

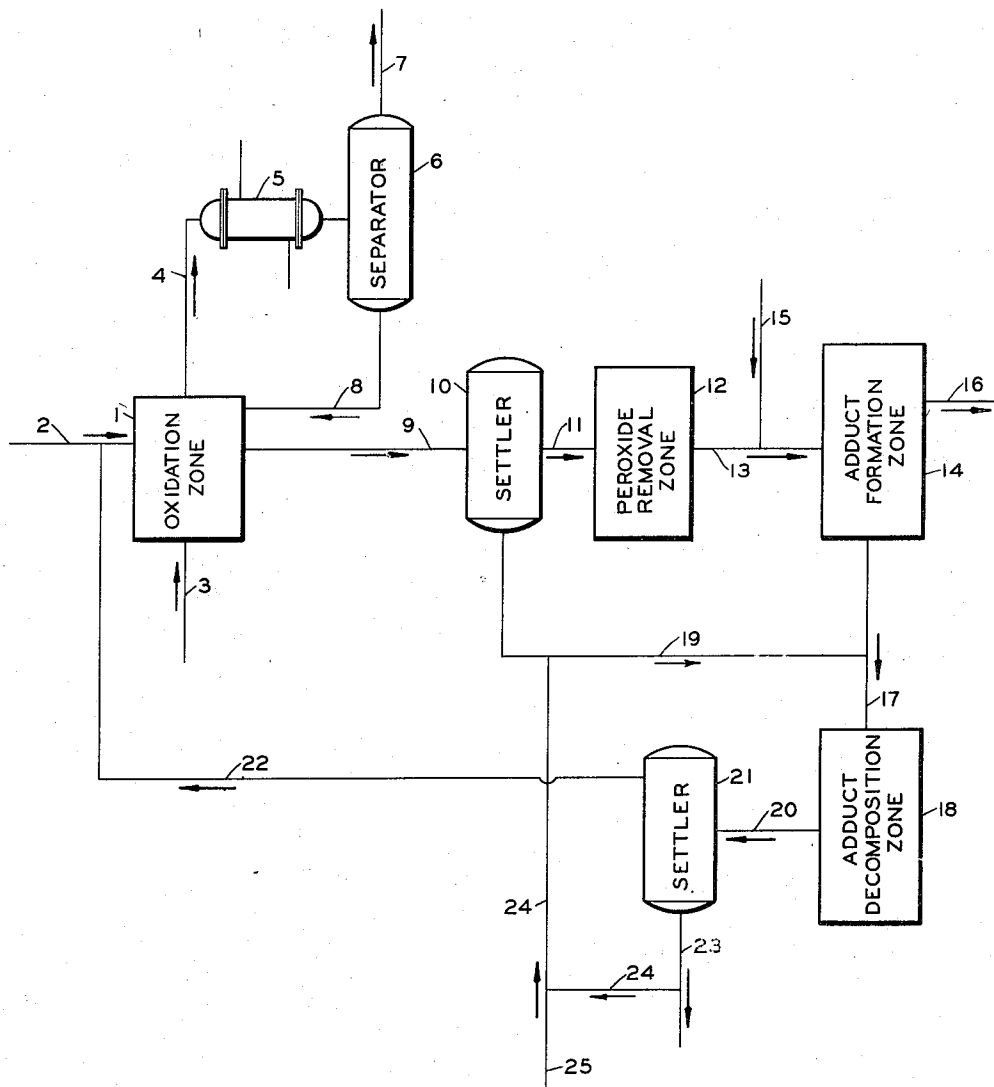
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SEPARATION PROCESS

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## UNITED STATES PATENT OFFICE

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## SEPARATION PROCESS

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This invention relates to a process for the separation of mixtures of organic compounds. In a specific aspect this invention relates to a process for separating mixtures of naphthenic hydrocarbons and oxygenated derivatives of naphthenic hydrocarbons. In a more specific aspect this invention relates to the resolution of the reaction products from a naphthenic hydrocarbon oxidation process.

In various chemical processes it is necessary to separate naphthenic hydrocarbons from oxygenated derivatives thereof. For example, in processes for the production of alcohols and ketones by the oxidation of naphthenic hydrocarbons one of the essential steps is the recovery of the alcohols and ketones from the unreacted hydrocarbons. Obviously, an efficient method of carrying out such a separation economically is highly desirable in order to obtain the unreacted hydrocarbons for further oxidation and the alcohols and ketones as products of the process.

