Oct. 3, 1939. M. G. GWYNN 2,174,510

METHOD OF CONTINUOUSLY HYDROFINING CARBONACEOUS VAPORS WITH SOLID SULPHUR SENSITIVE CATALYTIC SURFACES

Filed March 8, 1937 2 Sheets-Sheet 1

Fig. 1.

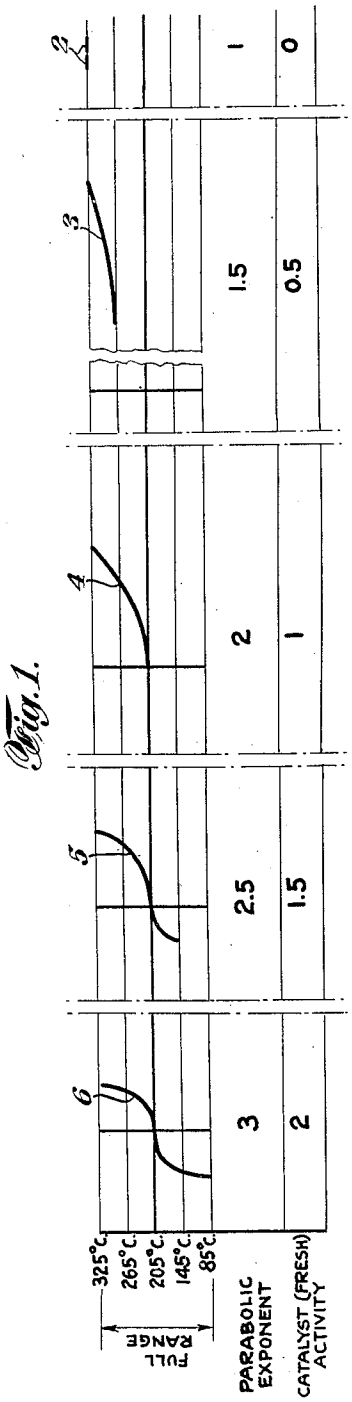
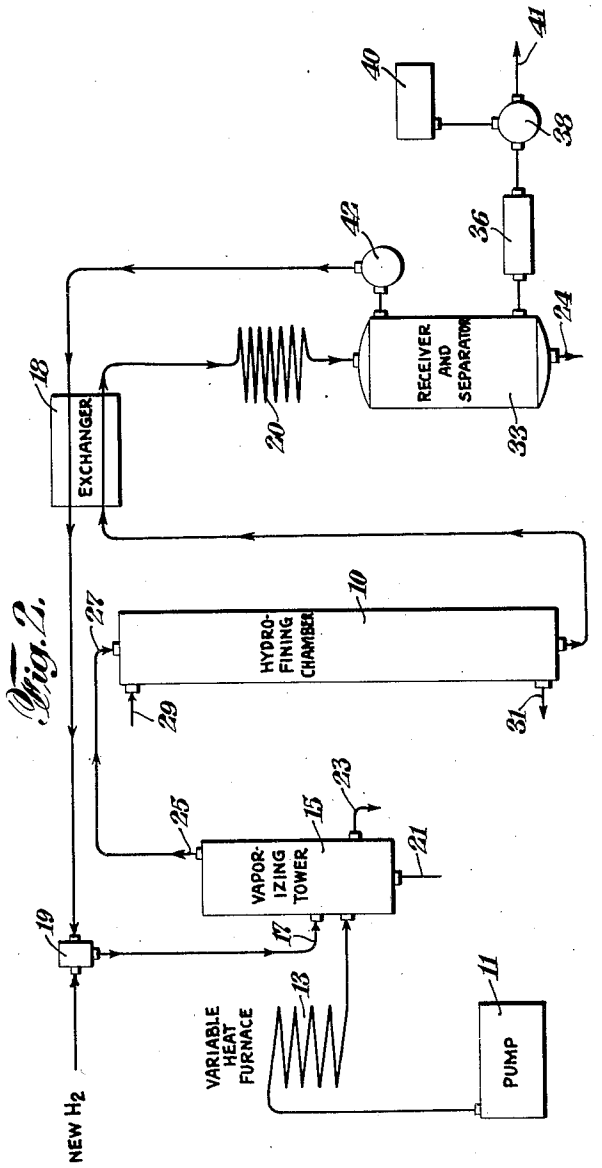


Fig. 2.



