

# UNITED STATES PATENT OFFICE

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## PROCESS FOR PURIFYING PIPERYLENE

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This invention relates to the refining of piperylene.

More particularly, this invention pertains to the removal of impurities from piperylene and piperylene fractions by the application thereto of one or more metals of group Ia and group IIa of the periodic table, as well as active alloys thereof.

An object of the present invention is the removal of certain impurities from piperylene and piperylene fractions by treatment with one or more finely divided alkali or alkaline earth metals, or active alloys thereof. Another object of the invention is the provision of certain methods whereby piperylene, and particularly light oil piperylene fractions, may be purified in a continuous manner by the application of alkali or alkaline earth metals without undue loss of unsaturated hydrocarbons in the form of soluble or insoluble polymers. Other objects and advantages of the invention will be apparent to those skilled in the art upon an inspection of the following description and claims.

Piperylene and piperylene fractions, particularly light oil piperylene fractions, frequently contain substantial quantities of impurities, such as acetylenic hydrocarbons and compounds; oxygenated compounds such as aldehydes and peroxides; and other impurities, which interfere with the use of such materials in most, if not all, industrial applications.

Thus, for example, a 75% light oil piperylene fraction obtained by the pyrolysis of petroleum in the gas phase at temperatures substantially above 1500° F., followed by condensation and fractionation, was found to contain 0.4% of acetylenes and 0.03% aldehydes, as well as certain other oxygenated impurities. This piperylene fraction, as well as the more highly concentrated piperylene obtained therefrom by the use of suitable concentrating methods, such as a 98% piperylene concentrate, is unsuited for the production of synthetic rubber of good quality due to the inhibiting action, and other undesirable properties, of the impurities contained therein.

As a result of extensive experimentation, I have discovered that piperylene and piperylene fractions, particularly light oil piperylene fractions, may be refined by the application in finely divided form of at least one metal of group Ia and group IIa of the periodic table, as well as active alloys thereof. Particularly desirable results are obtained by the use of finely divided alkali and alkaline earth metals.

Examples of such metals are lithium, sodium,

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potassium, rubidium, caesium, barium, strontium and calcium. Due to the availability and low cost of sodium and potassium, however, these metals are preferred for the use set forth herein.

Alloys of these metals, such as NaPb<sub>10</sub>, NaHg<sub>4</sub>, NaCa<sub>5</sub>, NaZn<sub>12</sub>, KNa and the like, also may be employed for the removal of undesired impurities from piperylene and piperylene fractions. In general, the alloys of the respective metals react with the impurities present in piperylene and piperylene fractions at a slower rate than the corresponding metals.

In general, therefore, it may be said that very finely divided metals in groups Ia and IIa of the periodic system, and their reactive alloys, may be used to refine piperylene and piperylene fractions.

The piperylene and piperylene fractions which may be refined by this method may be obtained from any desired source such as synthetically, for example by the removal of the elements of chlorine or hydrogen chloride from polychlorinated C<sub>5</sub> compounds, by the partial hydrogenation of certain C<sub>5</sub> acetylenes, by the dehydrogenation of certain pentanes and amylenes, by the dehydration of certain C<sub>5</sub> alcohols and glycols and by synthesis from furfural; by the pyrolysis of petroleum in the gaseous phase at temperatures above 1000° F., and more particularly above 1300° F., followed by condensation and fractionation; and by the pyrolysis of other carbonaceous materials. Other procedures also may be employed for the production of piperylene or piperylene fractions which may be refined by the methods to be more particularly described herein.

The piperylene fractions also may be initially concentrated to any desired extent prior to refining, and such concentration may be carried out by any desired method. This may include concentration by fractionation, azeotropic distillation, solvent extraction, a combination of solvent extraction and fractionation methods, and the formation of complexes between the diolefine and some active compound, such as cuprous chloride, followed by the removal of the non-diolefine portion of the fraction and the decomposition of the complex. Other concentrating methods also may be employed if desired.

