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CHEMICAL PROCESS AND PRODUCT

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6 Claims. (Cl. 260—681.5)

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This invention is concerned with the refining of unsaturated hydrocarbons.

More particularly, this invention is concerned with the removal of impurities from unsaturated hydrocarbons and unsaturated hydrocarbon fractions by the application of metals in group I*a* and group II*a* of the periodic table and certain active alloys or derivatives thereof in the presence of a polymerization inhibitor.

It is an object of the present invention to continuously purify unsaturated hydrocarbon fractions, and particularly diolefine fractions by treatment with one or more alkali or alkaline earth metals, or active alloys or derivatives thereof, in the presence of one or more polymerization inhibitors under carefully controlled conditions. Another object of the invention is the provision of certain methods whereby unsaturated hydrocarbon fractions and particularly diolefine fractions, may be purified in a continuous manner by the application of alkali or alkaline earth metals in the presence of one or more polymerization inhibitors 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.

Unsaturated hydrocarbons and unsaturated hydrocarbon fractions, particularly the latter, frequently contain substantial quantities of impurities, such as acetylenic compounds; oxygenated compounds such as aldehydes and peroxides; and the like; which interfere with the use of such materials in most, if not all, industrial applications.

Thus, diolefines and diolefine fractions, particularly the latter, frequently contain substantial quantities of acetylenes, such as monovinyl or other acetylene, oxygenated compounds such as aldehydes and peroxides, as well as certain other impurities.

As an example, a 41% light oil butadiene fraction obtained by the pyrolysis of petroleum in the gas phase at temperatures substantially above 1300° F., followed by condensation and fractionation, was found to contain 0.9% of acetylenes, mainly monovinylacetylene, and 0.045% aldehydes, as well as certain other impurities, including some C_3 and C_5 impurities. This butadiene fraction, as well as the more highly concentrated butadiene obtained therefrom by the use of suitable concentrating methods, such as 98% butadiene concentrate, is unsuited for the production of synthetic rubber of good quality due to the inhibiting

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action, and other undesirable properties, of the impurities contained therein.

As a result of extensive experimentation, I have discovered that unsaturated hydrocarbons and unsaturated hydrocarbon fractions, particularly diolefine fractions, may be refined, preferably in a continuous manner, by the application in finely divided form of at least one metal of group I*a* and group II*a* of the periodic table, as well as certain active alloys or derivatives thereof, in the presence of one or more polymerization inhibitors. Particularly desirable results are obtained by the use of finely divided alkali and alkaline earth metals in the presence of polymerization inhibitors.

Examples of refining metals which may be used for such purpose are lithium, sodium, 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 $NaPb_{10}$, $NaHg_4$, $NaCa_5$, $NaZn_{12}$, KNa, and the like, also may be employed for the removal of undesired impurities from unsaturated hydrocarbons and unsaturated hydrocarbon fractions in the presence of one or more polymerization inhibitors. In general, the alloys of the respective metals react with the impurities present in such hydrocarbons and hydrocarbon fractions at a slower rate than the corresponding metals.

Compounds of these metals which may be employed in the refining process described herein include hydrides, such as LiH, NaH, KH, RbH, and CaH; amides such as sodamide and potassium amide; and other reactive compounds, such as sodium methylate and sodium ethylate.

In general, therefore, it may be said that very finely divided metals in group I*a* and II*a* of the periodic system, their reactive alloys, and reactive derivatives, may be used to refine unsaturated hydrocarbons and unsaturated hydrocarbon fractions with very satisfactory results in the presence of one or more polymerization inhibitors. I find that these materials are particularly desirable for use in finely divided form in the presence of inhibitors for refining diolefines and diolefine fractions.

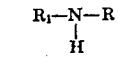
Inhibitors which are particularly effective agents for retarding the rate of polymerization of unsaturated hydrocarbons, and particularly diolefines and diolefine fractions, when refined with very finely divided metals in groups I*a* and II*a* of the periodic system, their reactive alloys,

and reactive derivatives, may be classified in the following groups.

