Patented Apr. 9, 1946

2,398,301

UNITED STATES PATENT OFFICE

2,398,301

REMOVAL OF HIGHLY UNSATURATED HYDROCARBON IMPURITIES FROM DIOLEFIN-CONTAINING MIXTURES

Ludo K. Frevel, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Michigan

No Drawing. Application July 26, 1943, Serial No. 496,184

14 Claims. (Cl. 260—681.5)

This invention concerns a method of treating mixtures comprising conjugated diolefins and one or more other hydrocarbons of equal or greater degree of unsaturation to decompose and remove said other hydrocarbons without loss of more than a minor amount of the conjugated diolefins. It pertains especially to the treatment of mixtures comprising conjugated diolefins and acetylenic hydrocarbons to remove the latter.

This application is a continuation-in-part of, and a substitute for, my co-pending application, Serial No. 467,782, filed December 3, 1942, and adds to the teachings of the latter.

Conjugated diolefins are produced in dilute form, but in large quantities, in various processes for the pyrolysis of petroleum fractions and other hydrocarbon starting materials. The diolefin-containing mixtures obtained in such processes usually comprise a variety of hydrocarbons other than the diolefins and separation of the latter in a form suitable for use in the preparation of synthetic rubber has proven difficult. For instance, cracked-oil gas, which is a well-known source of diolefins, usually comprises paraffinic hydrocarbons ranging from methane to hexane; olefins such as ethylene, propylene, butylenes, amylenes, and hexenes; diolefins such as allene, butadiene-1.3, methyl-allene, isoprene, and piperylene; and a small but appreciable amount of acetylenic hydrocarbons such as acetylene, methyl-acetylene, ethyl-acetylene and vinyl-acetylene; etc.

Although such mixture may be distilled to obtain fractions consisting for the most part of hydrocarbons having the same number of carbon atoms in the molecule and the diolefin content of each fraction may be concentrated by usual purification procedures, e. g. by extraction with solvents, the acetylenic hydrocarbons and other highly unsaturated hydrocarbon impurities of close to the same boiling point as the diolefin tend to accompany the latter during such treatments. For instance, butadiene-1.3 which has been recovered from cracked-oil gas by such conventional treatments usually retains a minor amount, e. g. less than 0.1 molecular equivalent, of acetylenic hydrocarbons such as methyl-acetylene, ethyl-acetylene and vinyl-acetylene, and may also retain a small but appreciable proportion of unconjugated diolefins such as allene or methyl-allene. Such impurities are objectionable when the diolefin is to be employed in the production of synthetic rubber. Although certain treatments, e. g. with chemical agents, are known whereby the acetylenic hydrocarbons may be removed, such treatments are expensive or difficult to carry out and are not well suited to commercial practice.

It is an object of this invention to provide a simple inexpensive method whereby vapor mixtures comprising a conjugated diolefin and, as impurities incident to the manufacture of the conjugated diolefin, a minor amount of one or more other unsaturated aliphatic hydrocarbons of equal or greater degree of unsaturation may be treated to remove the latter without excessive loss or destruction of the diolefin. For convenience, such impurities are referred to herein as "highly unsaturated hydrocarbon impurities." The highly unsaturated hydrocarbon impurities accompanying a conjugated diolefin are in most instances alpha.beta-unsaturated aliphatic hydrocarbons having no hydrogen atoms on the beta carbon atom, e. g. they are alpha-acetylenes or 1.2-diolefins. Other objects will be apparent from the following description of the invention.

I have found that the transition elements, iron and copper, when in finely divided or porous condition, and also the oxides of these metals have the property of causing a selective destruction of such highly unsaturated hydrocarbon impurities at temperatures below those at which conjugated diolefins are rapidly decomposed in the presence of these inorganic substances and that by passing a vaporized conjugated diolefin, containing such impurities, over the iron- or copper-containing substance at a suitable temperature, the highly unsaturated hydrocarbon impurities may be destroyed without excessive loss or destruction of the conjugated diolefin. Other more saturated hydrocarbons, such as simple olefins and paraffinic hydrocarbons, if present in the vapor mixture under treatment, are substantially unaffected.

It will be understood that not only the individual metals, copper and iron, but also alloys rich in these metals may be used to effect the selective decomposition of the above-mentioned highly unsaturated hydrocarbon impurities. Similarly, the oxides of these metals need not be pure. Examples of such metal oxides are cuprous oxide, cupric oxide, ferrous oxide, ferric oxide, ferroso-ferric oxide, mixtures of such oxides, and the spinel, $CuFe_2O_4$. Although both the finely divided metals and their oxides are effective for the purpose, the metal oxides, particularly the oxides of copper, are best adapted for commercial use and are preferred.