It is an object of this invention to provide a novel process for resolving mixtures of naphthenic hydrocarbons and oxygenated derivatives thereof.

It is another object of this invention to provide a novel process for separating naphthenic hydrocarbons from alicyclic alcohols and ketones.

It is another object of this invention to form addition products of thiourea and naphthenic hydrocarbons and thus to separate said hydrocarbons from admixture with oxygenated derivatives thereof.

Further and additional objects of my invention will be apparent from the disclosure and drawing hereinbelow.

It has been reported by Angla in *Compte Rendu*, vol. 224, pages 402-404, that certain naphthenic hydrocarbons and their alcohols and ketone derivatives form complexes or addition products with thiourea, but it is not apparent in what manner the addition products of thiourea and the alcohol and ketone derivatives of the naphthenic hydrocarbons were formed. I have verified the teachings of Angla and found such addition products of thiourea are formed when water is employed at certain conditions as an activator and solvent for the thiourea. On the other hand, when either a non-aqueous solvent-activator or water, at specific conditions, is employed, addition products or adducts of thiourea and naphthenic hydrocarbons are formed but no adducts of thiourea and the oxygenated derivatives of these hydrocarbons are formed.

Accordingly, I have found that naphthenic hy-

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drocarbons can be separated from oxygenated derivatives thereof by forming addition products or adducts of the former with thiourea while the oxygenated compounds remain unreacted.

The naphthenic hydrocarbons that are employed in my process are the saturated as well as the unsaturated type. In most instances these hydrocarbons do not contain more than 10 carbon atoms per molecule, but my invention is applicable to hydrocarbons containing a greater number of carbon atoms. Among the naphthenic hydrocarbons that form adducts with thiourea are cyclopentane, cyclohexane, cyclopentene, methylcyclopentane, methylcyclohexane, cyclohexene, cis-1,2-dimethylcyclopentane, trans-1,2-dimethylcyclopentane, and 1,1,3-trimethylcyclopentane. Among the oxygenated derivatives of naphthenic hydrocarbons that do not form adducts with thiourea in my process are cyclopentanol, cyclopentanone, cyclohexanol, cyclohexanone, 1,2-methylcyclohexanol, 1,3-methylcyclohexanol, 1,4-methylcyclohexanol, 1,4-methylcyclohexanone and 1,3-methylcyclohexanone.

The solvent-activators for my process are of the non-aqueous and aqueous types. Among the activators I employ are water and low-boiling oxygenated hydrocarbon derivatives. For example, methanol, ethanol, acetone, methyl ethyl ketone, propanol, secondary butyl alcohol, and the like have been found to be quite suitable in my process. Other activators are nitrogen-containing compounds which do not form adducts with thiourea, and in which thiourea is soluble to an appreciable extent, say five per cent or more, or which is substantially soluble, say five per cent or more, in a mutual solvent, preferably water, in which thiourea is likewise substantially soluble. It has been found that the nitrogen-containing compound can be ammonia, either as liquid ammonia or a concentrated aqueous solution containing from 14 to 28 per cent or more of ammonia, or it can be an ammonia derivative selected from those substituted ammonia compounds in which thiourea is soluble at least to the extent of five per cent by weight, or from those which are soluble in a mutual solvent to the extent of five per cent by weight, and in which mutual solvent the thiourea is likewise soluble, and such ammonia derivative can have the general formula of



wherein  $R_1$ ,  $R_2$  and  $R_3$  are selected from the group consisting of hydrogen and of the organic radi-

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cals consisting of alkyl, alkylene, hydroxy alkyl, acyl and amino alkyl radicals wherein any aliphatic carbon atom chain contains at least one but no more than five carbon atoms; provided that not more than two of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be hydrogen. Thus, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can all be the same or different organic radicals above-enu-  
merated, or any one or two of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be hydrogen with the remaining R<sub>1</sub>, R<sub>2</sub> and/or R<sub>3</sub> being one of the above radicals. Represent-  
ative of the substituted ammonia compounds are the alkyl amines wherein the alkyl group con-  
tains a total of from one to five carbon atoms, such as mono-n-propyl, monomethyl, dimethyl, trimethyl, monoethyl, diethyl, monopropyl, di-n-  
propyl, monobutyl and monopentyl amines; the alkylene amines wherein the alkylene group con-  
tains from two to five carbon atoms, such as ethyleneimine and the monoallyl, monopropylene and monobutylene amines; the alkyl-alkylene  
amines, such as dimethylaminopropene, monoethylaminopropene and monopropylaminoethyl-  
ene; the hydroxy alkyl amines, such as monoethanolamine, diethanolamine and monopropanol-  
amine; the amino alkyl amines, such as diethylenediamine, ethylenediamine; acyl amines or  
amides, such as formamide and acetamide; the amines having radicals selected from two or  
three of the above-enumerated radicals, such as hydroxypropylaminoethane, propylaminoethyl-  
ene, and methoxyaminobutane.