In addition, other refining methods also may be applied to piperylene and piperylene fractions to remove at least a portion of one or more impurities present prior to refining by methods to be more particularly described herein. Thus, such fractions may be contacted with acids or acidic solutions or materials to remove a portion of cer-

tain impurities or undesirable materials present.

Such concentrating and/or partial refining operations also may be applied to piperylene or piperylene fractions subsequent to the refining operations to be more particularly described herein.

The process is applicable to the refining of cis-piperylene, having a boiling point of approximately 43.6° C., trans-piperylene, having a boiling point of approximately 41.5° C., or mixtures thereof; or to the refining of any fraction or mixture containing at least one of the isomeric piperylenes.

I find that a solution of sodium, or a suspension or emulsion of very finely divided sodium, or a solution, suspension, or emulsion of one or more sodium alloys, is a particularly desirable agent for the continuous removal of certain undesirable impurities from piperylene and piperylene fractions. Excellent results are obtained by the use of a suspension of very finely divided sodium.

The alkali metals, particularly sodium and potassium, are very active catalysts for the polymerization of piperylene. Consequently, the use of such an active catalyst, particularly in finely divided (and hence most active) form, for the refining of piperylene and/or piperylene fractions would be expected to result in the conversion of the greater portion, if not all, of the piperylene present to polymers.

It should be emphasized that the success of the refining operations is dependent upon rigid adherence to certain operating conditions such as temperature, reaction time, concentration, and so forth, which will be discussed in considerable detail.

In addition, the use of polymerization inhibitors, as well as the method employed for conducting the refining operations, also has a very considerable influence upon the results obtained.

While the refining operations may be carried out in the absence of any added polymerization inhibitors, I prefer to employ one or more polymerization inhibitors in order to reduce the loss of piperylene in the form of polymers, as well as to broaden the permissible limits of certain of the reaction variables.

Inhibitors which are particularly effective agents for retarding the rate of polymerization of unsaturated hydrocarbons, and particularly piperylene and piperylene fractions, when refined with very finely divided metals in Groups Ia and IIa of the periodic system, and their reactive alloys, may be classified in the following groups.

1. Amines and nitrogen-containing inhibitors, particularly aryl amines such as

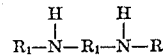
Alpha-naphthylamine,  
Thiodiaryl amines,  
p-Phenylene diamine,  
o-Phenylene diamine,  
2,4-diamino diphenylamine,  
Phenyl hydrazine,  
Benzamide,  
Cyclohexyl naphthyl amine, and  
Polybutyl amines.

Particularly desirable results may be obtained by the use of secondary aryl amines having the following general formula

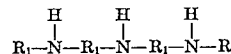


in which R<sub>1</sub> is a substituted or an unsubstituted aryl, aralkyl, cycloparaffinic, cycloolefinic, hydroaromatic or naphthenic ring or group, and in which R is a substituted or an unsubstituted aryl,

aralkyl, cycloparaffinic, cycloolefinic, hydroaromatic or naphthenic ring or group, and in which R is a substituted or an unsubstituted aryl, aryl-alkyl, alkyl-aryl, alkyl, cycloparaffinic, cycloolefinic, hydroaromatic, or naphthenic ring or group. Included are secondary amines such as for examples



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in which R and R<sub>1</sub> have the same meaning as before.

15 Secondary amines containing one or more aryl or substituted aryl groups are preferred, such as

- Diphenyl-p-phenylene diamine,  
Phenyl-beta-naphthylamine,  
20 Isopropoxydiphenyl amine,  
Aldol-alpha-naphthyl amine (and polymers thereof),  
Symmetrical di beta naphthyl-p-phenylenediamine,  
25 Trimethyl dihydroquinoline (and polymers thereof), and  
Ditolylamines, and mixtures thereof.

2. Phenolic compounds, such as

- 30 Dihydroxybenzenes (and substitution products thereof),  
Pyrogallol (and substitution products thereof),  
Pyrocatechol,  
Resorcinol,  
35 Xylenols,  
Catechol,  
Trihydroxybenzene (and substituents thereof),  
Nitrosophenol,  
Diaminophenol,  
40 Alpha-naphthol,  
Dihydroxynaphthalene,  
Hydroxy quinoline,  
Hydroxy tetrahydroquinoline,  
Polyhydric phenols,  
45 Polyhydroxy phenanthrene, and  
4-nitroso-2-methyl phenol.