The copper or iron, when used, is employed in a finely divided, or dispersed, or a finely porous form having a large surface relative to its absolute volume. The oxides of these metals often possess a finely porous structure, and they may be employed in either powdered or dispersed form, or in the form of porous lumps, granules, or filaments, etc. If desired, the metal or metal oxide may be deposited on a carrier such as kaolin, pumice, or alumina, etc., and be used as a dispersion on, or in, such carrier material. The carrier material should, of course, be one which is not itself a catalyst for the decomposition of conjugated diolefins at the operating temperature, and carrier materials which are not highly

absorptive of hydrocarbon vapors are preferred.

The principal products formed when the highly unsaturated hydrocarbon impurities present in the conjugated diolefin-containing mixtures are thermally decomposed in the presence of copper or iron are carbon and hydrogen, and it is clear that these metals act as catalysts for the selective reaction. Carbon and hydrogen are probably also the principal primary products when the decomposition is carried out in the presence of an oxide of copper or iron, and it is probable that these metal oxides also function as catalysts, but in this instance, the metal oxide is often reduced either to a lower oxide or to the metal, apparently by reaction with the hydrogen to form water.

The several metal oxides which may be employed differ as to the extent by which they are readily reduced during use in the process. Both cuprous oxide and cupric oxide tend to be reduced ultimately to a finely porous form of metallic copper. Ferric oxide is readily reduced to ferro-soferric oxide, Fe_3O_4, and it may be that the reduction sometimes continues to form some ferrous oxide or even metallic iron. However, the lower oxides of iron, i. e. Fe_3O_4 and FeO, although effective as catalysts for the selective thermal decomposition of the highly unsaturated hydrocarbon impurities, do not appear to have an appreciable oxidizing action toward such impurities under the reaction conditions employed. The observable function of ferric oxide and of the oxides of copper is that of serving as agents for the selective oxidation of the highly unsaturated hydrocarbon impurities to form carbon and water vapor and leave the conjugated diolefins largely unreacted.

Carbon produced in the reaction tends to accumulate in the catalyst bed, i. e. in the bed comprising the metal or metal oxide. It is a loose fluffy form of soot which does not interfere seriously with continuance of the reaction for the selective oxidation of the highly unsaturated hydrocarbon impurities by means of a metal oxide, but which may, and often does, interfere with the reaction for the selective thermal decomposition of said impurities unless the decomposition is accompanied by oxidation. It appears that the water vapor formed by the selective oxidation reaction at least momentarily frees adjacent metal oxide, or metal, surfaces of carbon and renders them available for continued reaction and that in the absence of such nascent water vapor the catalyst surfaces tend to become coated with carbon and rendered unavailable to the decomposition reaction. However, the invention is not limited by this theory as to the reason for the results which are observed.

In any instance, the catalyst becomes inactive after operating for some time, due presumably to its becoming coated with carbon or tar. When using ferric oxide or an oxide of copper in the process, the point at which the reaction for the destruction of the highly unsaturated hydrocarbon impurities ceases, or becomes sluggish, corresponds roughly to that at which the metal oxide has become reduced as described above. The carbon is then removed and the metal, or lower metal oxide, is re-oxidized by heating, e. g. to 350° C. or higher, in a current of air or other oxygen-containing gas. The resultant metal oxide, e. g. CuO or Fe_2O_3, is in condition for re-employment in the process.

It is because of the fact that ferric oxide and the oxides of copper are not rendered inactive by the carbon formed in the process and the further fact that such oxide is formed during the step of freeing the catalyst of carbon by oxidation, that these oxides are preferred over porous copper or porous iron as agents for effecting the selective decomposition of the highly unsaturated hydrocarbon impurities which often accompany conjugated diolefins.

