheric flash distillation. The solvent vapor in the tower 37 is condensed in a final condenser 38. A side stream fraction flows through a line 39 to a pump 40, where also the distillate from the condenser 38 is delivered through a pipe 41. The pump 40 delivers the recovered solvent back to the storage tank 25 through a pipe line 42.

The extract left after solvent recovery from the distilling column 37 is a residue representing from 4 to 5% of the charge of crude naphthalene to the tower 20. This residue leaves the column 37 through a line 45 and a pump 46, being discharged through a line 47 to a storage tank (not shown).

The purified washed naphthalene containing about 30% by weight of clean washing medium discharged from the conveyor 30 through the pressure valve 31 enters a closed tubular heater 50. The heating medium in this tubular heater can be either steam or circulating hot oil. In this heater the solvent processed or worked naphthalene is liquefied. The heating also brings this material up to the temperature required to distill off the 30% solvent remaining in the processed naphthalene. For this purpose, the tubular heater 50 is formed as a closed vapor-stage system and provided with a vapor dome 51 whence the vapors formed in the heater proper leave by way of a line 52 to enter an atmospheric distilling column 53. The liquid naphthalene together with whatever solvent has not vaporized leaves the heater 50 through a line 54, entering a pump 55 and being discharged through a line 56 into the distilling column 53 for solvent recovery. Solvent vapor is condensed in the condenser 57 and flows through a line 58 and a pump 59 for discharge through a line 60 to the storage tank 25.

The purified washed solvent-free liquid naphthalene left as a residue in the distilling column 53 has a good color and has a melting point of from 79.6° to 79.8° C. This residue represents from 95 to 96% of the crude naphthalene charged to tower 20. This liquid naphthalene leaves the tower 53 through a line 61, being moved by a pump 62 through a line 63, a tubular heater 64 and a pipe 65 into a vacuum distilling column 66 where the naphthalene is distilled at a reduced pressure on the order of from 50 to 75 millimeters of mercury (absolute pressure). The means for producing vacuum may comprise a steam jet 67. The temperature of distillation in the distilling column 66 is approximately the same as the temperature used for solvent recovery in the atmospheric distilling column 53 or, in other words, about 300° F. A low boiling naphthalene fraction amounting to 1% or less is recovered separately from a condenser 48 ahead of a barometric condenser 68, being discharged to storage through a line 69. This small low boiling naphthalene fraction apparently contains chemically unstable substances.

The main portion of the naphthalene leaves the distilling column 66 through a side pipe 70, flowing through a condenser 71, a line 72, a pump 73 and a line 74 to storage. This naphthalene fraction represents from 94 to 95% of the crude naphthalene entering the tower 20. This fraction is water white in color, has a mild odor and a melting point of 80° C. When subjected to a wash test, i. e. when a mixture of 11 cubic centimeters of chemically pure benzene, 7 cubic centimeters of melted naphthalene and 7 cubic centimeters of 95 to 98% chemically pure sulphuric

acid is shaken for 5 seconds and allowed to stand for 5 minutes, the acid will have a color value of less than 5.

The residue from the tower 66 flows through a line 75 to a pump 76 and is discharged through a line 77 to storage. This residue represents about 1% of the crude naphthalene charged into the tower 20 and can be accumulated and recycled separately or returned to the crude naphthalene storage. At least 95% of this residual 1% can be recovered as water white naphthalene having a melting point of 80° C. The extract residue leaving the tower 37 can also be accumulated and re-cycled. This extract residue, which amounts to about 4 to 5% in the case of a crude naphthalene having a melting point of 78° C., in turn has a melting point of 70° C. and is quite dark in color. When re-cycling this type of material it is necessary to use a solvent-solid ratio of about 1½ to 1 by weight. By using such a solvent ratio I have recovered from such extracted material 50% of its weight as pure naphthalene having a melting point of 80° C. The other half of the extract residue representing 2½% of the crude naphthalene heated has a melting point of 63° C. and is very dark in color.

Thus, starting with crude naphthalene having a melting point of 78° C., the ultimate yield of water white pure naphthalene having a melting point of 80° C. from the counter-current process described hereinabove will be as high as 97.5% when using the solvent and the solvent ratio described. The condensate leaving the tower 66 is the desired final product of the complete process, being a clean, permanently white stable naphthalene having a melting point of 80° C. which requires no further refining or purifying, as by chemical processes, no matter for what purposes the naphthalene is to be used.

It may be noted that all lines to and from the pumps handling liquid naphthalene are steam jacketed to prevent plugging by crystallization. Low steam pressure on the order of 5 or 10 pounds will furnish sufficient heat to maintain the naphthalene in liquid condition at all times.

Crude naphthalene having a melting point below 55° C. may advantageously be distilled fractionally before being purified by extraction as disclosed hereinabove. Thus, a crude naphthalene having a melting point of 46° C. may be distilled, the first 10% distilling over being discarded, and the next 60% being collected for further purification. This 60% fraction contains substantially the whole naphthalene content of the crude product, having a melting point of 62° C. and a distillation range of from 380° and 455° F. When purified by extraction according to the present invention, 42 out of the 60% may be recovered as white naphthalene having a melting point of 79.6° C.

Extraction treatment according to this invention can be carried out by other than counter-current means. For instance, a plurality of extraction towers may be charged with crude naphthalene and traversed successively by a current of extraction medium, the towers being cut out of the system in rotation for discharge of purified naphthalene and recharging with crude naphthalene.