3. Compound inhibitors, such as

- Acyl-substituted amino phenols,  
50 4-cyclohexyl amino phenol,  
p-Amino phenol,  
o-Amino phenol, and  
5-amino-2-hydroxytoluene.

4. Miscellaneous inhibitors, such as

- 55 Hydroquinone,  
Quinol,  
Nitroso naphthols,  
Quinhydrone,  
60 Reaction product of an aldehyde and an amine,  
p-Amino acetophenone,  
Dihydroxy anthraquinone, and  
Reaction product of a ketone with an amine.

Excellent results may be obtained when one or more inhibitors selected from a list comprising  
65 (1) secondary aryl amines such as phenyl beta-naphthylamine, diphenyl-p-phenylene diamine, isopropoxydiphenyl amine, aldolalpha-naphthylamine (and polymers thereof), symm. di-beta-naphthyl-p-phenylene diamine, trimethyl dihydroquinoline (and polymers thereof), and the ditolylamines; (2) phenolic compounds, such as p-tertiary butyl catechol and alkylated polyhydroxy phenols; and (3) reaction products  
70 of a ketone, such as acetone, and/or an aldehyde,

such as formaldehyde and acetaldehyde, with an amine, such as aniline, are employed in the refining process described.

In general, I prefer to employ less than 10%, by weight, of polymerization inhibitor, based on the unsaturated hydrocarbon or unsaturated hydrocarbon fraction in batch treating processes, and the maximum total volume of suspending liquid in the treating system at any one time in the case of continuous treating processes. Good results also have been obtained by the use of less than 5% inhibitor, and even less than 2% inhibitor, in certain cases, particularly when one or more of the inhibitors listed in the preceding paragraph are employed.

While the refining operations may be carried out in a satisfactory manner in a batchwise manner, I prefer to conduct such operations in a continuous or semi-continuous system in order to reduce the proportion of piperylene lost in the form of polymers, as well as to secure greater economy in the use of the reagent.

The preferred refining method disclosed herein differs fundamentally from all methods described heretofore for the refining of unsaturated hydrocarbon fractions in that the material in question is treated with a metal of group Ia or group IIa, or an active alloy of such metals, in finely divided or solution form in a continuous system and in the presence of one or more polymerization inhibitors. By the use of a continuous system, particularly in conjunction with the use of an inhibitor, the loss of piperylene due to side reactions or to polymerization is very markedly reduced, or almost completely eliminated.

As pointed out previously, this is of particular importance in the case of piperylene, which is quite susceptible to polymerization when placed in contact with certain active metals, as well as active alloys thereof. Thus, sodium is a very active catalyst for the polymerization of piperylene, and has been suggested as a catalyst for the conversion of piperylene to synthetic rubber in numerous references. The use of this material in very finely divided form for the refining of piperylene, therefore, must be carried out within well defined limits in order to prevent undue loss of piperylene due to polymerization. The success of the preferred refining method employing finely divided sodium, or other herein-mentioned active metals, or alloys, must be attributed largely to the continuous nature of operation, resulting in a minimum contact time between the piperylene and the reactant.

Although the process may be carried out in any desired manner, I prefer to conduct it in a vertical vessel or tower in which a certain height of a liquid suspension or solution of the active refining agent is maintained. The material to be refined then is passed upward in the vapor and/or liquid phase through this column of reagent at a rate sufficient to insure the removal of the desired quantity and type of impurities present at the temperature employed. The refined material preferably is taken off at the top in the vapor phase, temperature and pressure conditions being adjusted for this purpose.

Other methods of contacting the material to be treated and the refining agent also may be employed if desired. Thus, the unsaturated hydrocarbon may be passed through a horizontal treating unit, such as a pipe or bank of pipes, partially or completely filled with a suspension of the desired refining agent, or otherwise.