INVENTOR

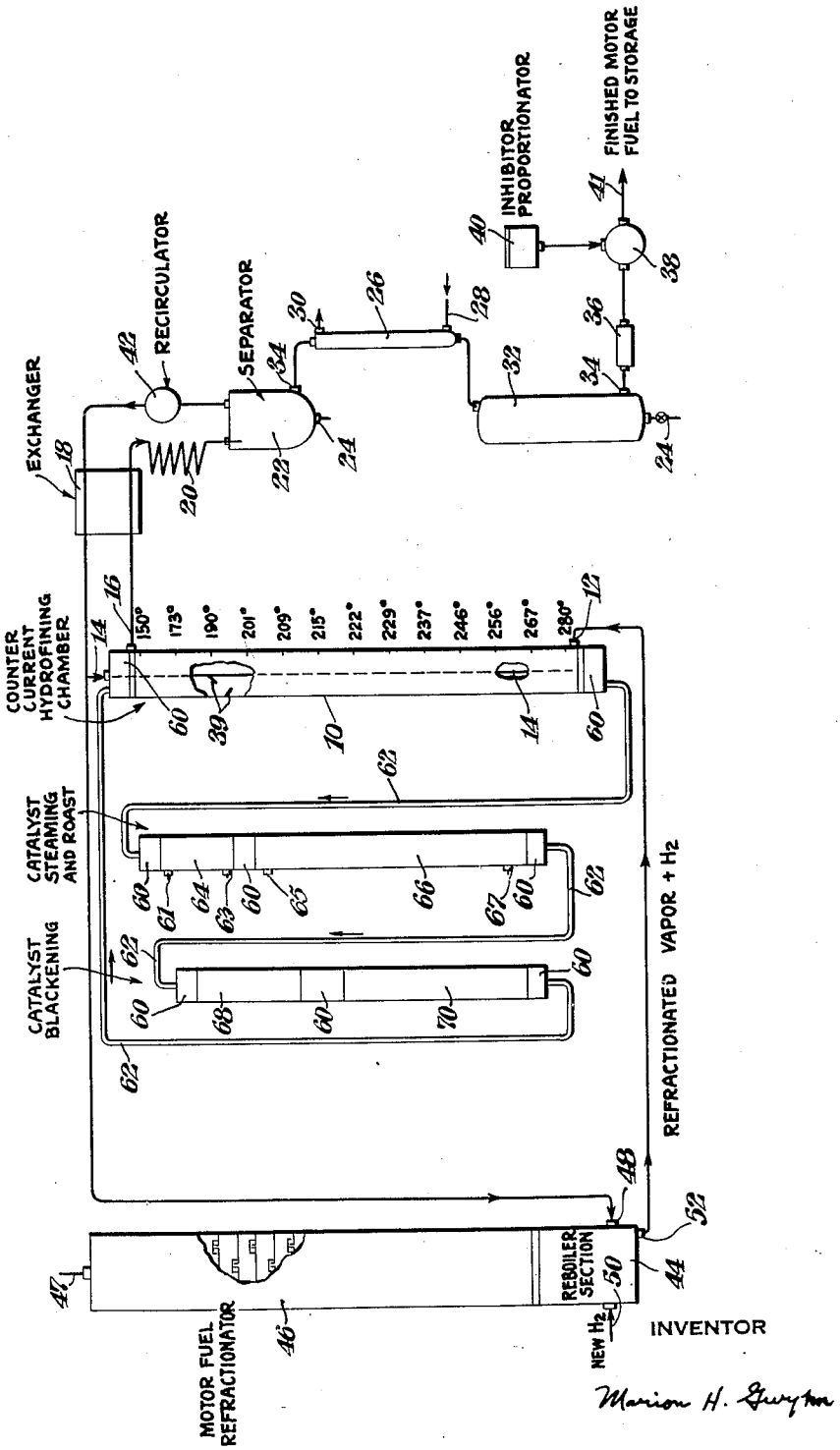
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Fig. 3



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METHOD OF CONTINUOUSLY HYDROFINING CARBONACEOUS VAPORS WITH SOLID SULPHUR SENSITIVE CATALYTIC SURFACES

Marion H. Gwynn, Leonia, N. J.