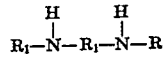
1. Amines and nitrogen-containing inhibitors, particularly aryl amines, such as

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

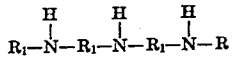
Particularly desirable results have been obtained by the use of secondary aryl amines having the following general formula



in which R_1 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 example



and



in which R and R_1 have the same meaning as before.

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

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

2. Phenolic compounds, such as

Dihydroxybenzenes, and substituents thereof
Pyrogallol, and substituents thereof
Pyrocatechol
Resorcinol
Xylenols
Catechol
Trihydroxybenzene, and substituents thereof
Nitrosophenol
Diaminophenol
Alpha-naphthal
Dihydroxynaphthalene
Hydroxy quinoline
Hydroxy tetrahydroquinoline
Polyhydric phenols
Polyhydroxy phenanthrene
4-nitroso-2-methyl phenol

3. Compound inhibitors, such as

Acyl-substituted amino phenols
4-cyclohexyl amino phenol
p-Amino phenol
o-Amino phenol
5-amino-2-hydroxytoluene

4. Miscellaneous inhibitors, such as

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

Excellent results have been obtained when one or more inhibitors selected from a list comprising (1) secondary aryl amines such as phenyl beta-naphthylamine, diphenyl-p-phenylene diamine, isopropoxydiphenyl amine, aldol-alpha-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 of a ketone, such as acetone, and/or an aldehyde, such as formaldehyde and acetaldehyde, with an amine, such as aniline.

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 2% inhibitor in certain cases, particularly when one or more of the inhibitors listed in the preceding paragraph are employed.

The diolefines and diolefine fraction employed in my process, such as butadiene, 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_4 compounds, by the partial hydrogenation of monovinylacetylene, by the dehydrogenation of butanes and/or butylenes, and by the dehydration of C_4 alcohols and glycols; by the pyrolysis of petroleum and petroleum hydrocarbons, such as 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 materials, such as by the pyrolysis of cyclohexane or by the pyrolysis of alcohols, such as the pyrolysis of ethyl alcohol. In the latter case, the process may include a combination of dehydrating and/or pyrolytic reactions. Thus, it may be carried out by passing the alcohol at suitable temperatures over suitable catalytic agents, such as for example alumina and the like, followed by secondary pyrolysis, or recombination steps, if desired. Other procedures also may be employed for the production of butadiene or butadiene fractions which may be refined by the methods to be more particularly described herein.

The diolefine or diolefine 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 diolefines and diolefine 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 certain impurities or undesirable materials present. Thus, light oil butadiene fractions may be contacted with sulfuric acid to remove at least a portion of the isobutylene present.

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

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 or active compounds, is a particularly desirable agent for the continuous removal of certain undesirable impurities from unsaturated hydrocarbons and unsaturated hydrocarbon fractions, and particularly from diolefines and diolefine fractions, when carried out in the presence of at least one polymerization inhibitor. Excellent results are obtained by the use of a suspension of very finely divided sodium containing an inhibitor.

The refining method disclosed herein differs fundamentally from all methods described heretofore for the refining of unsaturated hydrocarbons or unsaturated hydrocarbon fractions in that the material in question is treated with a metal of group I*a* or group II*a*, or an active alloy or compound of such metals, in finely divided or solution form in the presence of at least one polymerization inhibitor. By the use of a polymerization inhibitor, the loss of valuable hydrocarbons due to polymerization is very markedly reduced, or almost completely eliminated.