The suspending liquid employed for the refining agent may be of any desired type. Preferably, it does not react with the reagent or the material to be treated to any substantial extent, and preferably it does not introduce any additional impurities into the material to be treated. I find that hydrocarbons and hydrocarbon fractions are particularly desirable materials for use as suspending mediums for refining agents of the type described herein. Excellent results have been obtained by the use of aromatic hydrocarbons and aromatic hydrocarbon fractions for this purpose.

It is to be understood, of course, that the material to be treated may dissolve to some extent in the suspending medium, consequently the suspending medium actually employed in the operation of the process usually comprises a mixture of the material to be treated and the suspending medium initially introduced into the system. Thus, in the treatment of a light oil isoprene fraction with a xylene suspension of finely divided sodium in a continuous system operating at 50° C. and atmospheric pressure, the suspending medium contained 47% of the isoprene fraction by weight after equilibrium conditions had been established.

The material being treated also may serve as a suspending medium for the refining agent without the addition of any other material, if desired. Thus, a light oil piperylene fraction may be introduced into the desired tower or vessel, together with the finely divided refining agent, after which the piperylene fraction is passed into the suspension of the refining agent in the piperylene fraction at the desired temperature, the charging rate and more particularly the operating pressure being adjusted to maintain the treating agent at the desired level in the vessel.

It is to be understood, of course, that the portion of the material to be treated which has been dissolved in the suspending medium or which has been employed as the suspending medium in the substantial absence of other liquid materials, does not necessarily remain in the treating zone throughout the entire treating cycle. Rather, this material is in a state of dynamic equilibrium with the material being treated, a portion of it volatilizing continuously and being removed from the system, the material volatilized in this manner being replaced by the solution of a corresponding quantity of freshly added material to be treated. The major portion of the material to be treated, of course, passes upward through the suspending medium without dissolving therein.

The thickness of the layer of reagent through which the material to be treated is preferably passed depends upon a number of factors, such as the quantity and type of impurities present, the extent to which such impurities are to be removed, the type and degree of dispersion of the treating agent employed, the reaction temperature, the concentration of the treating agent in the suspending medium, and the like. In general, however, I prefer to employ a layer of reagent at least one foot thick and, more preferably, at least two feet thick. Excellent results are obtained by the use of a layer of reagent at least four feet thick.

It will be recognized that, other things being equal, the depth of reagent employed in the treating vessel controls the contact time between the material to be refined and the refining reagent.

The degree of dispersion of the treating agent also has a very profound effect upon the degree

of refining obtained. In the case of sodium, I prefer to employ a subdivided mass in which at least the majority of the particles present have a diameter of not more than 0.05" and, more preferably, not more than 0.03". Excellent results are obtained when at least the majority of the particles present have a diameter of not more than 0.02".

This subdivision may be carried out in any desired manner. Thus, in the case of sodium, a solution of this material in liquid ammonia may be introduced into an inert liquid, such as xylene, at room temperature or at elevated temperatures. The almost instantaneous volatilization of the ammonia present results in the dispersion of the sodium present in the xylene in an extremely finely divided state. Another method comprises spraying molten sodium into an inert liquid such as xylene or solvent naphtha. By suitable variations in the type and degree of fineness and/or dispersing ability of the spray nozzle employed, sodium of almost any desired degree of fineness may be obtained at will.

Another satisfactory method comprises melting the sodium under the surface of a suitable liquid, such as xylene, followed by violent agitation, such as with a turbo-mixer, and cooling with agitation. Other methods which may be used include extrusion through fine orifices, and the generation of an arc between sodium electrodes in an inert liquid.

Although almost any desired concentration of treating agent in the suspending medium may be employed, depending upon the type and concentration of the piperylene or piperylene fraction to be refined, the temperature, the depth of reagent employed, and the like, I generally prefer to employ a reagent containing less than 30%, and more particularly less than 20%, by weight of the treating agent. Excellent results are obtained when less than 15% by weight of the treating agent is suspended in the suspending medium.