As shown by the illustrative example described hereinabove, the present invention provides a process including a plurality of steps. The initial step includes comminuting naphthalene to make the same permeable to a liquid extraction medium. The second step comprises selectively ex-

tracting impurities from the comminuted naphthalene with a liquid medium having a maximum boiling point below that of naphthalene and containing a blend of liquids having different solvent powers in relation to naphthalene and to impurities present therein blended in such a ratio as to effect minimal dissolution of naphthalene while extracting the impurities completely. The extraction is preferably carried out progressively, being terminated by a displacement of extracting medium containing impurities with clean extraction medium. The naphthalene subjected to extraction may then be compressed, to express clean extraction medium adhering thereto. Up to this point the naphthalene has been treated in solid form and at atmospheric temperature, and the impurities have been removed from the naphthalene itself and from the extraction medium adhering thereto. The extraction medium preferably contains petroleum naphtha boiling between 100° and 275° F., to which may be added aliphatic esters, alcohols and ketones or aromatic hydrocarbons having a boiling range falling between 100° and 275° F., to increase the solvent power of the naphtha with respect to the naphthalene impurities. The amounts of solvents added to the naphtha are minor fractions, in order not to raise the solvent power of the blend for naphthalene. When naphthalene containing relatively large amounts of impurities is purified, a product having the same melting point of from 79.6° to 79.8° C. as that obtained, say, from crude naphthalene melting at 78° C. may be obtained by increasing the ratio of extraction medium to naphthalene. If temperatures below 60° F. prevail during the extraction, it may also be advantageous to increase the extraction medium-naphthalene ratio, since at lower temperatures the naphthalene particles appear less permeable to the extraction medium or the latter less efficient in removing impurities.

The third step includes heating the naphthalene subjected to extraction below its boiling point and above its melting point (if necessary) in order to expel extraction medium adhering thereto. The purified naphthalene thus obtained is of good color and may have a melting point of 79.6° to 79.8° C.

The fourth step, which is optional, includes a distillation of the naphthalene purified by extraction, the initial fraction of not more than one per cent being collected apart from the rest of the distillate, which consists of water white naphthalene having a melting point of 80° C., being chemically pure naphthalene suitable for any and all uses to which such naphthalene is put.

Naphthalene of a high degree of purity can thus be prepared without chemical action while keeping the naphthalene in solid state at atmospheric temperature. Naphthalene of various degrees of purity can be purified by the methods of this invention with excellent results. The only limitation imposed is that the crude naphthalene should not contain so great an amount of impurities as to be liquid when purified as outlined hereinabove.

Anthracene, phenanthrene, carbazol, mixtures thereof, and like materials can also be purified according to the present invention. Such materials are usually available in the form of crystals having relatively high melting points, as compared with naphthalene, and need not be melted and then solidified to be put into suitable form for extractive purification, although grinding or other reduction in particle size may be required.

Many details of procedure may be varied within a wide range without departing from the principles of this invention and it is therefore not my purpose to limit the patent granted on this invention otherwise than necessitated by the scope of the appended claims.

I claim as my invention:

1. A method of purifying naphthalene in the solid state including comminuting said naphthalene to make the same permeable to a liquid extracting medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an inert solvent for naphthalene capable of dissolving more than 2.5% naphthalene and having a boiling range falling between 100° and 275° F. and thereafter extracting impurities from said comminuted naphthalene with a liquid medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an inert solvent for naphthalene capable of dissolving more than 2.5% naphthalene and having a boiling range between 100° and 275° F., said extraction being effected by counter-currentwise flowing the liquid extraction medium through a moving column of comminuted naphthalene.

2. A method of purifying naphthalene in the solid state including comminuting said naphthalene to make the same permeable to a liquid extraction medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an aliphatic alcohol having a boiling range falling between 100° and 275° F. and thereafter extracting impurities from said comminuted naphthalene with a liquid medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an aliphatic alcohol having a boiling range between 100° and 275° F.

3. A method of purifying naphthalene in the solid state including comminuting said naphthalene to make the same permeable to a liquid extracting medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an aliphatic ester having a boiling range between 100° and 275° F. and thereafter extracting impurities from said comminuted naphthalene with a liquid medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an aliphatic ester having a boiling range of between 100° and 275° F.

4. A method of purifying naphthalene in the solid state including comminuting said naphthalene to make the same permeable to a liquid extracting medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an aromatic hydrocarbon having a boiling range falling between 100° and 275° F. and thereafter extracting impurities from said comminuted naphthalene with a liquid medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of an aro-

matic hydrocarbon having a boiling range falling between 100° and 275° F.

5. A method of purifying naphthalene in the solid state including comminuting said naphthalene to make the same permeable to a liquid extracting medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of ethyl acetate and thereafter extracting impurities from said comminuted naphthalene with a liquid medium containing from 80 to 95% of petroleum naphtha having a boiling range falling between 100° and 275° F. together with from 5 to 20% of ethyl acetate.

6. The method of purifying crude naphthalene containing naturally occurring tar acids and other contaminants to produce therefrom in a continuous process a purified naphthalene having a melting point of at least 79.6° C., which method comprises comminuting the crude naphthalene in solid form, advancing the comminuted naphthalene into and through an extraction zone, flowing countercurrently through said extraction zone an extraction solvent comprising at least 80% of petroleum naphtha having a boiling range of from 100° to 275° F. and maintained at a temperature of from 40° to 100° F., washing the advancing naphthalene prior to being displaced from said extraction zone with fresh extraction solvent, compacting said naphthalene to remove therefrom a portion of said fresh extraction solvent, heating the resulting naphthalene to remove the balance of said extraction solvent, fractionally distilling the solvent-free naphthalene and collecting the middle and final fractions of said naphthalene as the purified product, the steps named being carried out sequentially as recited and as a continuous process.

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