This is of particular importance in the case of diolefines, such as butadiene, which are quite susceptible to polymerization when placed in contact with certain active metals, as well as active alloys and derivatives thereof. Thus, sodium is a very active catalyst for the polymerization of butadiene and is employed for this purpose in several industrial processes, notably in Russia. The use of this material in very finely divided form for the refining of butadiene, therefore, must be carried out within well defined limits in order to prevent undue loss of butadiene due to polymerization. The success of the refining method employing finely divided sodium, or other active metals, alloys, or compounds, depends to a very considerable extent upon the presence therein of a polymerization inhibitor. It will be understood, of course, that an inhibitor must be very specific and powerful in action in order to retard the rate of polymerization of unsaturated hydrocarbons, such as butadiene, in the presence of a very active catalyst, such as finely divided sodium.

The refining operations may be carried out in any desired manner such as batch, multiple batch, batch countercurrent, continuous, and continuous countercurrent operations. Although the process may be carried out in a very satisfactory manner by each of these methods, I prefer to use the continuous or continuous countercurrent types of operation. However, it is to be understood that the refining process is not limited to any method of operation.

Although the continuous refining operations also 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 containing an inhibitor is maintained. This mixture of active refining agent and inhibitor will be referred to herein as the refining reagent. The material to be refined is passed upward 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.

Reference is made to my copending application, Serial No. 457,475, filed September 5, 1942, now U. S. Patent 2,398,810, issued April 23, 1946, disclosing and claiming the refining of unsaturated hydrocarbons and unsaturated hydrocarbon fractions with a finely divided active metal from groups I*a* and II*a* of the periodic system, or an active alloy or compound thereof, in a continuous system.

Other methods of contacting the material to be treated and the refining reagent 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, containing a suspension of the desired refining reagent, or otherwise.

The suspending liquid employed for the preparation of the refining reagent may be of any desired type, provided that it does not react with any of the constituents of the refining reagent or the material to be treated to any substantial extent, and provided that 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 reagents 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 dissolves 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 butadiene fraction with a xylene suspension of finely divided sodium containing an inhibitor in a continuous system operating at 50° C. and atmospheric pressure, the suspending medium contained 11% of the butadiene fraction by weight after equilibrium conditions had been established.

In a similar manner, when refining a light oil butadiene fraction in a continuous system with a xylene suspension of finely divided sodium containing an inhibitor at 50° C. and a pressure of 50 pounds per square inch, gauge, the composition of the suspending medium after equilibrium conditions had been established was 76% butadiene fraction and 24% xylene.

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

being adjusted to maintain the refining 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, bubbles up through the suspending medium without dissolving therein.

The thickness of the layer of refining 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 type and quantity of inhibitor employed, 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 refining 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 refining reagent at least four feet thick.

It will be recognized that, other things being equal, the depth of refining 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 fraction to be refined, the temperature, the depth of reagent employed, and the like, I generally prefer to employ a refining 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 type and concentration of the unsaturated hydrocarbon or unsaturated hydrocarbon fraction to be treated also has a considerable influence upon the method of operating the process. Thus, with a highly concentrated butadiene, such as 98% butadiene, the refining reagent should preferably contain a fairly low concentration of active agent, and a fairly high concentration of inhibitor, 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 unsaturated hydrocarbon, such as butadiene, in the reaction zone is less than 80% and, more preferably, less than 70%. Excellent results are obtained when the actual concentration of unsaturated hydrocarbon in the reaction zone is less than 60%.

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

The temperature at which the process is conducted also has a very considerable bearing upon the degree to which the 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 unsaturated hydrocarbon and the refining reagent in the reaction zone, I generally prefer to conduct the refining operations at temperatures below 100° C. and, more particularly, below 80° C. Excellent results are obtained by conducting the refining operations at temperatures below 70° C.

The rate at which the material to be refined is passed through the refining 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 refining reagent employed and by the rate at which the material to be treated is passed through the reagent.

The method employed for introducing the ma-

terial to be refined into the refining reagent 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 refining 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 refining 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 refining reagent.

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 reactor 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 refining reagent in any desired state of agitation.