In practicing the invention, a vapor mixture comprising a conjugated diolefin and a lesser amount, usually less than 0.1 molecular equivalent, of one or more at least equally unsaturated hydrocarbon impurities, e. g. alpha-acetylenes and/or unconjugated diolefins, is passed through a bed of the catalyst at a reaction temperature below about 375° C.; i. e. at a temperature below that at which conjugated diolefins are rapidly decomposed upon contact with the catalyst. The minimum temperature at which the treatment may satisfactorily be carried out varies somewhat depending upon the particular catalyst used. For instance, the decomposition of an alpha-acetylene may be carried out at a satisfactorily rapid rate in the presence of cuprous oxide at temperatures as low as 140° C. and in the presence of any of the other catalysts, e. g. copper, cupric oxide or iron or iron oxides, at about 200° C., or possibly at somewhat lower temperatures. As hereinbefore indicated, the activity of the catalyst increases with increase in the ratio of its surface to its absolute volume, e. g. as the particle size thereof is decreased, and it may be possible to prepare the catalysts in physical forms which will be effective at temperatures lower than those just mentioned. In practice, however, the treatment is usually carried out at temperatures between 220° and 350° C., and preferably between 275° and 325° C. The vapors are passed over the catalyst at a rate sufficient to avoid destruction of more than a minor amount, e. g. less than 20, and preferably less than 10, per cent of the conjugated diolefin. The time of contact with the catalyst should, of course, be sufficient to cause destruction of the major portion, and preferably all, of the highly unsaturated hydrocarbon impurities initially accompanying the conjugated diolefin.

The heat required to initiate the reaction may be supplied by direct heating of the catalyst bed or by preheating of the vapor mixture prior to flow into the bed. However, the reaction is highly exothermic and, once stated, further heating from an outside source may not be necessary. In some instances, cooling may be required in order to control the reaction temperature.

The treatment is usually carried out at atmospheric pressure or thereabout, but it may be carried out at lower or at much higher pressures, e. g. at pressures between 5 and 80 pounds per square inch, absolute. By carrying the treatment out at a pressure above atmospheric, e. g. between 30 and 80 pounds per square inch, absolute, the conjugated diolefin product may be readily cooled and liquefied without resorting to refrigeration or further compression of the same. The selective reaction for the destruction of the highly unsaturated hydrocarbon impurities occurs satisfactorily regardless of whether steam or other inert gases are present in the vapors under treatment and, if desired, the reaction may be carried out under substantially adiabatic conditions using steam as a diluent for controlling the reaction temperature. Accordingly, the present method for the removal of such impurities

from conjugated diolefin-containing vapor mixtures is adapted for use as a step in any of a variety of known processes for the pyrolysis of hydrocarbon starting materials to produce such diolefin-containing mixtures, certain of which known processes involve the use of steam as a diluent or involve operation at pressures other than atmospheric pressure.

By passing a vapor mixture comprising a conjugated diolefin and such highly unsaturated hydrocarbon impurity over the catalyst under the preferred conditions described above, the impurity may be entirely removed without appreciable loss of the conjugated diolefin or other hydrocarbons more saturated than the diolefins initially present.

The following examples describe certain ways in which the principle of the invention has been applied, but are not to be construed as limiting the invention.

EXAMPLE 1

A chamber of 3 centimeters internal diameter and 50 centimeters length was filled with cupric oxide in wire form and the copper oxide was reduced to metallic copper with hydrogen. A fraction of cracked-oil gas containing approximately 44.9 per cent by volume of butylenes (principally butylene-1), 53 per cent of butadiene-1.3 and 1.9 per cent acetylenes (principally methyl-acetylene, ethyl-acetylene and vinyl-acetylene) was heated to about 270° C. and was passed at a rate of 2.2 grams per minute into the bed of copper while maintaining the latter at the same temperature. The vapors passing from the bed were collected and analyzed. They were found to be entirely free of acetylenes and to contain 48 per cent by volume of butadiene-1.3.

EXAMPLE 2

In each of a series of experiments, a chamber having the dimensions given in Example 1 was filled with powdered cuprous oxide, and a fraction of cracked-oil gas containing the ingredients stated in Example 1 was heated and passed into the bed of cuprous oxide at a rate of 1.1 grams per minute. The gases issuing from the bed were collected and analyzed. The following table gives the per cent by volume of butadiene-1.3 and also of alpha-acetylenes in the gaseous mixture which was fed into the bed of cuprous oxide, the average temperature of the gases within the bed, and the per cent of butadiene-1.3 and of alpha-acetylenes in the gas after passage through the bed.

Table I

Run No.	Temp. within bed, ° C.	Untreated gas		Treated gas	
		Per cent butadiene	Per cent alpha-acetylenes	Per cent butadiene	Per cent alpha-acetylenes
1	145	51	2.1	54	0.4
2	190	51	2.1	53	0.0
3	280	51	2.1	50	0.0

EXAMPLE 3

In each of two experiments a fraction of cracked-oil gas containing the ingredients stated in Example 1 was passed through a heated chamber of 3 centimeters internal diameter and 50 centimeters length, which chamber was filled with cupric oxide in wire form. The gases issuing from the chamber were collected and analyzed. Table II gives the per cent by volume of butadiene-1.3 and of alpha-acetylenes in the gas mixture both before and after passage through the heated chamber. It also gives the rate at which the gas mixture was fed into the chamber and the average temperature within the chamber.