It is to be understood, of course, that the term suspending medium refers to the actual suspending agent employed during the treating operation, and includes any of material being treated which may dissolve in such agent.

The concentration of the piperylene or piperylene fraction to be treated also has a considerable influence upon the method of operating the process. Thus, with a highly concentrated piperylene, such as 98% piperylene, the reagent should preferably contain a fairly low concentration of active agent to minimize losses due to polymerization.

I generally prefer to employ a fraction of such concentration, and with such proportion of suspending medium, that the actual concentration of piperylene in the reaction zone is less than 80% and, more preferably, less than 70%. Excellent results are obtained when the actual concentration of piperylene in the reaction zone is less than 65%.

The process may be carried out at any desired pressure, such as atmospheric, subatmospheric, and superatmospheric pressures.

In many cases, particularly when piperylene in a fairly highly concentrated form is refined with a suspension or solution of a finely divided active metal, alloy, or compound of the type described herein, it is highly advantageous to conduct such operations at subatmospheric pressures, thereby reducing the concentration of piperylene present in the refining system at a given reaction temperature. This serves to reduce the quantity of

piperylene converted to polymers in the process, consequently it is a preferred embodiment of this invention.

The temperature at which the process is conducted also has a very considerable bearing upon the degree to which the piperylene or piperylene fraction is refined and the losses incurred due to polymerization. Although the optimum reaction temperature to be employed is dependent largely upon other factors, such as the concentration of both the piperylene and the refining agent in the reaction zone, I generally prefer to conduct the refining operations at temperatures below 100° C. and, more particularly, below 85° C. Excellent results are obtained by conducting the refining operations at temperatures below 75° C.

The rate at which the material to be refined is passed through the reagent has a very considerable effect upon the degree to which the impurities present are removed, although this is dependent to some extent upon other variables such as the concentration of refining agent in the suspending medium and the temperature at which the refining operations are being conducted. While it is difficult to establish exact limits for optimum throughputs under all conditions, I generally prefer not to exceed a throughput of material to be treated on an hourly basis of more than four times the weight of suspending medium employed and more preferably, not more than twice the weight of the suspending medium. Excellent results are obtained when not more than equal quantities of material to be treated, upon an hourly basis, are passed through the suspending medium.

It will be recognized that the contact time between the material to be treated and the reagent is determined both by the thickness of the layer of reagent employed and by the rate at which the material to be treated is passed through the reagent.

The method employed for introducing the material to be refined into the refining agent also has some influence upon the extent to which the unsaturated hydrocarbon or unsaturated hydrocarbon fraction is refined. In general, it may be said that a fine stream or jet of the liquid or gaseous material to be refined is desired. This may be accomplished by introducing the material to be treated into the reagent by means of suitable orifices, jets, nozzles, or other subdividing means. Porous objects or materials also may be employed for this purpose, such as porous ceramic or glass diffusing blocks or units.

As the refining agent may show some tendency to settle out in the bottom of the treating vessel or unit, the jets or nozzles by means of which the material to be treated is introduced into the unit may be so arranged as to prevent any undue settling of this material. In vertical vessels, this may be accomplished by locating these units in such a way as to impinge the inlet stream or streams upon the bottom of the treating vessel. The inlet jets also may be arranged tangentially to impart a swirling or circular motion to the treating reagent, if desired. Another method comprises locating the inlet jet or jets directly in the bottom of the reactor, or tangentially in the sides of the reactor, or both, to prevent any settling in the bottom of the reacting vessel and/or to impart any desired circular or other motion to the treating medium.

Any desired combination of these methods also may be employed, such as the use of a jet or jets directly impinging upon the bottom of the re-

actor in conjunction with the use of a tangential jet or jets to prevent the active agent from settling out and depositing on the walls of the reactor and/or to maintain the reaction medium in any desired state of agitation.

The reaction medium also may be maintained in the desired degree of agitation by the use of suitable stirring or mixing devices, or by the use of circulating pumps, or by combination of these methods, or otherwise. One or more of these methods also may be used in conjunction with one or more of the methods discussed previously to maintain the system in the desired degree of dispersion.