In addition to ammonia and its derivatives as above illustrated, the heterocyclic organic base amines can be employed as activators. Among such compounds can be pyrrole, pyridine, piperidine, morpholine, the picolines, the collidines, quinoline, isoquinoline, indole, pyrimidine, pyrrolidine, pyridazine, pyrazole, pyrazoline, pyrazine.

When water is employed as a solvent-activator, sufficient water is used to dissolve the thiourea and to produce an aqueous thiourea solution of more than 50 but less than 100 per cent saturation at the temperature of the adduct-forming reaction. At concentrations outside this range the results of my invention are not obtained. It is preferable that the aqueous thiourea solution be from 60 to 95 per cent saturated and more preferably from 70 to 85 per cent saturated.

In order to resolve a mixture of naphthenic hydrocarbons and oxygenated derivatives of naphthenic hydrocarbons, the mixture is contacted with the thiourea to effect adduct formation of the hydrocarbons and thiourea. Various methods of contacting may be employed. For example, a solution of thiourea in an activator may be contacted either concurrently or countercurrently with the mixture to be resolved. Also, a slurry or mixture of thiourea and thiourea-activator solution may be passed either concurrently or countercurrently with the mixture to be resolved. Additionally, either a fluidized fixed bed or a moving bed of thiourea may be employed, and the mixture to be resolved is passed into contact therewith.

The temperature at which the mixture to be resolved and thiourea are contacted is determined by the decomposition temperature of adducts of thiourea and the naphthenic hydrocarbons in the mixture to be resolved, since the reaction temperature must be below this decomposition temperature. Usually, a temperature below 75° C. is satisfactory, and I prefer to effect the adduct forming reaction at a temperature within the range of 10 to 35° C. To effect the

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formation of the adducts from 2 to 10 mols of thiourea per mol of hydrocarbon are employed.

The adducts of naphthenic hydrocarbons and thiourea are solid and ordinarily in a crystalline form. They are readily separable from the liquid oxygenated derivatives of naphthenic hydrocarbons by centrifuging, decanting, filtering or other suitable means, and, after such separation, the adducts are decomposed by heating to a decomposition temperature which is dependent upon the hydrocarbons in the adduct. Actually, the decomposition temperature is dependent in part upon the number of carbon atoms in the naphthenic hydrocarbon molecule, and the adducts containing the higher molecular weight hydrocarbons generally decompose at the higher temperatures than the adducts of the lower molecular weight hydrocarbons. The decomposition temperatures are higher than the temperatures at which the adducts are formed. When I employ the preferred temperature of 10 to 35° C. to form the adducts, I prefer to employ decomposition temperatures within the range of 30 to 80° C., but obviously higher temperatures may be employed, if desired.

Various methods of decomposing the adducts may be employed. For example, dry heating of the adducts or distillation of the adducts with either steam or other gases, such as nitrogen or carbon dioxide, may be employed, but these methods sometimes cause decomposition of the thiourea. Another method of decomposing the adducts involves the use of a hot, liquid hydrocarbon that does not form an adduct with thiourea, such as propane, butane, and the like. In the description of the accompanying drawing I will disclose another method for effecting decomposition of the thiourea adducts.

I will disclose my invention in greater detail with reference to the accompanying drawing. In this specific embodiment of my invention, cyclohexane is oxidized to cyclohexanol and cyclohexanone, and the resulting reaction mixture is resolved in accordance with my invention. The accompanying drawing is a schematic diagram of one method of effecting my invention. Conventional equipment, such as valves, compressors, control equipment, and the like has not been included in this drawing, but the inclusion of such equipment would be obvious to one skilled in the art.