Table II

No.	Rate of flow, gm./min.	Temp., °C	Untreated gas		Treated gas	
			Per cent butadiene	Per cent alpha-acetylenes	Per cent butadiene	Per cent alpha-acetylenes
1	2.2	270	53	1.9	53	0.9
2	2.9	300	53	1.9	54	0.0

EXAMPLE 4

In each of a series of experiments, a cracked-oil gas fraction containing the ingredients stated in Example 1 was passed through a heated chamber of 3 centimeters internal diameter and 50 centimeters length, which chamber was filled with a powder of the catalytic substance named in the following table. The gases issuing from the chamber were collected and analyzed. Table III names the catalyst used in each experiment, gives the rate of flow of the hydrocarbon mixture, and states the average temperature within the catalyst bed. The table states the per cent by volume of butadiene-1.3 and also of acetylenes in the mixture, both prior to and after passage over the catalyst.

Table III

Run No.	Catalyst	Temp., ° C.	Flow, gms./min.	Untreated gas		Treated gas	
				Per cent butadiene	Per cent acetylenes	Per cent butadiene	Per cent acetylenes
1	Fe	265	1.1	54	2.2	50	1.3
2	Fe_2O_3	202	0.7	63	2.0	64	1.0
3	do	253	0.7	63	2.0	59	0.0
4	Fe_3O_4	195	0.7	63	2.0	63	0.4
5	$CuAl_2O_4$	275	0.7	63	2.0	56	0.0

EXAMPLE 5

A granular catalyst consisting of cupric oxide supported on Silocel brick (i. e. brick formed of diatomaceous earth) and containing approximately 21.3 per cent by weight of cupric oxide was prepared by soaking the brick in an aqueous copper nitrate solution containing approximately 50 per cent by weight of $Cu(NO_3)_2.3H_2O$, thereafter draining and drying the brick, and decomposing the copper nitrate to form copper oxide by heating the granular material to about 500° C. in a current of air. An iron tube of 1 inch internal diameter was filled to a depth of 30 inches with the granular catalyst. 97.5 grams of a cracked-oil gas fraction containing the ingredients stated in Example 1 and having an acetylene content of 1.9 per cent by volume was passed through the tube at a rate of 2.5 grams per minute while heating the mixture within the catalyst chamber at a temperature of approximately 300° C. After passage through the catalyst chamber, the remaining hydrocarbons were

condensed and analyzed. The recovered hydrocarbons weighed 95.3 grams, were entirely free of acetylenes, and consisted of approximately equal parts by weight of butylene and butadiene-1.3. There was also obtained in the condensate 1.6 grams of water. Approximately 1.7 grams of carbon was formed during the treatment.