The refining reagent 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 a 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 butadiene fractions containing monovinylacetylene, other acetylenes, aldehydes, and other oxygenated impurities, the sodium will react with at least a portion of the monovinylacetylene present to form sodium monovinylacetylide, and may react with certain of the oxygenated derivatives to form corresponding 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 butadiene fractions with a suspension of finely divided sodium in the presence of an inhibitor is characterized by the gradual accumulation of insoluble polymers derived from the impurities present in the unsaturated hydrocarbon. These 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 monovinyl acetylide and/or other metallic 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. Any inhibitor present also may be recovered.

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 refining reagent 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 com-

pletely 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 active agent), while the outgoing material to be refined is contacted with fresh or more highly concentrated reagent (minimum concentration of impurities—maximum concentration of active agent). Thus the two objectives to be sought, namely, practically complete, or complete, utilization of the active agent 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 active agent 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 refining 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 refining 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 are converted on prolonged contact with the refining reagent 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 examples.

Example 1

A 3800 gram portion of a 40% light oil butadiene fraction containing 1.02% acetylenes and 0.05% aldehydes was treated in an autoclave at a temperature of 50° C. with a suspension of 23 grams of very finely divided sodium in 200 cc. of benzene containing 10 grams of phenyl beta-naphthylamine. The reaction was continued for a period of 15 minutes, after which the butadiene fraction was removed from the autoclave by distillation. The refined butadiene fraction contained only 0.05% acetylenes while the aldehydes had been removed completely. Analyses of both the refined fraction and the residue remaining in the reaction vessel indicated a negligible loss of butadiene during the refining process.

Example 2

A 50% light oil butadiene fraction containing 1.1% acetylenes and 0.05% aldehydes, was passed continuously in the gaseous state into a zylene suspension of finely divided sodium containing 0.5% by weight of phenyl beta-naphthylamine. The operations were carried out in a 2" column at a temperature of 50° C. and atmospheric pressure. The finely divided sodium was prepared by agitation of molten sodium under the surface of xylene by means of a turbo-mixer, followed by cooling with continuous agitation. Under the operating conditions employed, the actual refining medium comprised a 10% sodium suspension in a suspending medium containing approximately 90% xylene and 10% butadiene fraction. The height of refining reagent employed was 5 feet.

The refining operation was continued for a period of 30 hours, the butadiene fraction being charged at the rate of approximately 900 grams per hour.

The refined butadiene fraction obtained contained only 0.002% acetylenes and less than 0.001% aldehydes. Only negligible quantities of the butadiene was lost in the form of soluble polymers, and otherwise.

Example 3

A 50% light oil butadiene fraction containing 1.0% acetylenes and 0.04% 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. and a pressure of 50 pounds per square inch, gauge. The treating medium contained 0.05% of a substituted polyphenol as a polymerization inhibitor.

Under the operating conditions employed, the actual suspending medium was a mixture of 24% of xylene and 76% of the butadiene fraction. The quantity of finely divided sodium employed was 130 grams, representing a 7% suspension in the indicated suspending medium.

The run was continued for a total of 31 hours at an average charging rate of 840 grams per hour, the total quantity of butadiene fraction charged being approximately 24,000 grams.

The refined butadiene fraction contained only 0.02% acetylenes and <0.001% aldehydes. The quantity of soluble polymers produced was 29 grams, or approximately 0.1% by weight of the total fraction refined.

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

The term "polymerization inhibitor" is intended to include one or more compounds or materials which serve to retard, or entirely prevent, the polymerization of unsaturated hydrocarbons in the presence of an active refining agent.

The term "a metal of group I*a* and group II*a* of the periodic system" is intended to include lithium, sodium, potassium, rubidium, caesium, barium, strontium, and calcium, as well as active alloys or compounds containing one or more of such metals as an essential ingredient.

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, which is intended to be limited only as required by the prior art.