Referring now to the accompanying drawing, cyclohexane enters oxidation zone 1 via line 2 and oxygen, air or other oxygen-containing gas enters zone 1 via line 3. The conditions in zone 1 are such that the cyclohexane is oxidized to form cyclohexanol and cyclohexanone. The temperature is ordinarily within the range of 150 to 200° C. and the pressure is such that the hydrocarbon is maintained in the liquid phase, say from 350 to 450 pounds per square inch. The oxygen or oxygen-containing gas is bubbled through the liquid reaction mixture and the hydrocarbon residence time in the reactor is such that a per pass conversion of hydrocarbon within the range of 3 to 20 per cent is effected. Oxidation catalysts are not necessary for the reaction, but, if desired, catalysts such as manganese, lead or nickel salts of organic acids may be used. It is also desirable to have present in the oxidation reactor a small amount of oxidation initiator. Suitable compounds for this purpose are organic oxygen-containing compounds, such as aldehydes and ketones, and they are believed to function through the intermediate formation of organic

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peroxides. In any event, they reduce and sometimes eliminate the induction period commonly observed in connection with oxidation reactions.

Gaseous effluent from oxidation zone 1 is withdrawn via line 4 and passed to condenser 5 where it is cooled to about atmospheric temperature or lower. The cooled effluent is passed to separator 6 from which uncondensed gases are removed via line 7. Liquid condensate from separator 6 is returned to oxidation zone 1 via line 8. Liquid effluent from oxidation zone 1 is withdrawn via line 9 and passed to settler 10 wherein an organic phase is separated from an aqueous phase. The lighter organic phase is withdrawn via line 11 to peroxide removal zone 12. Ordinarily, the oxidation products from such a process contain small amounts of organic peroxides and it is desirable to remove these peroxides from the reaction product to preclude danger of explosion. These organic peroxides are removed from the reaction mixture by any suitable method, such as by controlled heating of the reaction products at closely controlled temperatures. After removal of the organic peroxides the organic phase in zone 12 is passed to adduct-formation zone 14 to which a saturated solution of thiourea in methanol is introduced via line 15. In adduct-formation zone 14 the solid adducts of thiourea and cyclohexane are formed, and these adducts are separated from unreacted liquid by any suitable means, such as by filtering, centrifuging, decanting and the like. After this separation, unreacted liquids which contain cyclohexanol and cyclohexanone are withdrawn from zone 14 via line 16, and these oxygenated organic compounds may be subjected to further treatment steps to recover the alcohol and ketone either separately or in a mixture. For example, the liquid in line 16 may be distilled to obtain methanol overhead after which the remaining liquids are cooled to crystallize out and to separate thiourea. The liquid remaining contains cyclohexanol and cyclohexanone. Obviously any other method for effecting such a separation is within the scope of my invention. The solid adducts of thiourea and cyclohexane are withdrawn from zone 14 and passed via line 17 to adduct-decomposition zone 18 wherein the adducts are decomposed at a temperature within the range of 30 to 80° C. to recover the thiourea and the cyclohexane. Aqueous phase from settler 10 is passed to zone 18 via lines 19 and 17. This aqueous phase contains relatively small concentrations of cyclic ketones, cyclic alcohols and other oxidation products, such as aldehydes, lactones and hydroxy acids. Certain of these compounds, particularly the aldehydes and ketones, serve satisfactorily as oxidation carriers in oxidation zone 1. Since they are present in rather low concentrations in the aqueous phase from settler 10, recovery thereof is usually a rather costly operation. In accordance with my invention, the aqueous phase from settler 10 is employed to decompose the adducts in decomposition zone 18. Zone 18 ordinarily contains suitable agitating means, such as a mixer or other activating devices. The temperature in zone 18 is within the range of 30 to 80° C., and in this zone the adducts are decomposed to liberate cyclohexane which appears as a separate organic phase. The thiourea resulting from the decomposition of the adduct dissolves in the water. Also, the liberated cyclohexane dissolves some of the oxygen-containing compounds from the aqueous phase. The reaction effluent from zone

18 is passed via line 20 to settler 21 wherein the cyclohexane containing dissolved oxygenated compounds separates as a lighter phase, and it is withdrawn via line 22 and thus returned to oxidation zone 1. In oxidation zone 1 the oxygenated compounds dissolved in the cyclohexane act as initiators for the oxidation reaction. Aqueous phase containing dissolved thiourea is withdrawn from settler 21 via line 23 for recovery of the thiourea therefrom. Part of this aqueous phase is recycled via line 24 in order to allow the dissolved thiourea to build up to the desired concentration for recovery and also to increase the recovery of oxygenated compounds from the aqueous phase. As required, additional water is added to the system via line 25.