Application March 8, 1937, Serial No. 130,478

11 Claims. (Cl. 196—28)

This invention is a continuation in part of my pending application Serial Number 650,997 entitled Method of refining hydrocarbon distillates, filed January 10, 1933, now Patent 2,073,578 granted March 9, 1937.

My invention relates to the refining of carbonaceous vapors with solid sulphur sensitive catalytic surfaces under novel gradient conditions, particularly to the hydrofining of light petroleum distillates (and those free or freed of asphaltic materials) which refining may be used alone or in conjunction with the old methods of refining.

The essential feature of this hydrofining is the use of solid sulphur sensitive surfaces comprising a catalytic metal, e. g., nickel, under gradient and substantially nonpyrolytic conditions, particularly gradients of temperature and hydrogen excess or their equivalents. Two forms of the invention are described, one the stationary catalyst form, and the other the countercurrent form. When present, labile sulphur compounds are removed or converted into less troublesome components, and gum forming unsaturated compounds converted to useful compounds without loss of yield. The process eliminates wholly or in part the use of sulphuric acid.

In either form the invention is carried out in the vapor phase preferably under a gradient of temperatures and of hydrogen excess. In the countercurrent form the catalyst is preferably continuously moved countercurrent to the mixture of carbonaceous vapor and hydrogen as shown in Fig. 3. In this form the catalyst becomes progressively spent, the most spent portions are preferably contacted with the unhydrofined carbonaceous vapor, and the least spent or fresh portions are preferably contacted with those carbonaceous vapor hydrogen mixtures most completely hydrofined.

Also contributing to my invention is one or more of the following: the division of the hydrofining into two different operations; the separate treatment or selection of fractions within a distillate; effective means for preparing and reactivating the catalytic surface; the selection of effective nonhydrofining treatments to be used in connection with the hydrofining, such as the subsequent addition of antioxidant and/or antiknock reagents. Later described are examples of these means and of novel apparatus highly useful in practicing the invention, particularly that apparatus exemplified in Fig. 3.

I use the term hydrofining generically to comprise hydrogenation and/or desulphurization, generally both when sulphur is present. Sulphur immune catalyses are characteristically liquid phase processes requiring high pressures and pyrolytic temperatures, whereas my hydrofining is preferably in the vapor phase at pressures below those generally used above, and at low temperatures which essentially exclude pyrolysis. My hydrofining is more truly a refining or treating process than the high pressure-temperature sulphur immune pyrolytic catalysis.

For practical hydrofining with my readily reducible sulphur susceptible catalysts, especially when the vapors are accompanied by similar carbonaceous compounds in the liquid phase, the distillates are preferably free of ultra microscopic colloids, depositing "carbon", marked coloration, and even very high molecular weight hydrocarbons. It is not necessary that the distillates be water white. Vaporization from a vaporizing chamber tends to rid a distillate of extreme heavy ends, oxidation products due to age, and other impurities harmful to the catalyst. I also find that the unsaturates themselves prematurely deactivate a metallic catalyst unless contacted under my gradient conditions.

My gradient operation maximizes and fixes sulphur "poisoning". This is a necessary deactivation, a purpose of my invention. At the same time the gradient operation minimizes the unnecessary or premature deactivations. These things are marked advances over the prior art, which has been dominated by the traditional phase rule practice of a constant temperature, pressure and contact time within a given operation.