It should be pointed out, however, that the use of such agitation methods is not required in most cases. Thus, excellent results have been secured by conducting the refining operations in a tower, the material to be treated being introduced into the bottom of the tower by means of a small orifice. The passage of the fraction being treated in the gaseous state upward through the column was found to maintain the system in the desired degree of agitation.

The refining agent, particularly when finely divided sodium is employed for this purpose, usually acts both as a reactant and as a polymerizing agent for the removal of undesired impurities. Thus, in the case of light oil piperylene fractions containing acetylenes, aldehydes, and other impurities, the sodium usually will react with at least a portion of the acetylenes present to form sodium acetylides, and may react with certain of the oxygenated derivatives to form corresponding metallic derivatives. At least a portion of the acetylenic hydrocarbons present also are polymerized to form polymers, or copolymers with other unsaturated hydrocarbons present, which frequently are insoluble in nature. Certain of the oxygenated derivatives, such as aldehydes, also may be polymerized to form polymers which may be insoluble in type.

As a result, the refining of piperylene fractions with a suspension of finely divided sodium is characterized by the gradual accumulation of insoluble polymers in the refining medium. This may be removed in any desired manner, such as by filtration, which may be carried out continuously during the refining operation, or may be carried out in a batchwise manner after the termination of the refining step.

As the removal of the insoluble polymers also is attended by some loss of refining agent, even when the latter is in a very fine state of subdivision, it is advisable in many cases to continue the refining operations until the refining agent has been largely or completely exhausted before filtering.

The solid or semi-solid filtered products may be treated to recover any desired materials or they may be disposed of in any suitable manner. Thus, any unchanged refining agent, such as sodium, may be recovered by melting and coalescing operations, or by amalgamation with mercury, or otherwise. Certain of the reaction products, such as sodium acetylides, may be decomposed with water to regenerate the corresponding acids or they may be reacted with carbon dioxide to form unsaturated acids, or otherwise.

A convenient method for the disposal of the insoluble polymers comprises treatment with carbon dioxide, suitably in the presence of traces of moisture, followed by filtration.

As the cost of the treating process is largely

a function of the quantity of the reactive agent employed in the refining operations, the efficient utilization of such agent is of considerable importance. A desirable method for insuring optimum utilization of the treating agent is to carry out the operations in a continuous countercurrent manner, the reagent moving through the system in a manner countercurrent to that of the material to be treated.

This may be illustrated by means of a consideration of a simple continuous countercurrent system comprising two treating towers or vessels. The material to be treated is passed into the first tower, which contains a partially exhausted reagent. This serves to remove a substantial portion of the impurities present, after which the partially refined material passes into the second tower, which contains a fresh, or more highly concentrated, reagent. This serves to remove the impurities present to the desired extent. The process is continued until the reagent in the first tower is almost, or completely, exhausted, after which it is discarded and the partially exhausted reagent from the second column substituted for it. Fresh reagent then is added to the second column.

In this manner the material to be treated and the treating agent pass through the system countercurrent to each other, the first continuously and the second in a discontinuous manner.

This may be modified such as by the continuous addition of fresh reagent to the second tower, the continuous transfer of partially exhausted reagent to the first tower, and the continuous withdrawal of more completely exhausted, or exhausted, reagent from the first tower. A completely continuous countercurrent treating system thus is achieved.

Any desired modification of these methods may be employed, and any number of treating towers or units may be used. It will be observed that in each of the cases discussed, the incoming material to be refined is contacted with partially exhausted reagent (maximum concentration of impurities—minimum concentration of reagent), while the outgoing material to be refined is contacted with fresh or more highly concentrated reagent (minimum concentration of impurities—maximum concentration of reagent). Thus the two objectives to be sought, namely, practically complete, or complete, utilization of the reagent and substantial, or practically complete, removal of impurities from the material to be refined, are achieved.