The following examples are illustrative of my invention.

#### EXAMPLE I

One part by volume of each of the hydrocarbons listed in Group I was added to about 10 parts by volume of a saturated solution of thiourea in methanol at room temperature, and solid addition products were formed.

##### Group I

Cyclohexane  
Cyclopentane  
Cyclopentene  
Methylcyclopentane  
1,1,3-trimethylcyclopentane  
Methylcyclohexane  
Cyclohexene  
Cis-1,2-dimethylcyclopentane  
Trans-1,2-dimethylcyclopentane

#### EXAMPLE II

One part by volume of each of the hydrocarbons listed in Group I was added to about 10 parts by volume of a saturated solution of thiourea in monoethylamine at room temperature, and solid addition products were formed.

#### EXAMPLE III

One part by volume of each of the compounds listed in Group II was added to about 10 parts by volume of a saturated solution of thiourea in methanol at room temperature, and solid addition products did not form within 24 hours.

##### Group II

Cyclohexanol cyclohexanone  
1,2-methylcyclohexanol  
1,3-methylcyclohexanol  
1,4-methylcyclohexanol  
1,4-methylcyclohexanone  
1,3-methylcyclohexanone

#### EXAMPLE IV

One part by volume of each of the compounds listed in Group II was added to about 10 parts by volume of a saturated solution of thiourea in monoethylamine at room temperature, and solid addition products did not form within 24 hours.

#### EXAMPLE V

One part by volume of each of the mixtures listed in Group III, each of said mixtures containing 50 per cent cyclohexane, was added to about 10 parts by volume of saturated solutions of thiourea in methanol and in monoethylamine at room temperature. In each case the cyclohexane formed a solid adduct with thiourea, and, after filtering, the filtrate contained the oxygen-containing compound.

Cyclohexane and 1,3-methylcyclohexanol  
 Cyclohexane and 1,4-methylcyclohexanol  
 Cyclohexane and 1,2-methylcyclohexanol  
 Cyclohexane and 1,4-methylcyclohexanone  
 Cyclohexane and 1,3-methylcyclohexanone  
 Cyclohexane and cyclohexanol  
 Cyclohexane and cyclohexanone

## EXAMPLE VI

Aqueous solutions of thiourea were prepared containing 50, 80 and 100 per cent of the thiourea required for saturation. To about 10 parts by volume of each of these solutions was added one part by volume of each of cyclohexane, cyclohexanone and cyclohexanol at room temperature. With a 100 per cent saturated aqueous thiourea solution, each of these compounds formed a precipitate. With a 50 per cent saturated aqueous thiourea solution, none of these compounds formed a precipitate upon being shaken and standing for 16 hours. With an 80 per cent saturated aqueous thiourea solution, cyclohexane formed a precipitate in one minute, but cyclohexanol and cyclohexanone did not form a precipitate upon being shaken and standing for 16 hours.

Numerous variations and modifications of my invention will be readily apparent to those skilled in the art from any disclosure hereinabove.

I claim:

1. The method for resolving mixtures of naphthenic hydrocarbons and oxygenated derivatives of naphthenic hydrocarbons which comprises contacting said mixture with thiourea in the presence of an addition reaction activator selected from the group consisting of (a) low-boiling oxygenated hydrocarbon derivatives; (b) nitrogen-containing activators; and (c) water in amount such that an aqueous thiourea solution containing from 60 to 95 per cent of the thiourea required for saturation is employed, and separating solid addition products of said naphthenic hydrocarbons and thiourea from the resulting mixture.

2. The method for resolving a mixture of naphthenic hydrocarbons and oxygenated derivatives of naphthenic hydrocarbons which comprises contacting said mixture with thiourea in the presence of a low-boiling aliphatic alcohol at a temperature below 75° C., and separating solid addition products of said naphthenic hydrocarbons and thiourea from the resulting mixture.

3. A method according to claim 2 wherein the alcohol is methanol.

4. The method for resolving a mixture of naphthenic hydrocarbons and oxygenated derivatives of naphthenic hydrocarbons which comprises contacting said mixture with thiourea in the presence of an alkyl amine at a temperature below 75° C., and separating solid addition products of said naphthenic hydrocarbons and thiourea from the resulting mixture.