I find that reactant and catalyst activity are complemental to temperature, and it is the product of activity and temperature which I strive to maintain constant or relatively so. Neither of these factors can be changed without changing the product thereof, the latter apparently being the essential factor so far as constancy is concerned. The time gradient of temperature as discussed later is ascending, and compensates the progressive decrease of catalyst activity, for which I have developed a measure as indicated in Fig. 1.

My hydrofining may be carried out to various extents. A relatively small extent or duration of contact is generally sufficient to remove the more labile impurities, such as mercaptans, and so render the product "doctor" sweet. The olefines need not be completely hydrogenated. Other treatments may be used in conjunction with my hydrofining such as those means known to the art. If for reasons of economy, minor quantities of gum forming unsaturates remain after my

hydrofining, these may be removed or inhibited by other means. The contact with liquid caustics and the addition of antioxidants are useful after-treatments to my hydrofining. For example I may add the soluble and gum inhibiting derivatives of para-aminophenol in very small quantities to a motor fuel distillate after my hydrofining when the olefines are incompletely hydrogenated. Examples of such derivatives are monobenz¹-para-aminophenol, dibenzyl - para-aminophenol, parahydroxyphenyl morpholine, and in a quantity for instance on the order of 0.005%.

The product of my hydrofining is extraordinarily responsive to the subsequent addition of fractional percentages of reagents such as antioxidant and antiknock reagents, this being one of the purposes of the invention. My hydrofining selectively and in general entirely removes components which are apt to precipitate or offset the effect of antioxidants, and which are proknock. The more labile sulphur compounds, particularly polysulphides, are markedly proknock and often prooxidant. My hydrofining also retains and improves many of the natural gum inhibitors of the distillate. Thus I may use antioxidants or inhibitors of unusually low solubility. I may also use the somewhat more soluble inhibitors or antioxidants with less danger of precipitation or change. The more powerful gum inhibiting antioxidants are among those of the least solubility in hydrocarbon motor fuel, for instance para ethyl aminophenol or pyrogallol. Other of the less simple phenols and/or nitrogen derivatives of benzenes may be used.

The usual motor fuel distillate is generally finished "sweetened" with alkali in some form. The utmost care is required to eliminate traces of alkali from the final product. Yet traces of alkali precipitate or are otherwise detrimental to some of the best gum inhibitors such as monobenzyl para aminophenol. My hydrofined product is free from traces of alkali as well as free from precipitating sulphur compounds.

Diagrammatically shown in the drawings are three forms of apparatus or control for sulphur sensitive hydrofining under gradient conditions. Fig. 1 represents four types of time gradients of temperature and the relation of these to catalyst activity. The gradients may be used directly in the stationary catalyst form of my invention. Fig. 2 represents the stationary catalyst form of the invention. Fig. 3 represents the countercurrent form of the invention. The hydrofining chamber and reactivation unit are directly connected to the motor fuel refractionator, and are shown in more detail. Fig. 3 is better representative of large scale conditions than Fig. 2.

Generally it is preferable to introduce reserve or fresh catalyst at the rear or cool stage of contact, comprising relatively countercurrent operation with either continuous or discontinuous introduction of the catalyst.

A series of temperatures as ordinarily used in the prior catalytic art is herein termed a space gradient, in distinction to a time gradient which represents the increase of average temperature of the space gradient if any with increasing deactivation of the catalyst as a whole. A time series of temperatures is an ascending gradient. I use the term gradient to mean discontinuous steps or changes as well as continuous change. The space gradient is ascending and/or descending. The usual space gradient is ascending but controls reactant rather than catalyst changes. A descending gradient of temperature for the vapors is useful during relatively countercurrent contact with fresher and fresher catalyst.

The space gradient is an essentially instantaneous gradient, consisting of a series of temperatures which a molecule of the vapor undergoes during its short period of catalyst contact. This gradient is generally of the wider range in the low temperature, liquid phase, hydrogenating rather than desulphurizing operations.

The time gradient constitutes that rise of temperatures as a whole over a single cycle of active life of the catalyst. It is generally of the wider range in the vapor phase, and in desulphurization rather than hydrogenation operations.