I claim:

1. A process for refining a light oil diolefine fraction containing diolefine material and contaminated with impurity including acetylenic material comprising passing said fraction through a dispersion of at least one finely divided metal selected from the group consisting of metals of group IA and group IIA of the periodic system in the presence of a polymerization inhibitor at a temperature below 100° C. while maintaining the concentration of diolefine material in the reaction zone at less than 80% and a rate of flow per hour of said fraction through said dispersion of not more than four times the weight of dispersion medium employed, said dispersion being at least one foot thick in the direction of flow of said fraction, and removing said diolefine material from contact with said dispersion prior to the polymerization of the larger part thereof, said removed diolefine material being less contaminated with impurity including acetylenic material.

2. A process for refining butadiene contaminated with impurity including monovinyl acetylene comprising passing said contaminated butadiene at a temperature below 100° C. and in the presence of less than 10% by weight of a polymerization inhibitor through a dispersion of at least one finely divided metal selected from the group consisting of metals of group IA and group IIA of the periodic system at a rate of flow per hour of less than four times the weight of dispersion medium employed while maintaining the concentration of butadiene in the reaction zone at less than 80%, the depth of said dispersion being at least one foot thick in the direction of flow of said butadiene, and removing said butadiene from contact with said dispersion prior to the polymerization of a large proportion thereof, said removed butadiene being less contaminated with monovinyl acetylene.

3. A process for refining butadiene contaminated with impurity including acetylenic material which comprises passing said contaminated butadiene through a dispersion containing up to 30% by weight thereof of a finely divided alkali metal in the presence of up to 5% by weight of a polymerization inhibitor at a temperature below 80° C. while maintaining the concentration of butadiene in the reaction zone at less than 70%, said dispersion being at least two feet thick and the rate of flow of said contaminated butadiene through said dispersion being not more than twice the weight per hour of the dispersion medium employed, and removing said butadiene from contact with said dispersion prior to the polymerization of a large proportion thereof, said removed butadiene being less contaminated with impurity including acetylenic material.

4. A process for refining a light oil butadiene fraction contaminated with acetylenic material 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 80° C. while maintaining the concentration of butadiene in the reaction zone at less than 70%, said dispersion being at least two feet in thickness in the direction of flow of said butadiene and being maintained in agitation by the passage of the contaminated butadiene therethrough at a rate of flow per hour equivalent to less than twice the weight of dispersion medium employed, and removing said butadiene from contact with said dispersion prior to the polymerization of a substantial proportion thereof, said removed butadiene being in a form less contaminated with acetylenic material.

5. A process for refining butadiene contaminated with impurity including acetylenic material comprising passing said contaminated butadiene upwardly in vapor phase through a dispersion containing less than 30% by weight of finely divided alkali metal and containing less than 10% by weight of a polymerization inhibitor at a temperature below 100° C. while maintaining the concentration of butadiene in the reaction zone at less than 80% by weight, the depth of said dispersion being at least one foot in thickness in the direction of flow of said butadiene and the rate of flow per hour of said butadiene being not more than four times the weight of dispersion medium employed, and removing gaseous butadiene from contact with said dispersion prior to the polymerization of a large proportion thereof, said removed butadiene being less contaminated with impurity including acetylenic material.

6. A process for refining butadiene contaminated with impurity including acetylenic material comprising passing said contaminated butadiene through a dispersion containing less than 30% of finely divided sodium the majority of the particles of which have a diameter of not more than 0.05" at a temperature below 100° C. while maintaining the concentration of butadiene in the reaction zone below 80%, said dispersion being at least one foot thick in the direction of flow of said butadiene and containing less than 10% by weight of a polymerization inhibitor, the rate of flow per hour of said butadiene being not more than four times the weight of dispersion medium employed, and removing said butadiene from contact with said dispersion prior to the polymerization of a large proportion thereof, said removed butadiene being less contaminated with said impurity including acetylenic material.

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