5. A method according to claim 4 wherein the alkyl amine is monoethylamine.

6. The method for resolving a mixture of naphthenic hydrocarbons and oxygenated derivatives of naphthenic hydrocarbons which comprises contacting said mixture with thiourea in the presence of water in an amount such that an aqueous thiourea solution containing from 60 to 95 per cent of the thiourea required for saturation is employed, at a temperature below 75° C., and separating solid addition products of said

naphthenic hydrocarbons and thiourea from the resulting mixture.

7. A method according to claim 6 wherein an aqueous thiourea solution of 70 to 85 per cent saturation is employed.

8. The method for resolving a mixture comprising cyclohexane and at least one of alcohol and ketone derivatives thereof which comprises contacting said mixture with thiourea in the presence of methanol at a temperature within the range of 10 to 35° C., separating solid addition product of cyclohexane and thiourea from the resulting mixture and regenerating cyclohexane therefrom.

9. The method for resolving a mixture comprising cyclopentane and at least one of alcohol and ketone derivatives thereof which comprises contacting said mixture with thiourea in the presence of methanol at a temperature within the range of 10 to 35° C., separating solid addition product of cyclopentane and thiourea from the resulting mixture and regenerating cyclopentane therefrom.

10. The method for resolving a mixture comprising methylcyclopentane and at least one of alcohol and ketone derivatives thereof which comprises contacting said mixture with an aqueous thiourea solution of 70 to 85 per cent saturation at a temperature within the range of 10 to 35° C., separating solid addition product of methylcyclopentane and thiourea from the resulting mixture and regenerating methylcyclopentane therefrom.

11. The method for resolving a mixture comprising methylcyclohexane and at least one of alcohol and ketone derivatives thereof which comprises contacting said mixture with thiourea in the presence of monoethylamine at a temperature within the range of 10 to 35° C., separating solid addition product of methylcyclohexane and thiourea from the resulting mixture and regenerating methylcyclohexane therefrom.

12. The method for resolving a mixture comprising dimethylcyclopentane and at least one of alcohol and ketone derivatives thereof which comprises contacting said mixture with thiourea in the presence of monoethylamine at a temperature within the range of 10 to 35° C., separating solid addition product of dimethylcyclopentane and thiourea from the resulting mixture and regenerating dimethylcyclopentane therefrom.

13. The process for recovering oxygenated organic compounds resulting from the partial oxidation of cyclohexane which comprises separating liquid effluent from such oxidation into an organic phase and an aqueous phase, contacting said organic phase with a saturated solution of thiourea in methanol at a temperature within the range of 10 to 35° C., and separating cyclohexanol and cyclohexanone from the resulting mixture.

14. The process for recovering oxygenated organic compounds resulting from the partial oxidation of cyclohexane which comprises separating liquid effluent from such oxidation into an organic phase and an aqueous phase, said aqueous phase containing a minor amount of dissolved oxidation products, contacting said organic phase with a saturated solution of thiourea in methanol at a temperature within the range of 10 to 35° C., separating cyclohexanol and cyclohexanone from the resulting mixture, regenerating cyclohexane from resulting addition products of cyclohexane and thiourea by contacting said

addition products with aqueous phase from said first separation step, separating resulting effluent into an aqueous phase and an organic phase containing cyclohexane and a small amount of dissolved oxidation products, and recycling said last-mentioned organic phase to the step for the partial oxidation of cyclohexane thereby concomitantly recovering oxidation products which would otherwise be lost and supplying initiators for said partial oxidation of cyclohexane.

15. The process for recovering oxygenated organic compounds resulting from the partial oxidation of cyclohexane which comprises separating liquid effluent from such oxidation into an organic phase and an aqueous phase, said aqueous phase containing a minor amount of dissolved partial oxidation products contacting said organic phase with a saturated solution of thiourea in methanol at a temperature within the range of 10 to 35° C., separating cyclohexanol and cyclohexanone from the resulting mixture as products of the process, decomposing resulting addition products of cyclohexane and thiourea at a temperature within the range of 30 to 80° C. in the presence of aqueous phase from said first sep-

aration step, separating resulting effluent into an aqueous phase and an organic phase containing cyclohexane and said partial oxidation product from said first-mentioned aqueous phase, and recycling said last-mentioned organic phase to the step for the partial oxidation of cyclohexane thereby concomitantly recovering said partial oxidation product and supplying an initiator for said partial oxidation of cyclohexane.

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