As the limiting factor affecting the utilization of the reagent is the proportion of insoluble polymers and/or residues which can be contained therein without seriously impairing its flowing properties, or the passage of the gaseous material to be treated therethrough, it frequently happens that the quantity of insoluble material present is insufficient to interfere seriously with the operation of the process when the refining agent present has been almost completely exhausted. In this case, the operation of the unit may be continued by the addition thereto of an additional quantity of the refining agent, and this process may be continued until the concentration of insoluble material in the reagent renders it too viscous to be used further in the process in a satisfactory manner.

In this connection, it is well to point out that the insoluble products formed during the reaction have a tendency to stabilize the sodium suspension and act to reduce the rate of settling of the finely divided sodium in certain cases.

As this is desirable, the incomplete removal of insoluble products from the reagent may be indicated, or even the addition of a certain quantity of such materials to a fresh reagent.

Soluble polymers also usually are formed in small amounts during the refining operations. As certain of these soluble and/or liquid polymers may be converted on prolonged contact with the refining agent to viscous and/or insoluble products, their removal from the suspending medium, suitable at the end of a refining cycle and prior to the return of the suspending agent to the system, may be indicated. On the other hand, certain of these soluble polymers are sufficiently stable to act as a suspending medium for the refining agent.

The process may be more completely illustrated by means of the following example.

#### Example

A 70% light oil piperylene fraction containing 0.191% acetylenes and 0.031% aldehydes, was passed continuously into the bottom of a 2' steel column containing a xylene suspension of very finely divided sodium at a temperature of 50° C.

Under the operating conditions employed, the actual suspending medium was a mixture of 462 grams (28.9%) of xylene and 1138 grams (71.1%) of the piperylene fraction. The quantity of finely divided sodium employed was 108 grams, representing a 6.8% suspension in the indicated suspending medium. The suspending medium contained 3 grams of phenyl beta-naphthylamine as a polymerization inhibitor.

The run was continued for a total of 37 hours at an average charging rate of 525 grams per hour, the total quantity of piperylene fraction charged being 21,885 grams.

The refined piperylene fraction contained only 0.02% acetylenes and less than 0.001% aldehydes, and was water-white in color.

The impurities present, particularly the acetylenes and the aldehydes were converted both to sodium derivatives and to insoluble polymers.

In the specification and in the claims, the following terms have the indicated meanings.

The term "finely divided" is intended to mean a material reduced to such a state of fineness that the preponderating part is composed of particles having a diameter of less than 0.05", as well as materials in the colloidal or dissolved form.

While reagents and procedures of a particular nature have been specifically described, it is to be understood that these are given by way of illustration. Therefore, changes, omissions, additions, substitutions, and/or modifications may be made within the scope of the claims without departing from the spirit of the invention.

I claim:

1. A process for refining piperylene contaminated with impurity including acetylenic material and aldehydes, comprising passing said contaminated piperylene at a temperature below 100° C. through a dispersion of a finely divided metal selected from the group consisting of metals of group Ia and group IIa of the periodic system and alloys thereof, said dispersion containing less than 30% by weight thereof of said finely divided metal and being at least one foot in thickness in the direction of flow of said contaminated piperylene, maintaining the concentration of said piperylene in the reaction zone less than 80% by weight of the total material present, while maintaining the rate of flow per hour of

said contaminated piperylene through said dispersion at less than four times the weight of dispersion medium employed, and removing said piperylene less contaminated with said impurity from said reaction zone sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

2. A process for refining piperylene contained in admixture with impurity including acetylenic material which comprises passing said admixture at a temperature below 100° C. and in the presence of a polymerization inhibitor through a dispersion of a finely divided metal selected from the group consisting of metals of group Ia and group IIa of the periodic system and alloys thereof, said dispersion containing less than 30% by weight thereof of said finely divided metal and being at least one foot in thickness in the direction of flow of said admixture, maintaining the concentration of said piperylene in the reaction zone less than 80% by weight of the total material present, while maintaining a rate of flow per hour of said admixture through said dispersion of less than four times the weight of dispersion medium employed, and removing said piperylene less contaminated with said impurity from said reaction zone sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