EXAMPLE 6

A granular catalyst of from 4 to 10 mesh particle size and containing 25 per cent by weight of cupric oxide supported on Silocel brick was prepared as in Example 5. An iron chamber of 10 inches internal diameter and 20 inches depth was filled with the catalyst. The catalyst bed was brought to a temperature of about 300° C. by passage of a mixture of air and superheated steam therethrough, at which time the introduction of air was discontinued, the chamber was swept free of air with the steam, and the treatment of a diolefin-containing hydrocarbon vapor mixture to free the same of acetylenes was started. The hydrocarbon mixture contained about 49 per cent by volume of butylenes, about 49 per cent of butadiene-1.3 and 2 per cent of acetylenes (principally methyl-acetylene, ethyl-acetylene and vinyl-acetylene). The procedure in carrying out the treatment was to pass the mixture (together in most instances with sufficient steam to avoid the possibility of local overheating within the catalyst bed due to the heat of reaction) over the catalyst at the pressure given in the following table while maintaining the mixture within the bed at temperatures between 280° and 320° C. The vapors issuing from the bed were cooled, while under pressure, to condense the hydrocarbons and the latter were continuously analyzed for acetylenic hydrocarbons. The hydrocarbon products consisted almost entirely of butylene and butadiene-1.3 up to the time when the catalyst had become so badly fouled that acetylenes began to appear in the products. Operation in the manner just described was interrupted before the proportion of acetylenes in the mixture issuing from the bed had risen to a value of 0.05 per cent by volume, and the catalyst was freed of carbon and reactivated by a "burning off" operation. In this burning off operation, a mixture of air and sufficient steam to prevent excessive temperature rises within the catalyst bed is passed through the latter until the bed is substantially free of carbon and the copper is re-oxidized to copper oxide. This operation is usually carried out at temperatures between 400° and 600° C., but higher temperatures, e. g. about 1000° C., have been used without damage to the catalyst. For convenience, the burning off operation was carried out at about the same vapor pressure as that employed in freeing the hydrocarbon mixture of acetylenes. After completing the burning off operation, passage of the mixture of hydrocarbon vapors and steam over the catalyst was resumed. These alternate operations of passing the hydrocarbon mixture over the catalyst and of burning off the latter were repeated fourteen times without appreciable decrease in the activity of the catalyst. The data accumulated is summarized in the following table which gives the pounds of the hydrocarbon vapors, and also of steam, fed into the catalyst bed per hour, the pressure at which the treatment was carried out, the total weight of hydrocarbons fed into the bed in each cycle of the process, the length of time over which the hydrocarbon mixture was passed through the catalyst in each cycle and the time of heating in each "burn off" operation. It may be mentioned that during the operations for the removal of acetylenes from the hydrocarbon mixture the proportion of steam was varied for purpose of temperature control and that there were brief periods in which the introduction of steam was interrupted. In the table, the step of treating the hydrocarbon mixture to remove acetylenes is referred to as operation "A" and the step of burning off the catalyst is referred to as operation "B."

Table IV

Cycle No.	Operation	Rates of flow: Hydrocarbons, lbs./hr.	Rates of flow: Steam, lbs./hr.	Abs. pressure, lbs./in.²	Lbs. of hydrocarbons treated	Duration of treatment, hrs.
1	A	7	60	21-23	28	4
	B			21-23		1.25
2	A	7	60	21-23	42	6
	B			21-23		1.5
3	A	7.6	16	21-23	19	2.5
	B			21-23		1.5
4	A	7.3	0-20	21-23	44	6
	B			21-23		1.75
5	A	11.1	20-0	21-23	50	4.5
	B			21-23		2
6	A	9.2	12	21-23	60	6.5
	B			21-23		1.3
7	A	13.4	6-0	21-23	47	3.5
	B			21-23		3
8	A	13.4	5-20	35-55	57	4.25
	B			35-55		3.5
9	A	26.3	0-30	35-55	97.5	3.7
	B			35-55		4.5
10	A	28.6	30-50	35-55	71.5	2.5
	B			35-55		3.75
11	A	52	48	35-55	13	0.25
	B			35-55		2.3
12	A	27.7	Unknown	35-55	83	3
	B			35-55		3
13	A	47.5	Unknown	35-55	95	2
	B			35-55		2.75
14	A	60	Unknown	35-55	70	1.17

EXAMPLE 7

A fraction of cracked-oil gas which had been freed of acetylenes, as in Example 1, and which consisted substantially of equimolecular amounts of butylene and butadiene-1.3 was treated with allene in amount corresponding to 7.45 per cent of the weight of the resultant mixture. One portion of the mixture was passed through a heated

chamber of 3 centimeters internal diameter and 50 centimeters length, which chamber was filled with cupric oxide in wire form. Another portion of the mixture was passed through a heated chamber having the same dimensions, but filled with ferric oxide powder. In each experiment the rate of flow was 0.3 liter of the gas mixture (measured at 25° C. and atmospheric pressure) per minute. In each instance, the gas issuing from said chamber was collected and analyzed for allene. The following table names the catalyst used in each experiment, states the average temperature within the bed of catalyst and gives the per cent by weight of allene in the treated gas.

Table V

Run No.	Catalyst	Temp., °C.	Per cent allene in treated gas
1	CuO	300	2.9
2	Fe_2O_3	290	2.0

EXAMPLE 8

Two comparative experiments were carried out as in Example 7, except that the catalyst used in each of these experiments was copper oxide in wire form and the gas subjected to the treatment consisted substantially of equimolecular proportions of butylene and butadiene-1.3 together with 1.75 per cent by weight of allene. The rates of flow and the volume of the catalyst bed were the same as in Example 7. These two experiments differed from one another only as to the temperature of the catalyst bed and the results obtained. Table VI states the average temperature within the catalyst bed for each experiment and gives the per cent by weight of allene retained in the gas after passage through the bed of catalyst.