My gradient conditions tend to relatively or approximately equalize the hydrofining in each of the stages of hydrofining, particularly in the stages when the catalyst is quite active. When the catalytic surfaces are nearly spent it may be impracticable to maintain the former high level of hydrofining. The resulting hydrofined product may be further treated however, preferably hydrofined to bring it up to the standard.

I prefer to hydrofine motor fuel distillate, at least until the distillate is sweet to the doctor test. I also prefer to incompletely hydrofine, even as a standard. An incompletely hydrofined product may be further hydrofined with solid sulphur sensitive catalytic surfaces, preferably in fewer stages than the first hydrofining. For instance, an ascending space gradient of negative acceleration in the liquid phase and with a nickel catalyst and at an elevated temperature, e. g., 130° C., constitutes an effective means of hydrofining the light distillates with a minimum change in knock rating and solvent power, especially in distillates high in unsaturates and comparatively low in sulphur.

The relative or approximate equalization of hydrofining allows the catalyst to work at a relatively constant or uniform rate, which minimizes unnecessary catalyst deactivation and side reactions. These highly beneficial effects, together with a maximizing or speeding of necessary catalyst deactivation (sulphiding) and main reactions, appear to be only accomplished under my gradient conditions. Time gradients of temperature are the principal but not the only means of attaining my gradient conditions. Differential regulation of the hydrogen excess and pressure is useful. In both the stationary and countercurrent form of my invention the temperature and the hydrogen excess is regulated. Gradients of temperature, of hydrogen excess and of pressure may be effectively used together in the stationary form.

In carrying out my invention, I note a tendency for one carbonaceous molecule to adsorb on each sulphur sensitive catalytic unit, be that a metal compound or atom. The metal after conversion to sulphide or oxysulphide tends to more readily lose its adsorbed carbonaceous molecule. However, if the hydrogen excess is decreased and the pressures are increased as the catalyst temperature rises, then the total adsorption upon the catalytic surface remains relatively constant throughout the temperature rise. This yields practical results particularly in the stationary form of my invention. When hydrofining at constant pressure, both desulphurizing and hydrogenating diminish in the final and hotter stages of hydrofining. Along with this I have noted an apparent marked increase in yield above theory. This was found to be due to a decrease in the adsorption of carbonaceous

compounds on the catalytic surface, probably an index of a decrease in true contact time. By decreasing the hydrogen excess and/or increasing the pressure, the apparent abnormality of yield is corrected, and the desulphurizing and hydrogenating diminution is checked. Increasing the pressure alone aids the hydrogenating more than the desulphurizing.

As will be noted in the examples, the time gradient range for this work is preferably more than 100° C. with nickel and like catalysts, though less with the low activity catalysts. Fresh nickel will actively desulphurize distillate vapors below 200° C., and will be useful at 300° C. and greater when near spent. The preferred range of the temperature gradients in my invention is between about 20° C. and 200° C. The range of the time gradient in the stationary form of my invention is about proportional to the catalyst activity under otherwise similar conditions.

Fig. 1 diagrammatically shows several types of time gradients directly useful in the stationary form of my invention and indirectly useful in determining the cooling curve for the countercurrent form. Fig. 1 also shows the relation between these gradients and quantitative catalyst activity. The ordinates represent temperature in degrees centigrade. The unit full temperature range is 120° C. The abscissae represent time, which may vary in each case depending chiefly on the percentage of sulphur removed from the distillate. For instance a typical unit time is one day. In the cubic parabola 6, with unit of time one day, the total time from 85° C. to 325° C. is two days, and the equation is

$$\frac{T-205^\circ\text{ C.}}{120^\circ\text{ C.}}=(t_{85^\circ}-1)^3$$

where T is any temperature between 85° C. and 325° C., and t is the time in days from the start at 85° C. The parabolic exponent is 3.