3. A process for refining piperylene contained in admixture with impurity including an aldehyde which comprises passing said admixture at a temperature below 100° C. and in the presence of a polymerization inhibitor through a dispersion of a finely divided metal selected from the group consisting of metals of group Ia and group IIa of the periodic system and alloys thereof, said dispersion containing less than 30% by weight thereof of said finely divided metal and being at least one foot in thickness in the direction of flow of said admixture, maintaining the concentration of said piperylene in the reaction zone less than 80% by weight of the total material present, while maintaining a rate of flow per hour of said admixture through said dispersion of less than four times the weight of dispersion medium employed, and removing said piperylene less contaminated with said impurity from said reaction zone sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

4. A process for refining piperylene contained in admixture with impurity including acetylenic material which comprises passing said admixture at a temperature below 100° C. and in the presence of a polymerization inhibitor through a dispersion of a finely divided alkali metal, said dispersion containing less than 30% by weight thereof of said finely divided metal and being at least one foot in thickness in the direction of flow of said admixture, maintaining the concentration of said piperylene in the reaction zone less than 80% by weight of the total material present, while maintaining a rate of flow per hour of said admixture through said dispersion of less than four times the weight of dispersion medium employed, and removing said piperylene less contaminated with said impurity from said reaction zone sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

5. A process for refining piperylene contained in admixture with impurity including acetylenic material which comprises passing said admixture at a temperature below 100° C. and in the pres-

ence of a polymerization inhibitor through a dispersion of a finely divided alkaline earth metal, said dispersion containing less than 30% by weight thereof of said finely divided metal and being at least one foot in thickness in the direction of flow of said admixture, maintaining the concentration of said piperylene in the reaction zone less than 80% by weight of the total material present, while maintaining a rate of flow per hour of said admixture through said dispersion of less than four times the weight of dispersion medium employed, and removing said piperylene less contaminated with said impurity from said reaction zone sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

6. A process for refining a light oil piperylene fraction contaminated with acetylenic material and aldehyde which comprises passing said fraction upwardly through a dispersion containing up to 20% by weight thereof of a finely divided alkali metal in the presence of less than 5% by weight of a polymerization inhibitor at a temperature below 85° C. while maintaining the concentration of piperylene in the reaction zone at less than 70% by weight of the total material present, said dispersion being at least two feet in thickness in the direction of flow of said piperylene and being maintained in agitation by the passage of the contaminated piperylene therethrough at a rate of flow per hour equivalent to less than twice the weight of dispersion medium employed, and removing piperylene in vapor phase from said reaction zone in a form less contaminated with acetylenic material and aldehyde and sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

7. A process for refining piperylene contaminated with impurity including acetylenic material comprising passing said contaminated piperylene through a dispersion containing less than 30% of finely divided sodium the majority of the

particles of which have diameters of not more than 0.05'' at a temperature below 100° C. while maintaining the concentration of piperylene in the reaction zone below 80% by weight of the total material present, said dispersion being at least one foot thick in the direction of flow of said piperylene and containing less than 10% by weight of a polymerization inhibitor, the rate of flow per hour of said piperylene being not more than four times the weight of dispersion medium employed, and removing piperylene in vapor phase from said reaction zone less contaminated with said impurity including acetylenic material and sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

8. A process for the purification of a light oil piperylene fraction containing piperylene together with impurity at least a portion of which is in the form of acetylenic material which comprises passing said fraction in vapor phase at a temperature below 75° C. upwardly through a reaction zone containing a dispersion of finely divided sodium the preponderating part of which consists of particles having diameters of not more than 0.02'', said dispersion containing less than 15% by weight thereof of said finely divided sodium and being at least four feet in thickness in the direction of flow of said fraction, maintaining the concentration of said piperylene in said reaction zone less than 65% by weight of the total material present, while maintaining a rate of flow per hour of said fraction through said dispersion of less than equal the weight of dispersion medium employed, and removing piperylene in vapor phase from the top of said reaction zone less contaminated with impurity including acetylenic material and sufficiently rapidly to prevent a large loss of said piperylene due to the polymerization thereof.

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