Table VI

Run No.	Temp., °C.	Per cent allene in treated gas
1	300	0.5
2	330	0.0

In the following claims where a substance is referred to as being "finely divided" it will be understood that it may be in the form of a powder, or fine grindings, or turnings, or it may be deposited in dispersed form on or within a solid carrier material, or it may be in the form of lumps, granules or rods, etc., having a fine porous structure.

Other modes of applying the principle of the invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. The method which comprises passing a vapor mixture, containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing, as an impurity incident to the manufacture of the conjugated diolefin, a minor amount of a different and at least equally unsaturated hydrocarbon, into contact with a finely divided substance selected from the class consisting of copper, iron, and the oxides of said metals at a reaction temperature below 375° C., whereby said unsaturated hydrocarbon impurity is largely destroyed leaving the conjugated diolefin in a form substantially free of the same.

2. The method which comprises passing a vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of an alpha-beta-unsaturated aliphatic hydrocarbon having no hydrogen atoms attached to the beta-carbon atom thereof into contact with a finely divided substance selected from the class consisting of copper and iron and the oxides of said metals at a reaction temperature below 350° C., the rate of vapor flow being sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin during passage of the vapors through the bed of said finely divided substance.

3. The method as described in claim 2, wherein the unsaturated hydrocarbon having no hydrogen atoms on a beta carbon atom thereof is a 1.2-diolefin.

4. The method as described in claim 2, wherein the unsaturated hydrocarbon having no hydrogen atoms on a beta carbon atom thereof is a 1.2-diolefin and the finely divided substance is a copper oxide.

5. The method as described in claim 2, wherein the conjugated diolefin is butadiene-1.3, the unsaturated hydrocarbon having no hydrogen atoms on a beta carbon atom thereof is allene, and the finely divided substance is a copper oxide.

6. A method of treating a vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of an alpha-acetylene to remove the latter which comprises passing the mixture into contact with a finely divided substance selected from the class consisting of copper, iron, and the oxides of said metals, at a reaction temperature below 375° C.

7. A method of treating a vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of at least one alpha-acetylene to destroy and remove the latter which comprises passing the mixture through a bed of a finely divided substance selected from the class consisting of copper and iron and the oxides of said metals at a reaction temperature below 325° C., the rate of vapor flow being sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin during passage of the vapors through the bed.

8. A method of treating a hydrocarbon vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a smaller amount of at least one alpha-acetylene to destroy and remove the latter which comprises passing such vapor mixture through a catalyst bed comprising, as an active ingredient, a finely divided substance selected from the class consisting of copper, iron, and the oxides of said metals, at a reaction temperature below 325° C. and at a rate of vapor flow sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin, and periodically interrupting the flow of the vapor mix-

ture and removing carbon from said bed by burning the carbon with an oxygen-containing gas.

9. A method of treating a vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of an alpha-acetylene to destroy and remove the latter which comprises passing the mixture over an oxide of copper at a reaction temperature below 375° C. and at a rate of flow sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin.

10. A method of treating a vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of an alpha-acetylene to destroy and remove the latter which comprises passing the mixture over cuprous oxide at a reaction temperature between 140° and 350° C. and at a rate of flow sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin.

11. A method of treating a hydrocarbon vapor mixture containing butadiene-1.3 as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and a minor amount of at least one alpha-acetylene having from three to four carbon atoms in the molecule to destroy and remove the alpha-acetylene, which comprises passing the mixture over an oxide of copper at a reaction temperature between 275° and 325° C. and at a rate of flow sufficient to avoid destruction of more than 10 per cent of the butadiene.

12. A method of treating a vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of an alpha-acetylene to destroy and remove the latter which comprises passing the mixture over an oxide of iron at a reaction temperature below 375° C. and at a rate of flow sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin.

13. A method of treating a hydrocarbon vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and also containing a minor amount of at least one alpha-acetylene to destroy and remove the latter which comprises passing the mixture over an oxide of iron at a reaction temperature between 225° and 350° C. and at a rate of flow sufficient to avoid destruction of more than 10 per cent of the conjugated diolefin.

14. A method of treating a hydrocarbon vapor mixture containing butadiene as the principal hydrocarbon ingredient having a degree of unsaturation as great as that of a diolefin and a minor amount of at least one alpha-acetylene having from 3 to 4 carbon atoms in the molecule to destroy and remove the alpha-acetylene, which comprises passing the mixture over an oxide of iron at a reaction temperature between 275° and 325° C. and at a rate of flow sufficient to avoid destruction of more than 10 per cent of the butadiene.

LUDO K. FREVEL.