In the curve 6 the ordinate is the time when the catalysis reaches 205° C. and the equation for the upper right hand branch of the curve is

$$\frac{T-205^\circ\text{ C.}}{120^\circ\text{ C.}}=t_{205^\circ}{}^3$$

where t 205° is the time after reaching 205° C.

Likewise in the parabola 4, neglecting negative legs of the curve, the equation is

$$\frac{T-205^\circ\text{ C.}}{120^\circ\text{ C.}}=t_{205^\circ}{}^2$$

To scale with the cubic parabola 6, the unit time for the parabola 4 is somewhat more than 2 days. The parabolic exponent is 2.

In the intermediate curve 5, herein termed the mean hyper parabola, the parabolic exponent is 2.5. This is a very useful form.

A parabolic exponent of unity would represent a straight line parallel to the abscissa at T=325° C. This is a gradientless curve 2. Intermediate to this extreme and unreal form and the parabola is the mean hypoparabola 3 of parabolic exponent 1.5.

There are all gradations betwen the extreme unreal forms. The gradations between 6 and 4 are generically herein termed hyperparabolic.

The full range of curve 6 is shown as 240° C.; of curve 5, 180° C.; of curve 4, 120° C.; of curve 3, 60° C. Dividing the full range of each by 120° C. gives 2, 1.5, 1, 0.5 respectively. This is the same as the parabolic exponent less one, which is a measure of curvature complexity, and in my belief a measure of the fresh catalyst activity or sensitivity. The practical ranges are generally less than the full ranges. Temperatures somewhat above 325° C. may be used when hydrofining motor fuel or such distillates. 250° C. to the temperature at which substantial pyrolysis occurs, represents a practical upper limit. When the catalysis is at the abscissa, the catalyst activity is unity, irrespective of the state of the catalyst, whether fresh as at the beginning of curve 4 or half spent as at the mid point of curve 6. The abscissa may vary substantially from 205° C. Initial desulphurizing apparently occurs by means of adsorption of the sulphur compound to the catalytic suface. At temperatures higher than the abscissa temperature, this adsorption is followed by partial desorption and chemical reaction to form a sulphide of the catalytic metal.

The theoretical speculations herein are mainly for the purpose of guiding actual or prospective practitioners of the invention, particularly in the fine points thereof. The invention is practical and useful regardless of the absolute truth or fallacy of the speculations, and is not to be unduly limited by the theory or examples.

It appears however that the general complexity and range of the time gradient is a measure of and is determined by the activity or sensitivity of the fresh catalyst to an approximation at least.

These Fig. 1 curves are useful in determining the cooling in the countercurrent form of my invention. For the same fresh catalyst activity, the complexity of the countercurrent curvature is generally simpler, that is the graph is straighter. Both the practical and full ranges appear to be correspondingly less. The countercurrent form of my invention tends to maintain the activity of the catalysis relatively constant throughout the contact. I may regulate the cooling to compensate the net increase of the catalyst activity from which the reactant activity has ben subtracted. In the stationary form reactant activity is not subtracted.

The practical limits of catalyst activity in the fresh state for my invention appears to be greater than about 0.5 but less than about 1.8. An activity of 2.0 appears to be a limiting and ideal and unreal form. My copending applications Serial Numbers 86,741 and 117,515 are particularly useful in preparing catalytic surfaces for my invention. Nickel peroxide catalyst as prepared therein appears to have an activity of near 1.7, cobalt peroxide an activity somewhat above 1.5. My copending application Serial Number 86,741 also discloses the preparation of copper, silver, lead with respectively decreasing activities ranging from near 1.5 for copper down to near unity for lead. All these oxides are hydrated. I may use them all. My Serial Number 86,741 discloses the preparation and reactivation of black catalytic surfaces, which are hydrated readily reducible oxides or peroxides. The preferred step is anodic peroxidation in a low activity coefficient electrolyte in whose anolyte hydroxyl is the predominant ion. These catalysts and their metals and the anodic peroxidation are extraordinarily well adapted to sulphur sensitive motor fuel hydrofining. The precipitated sulphides of these metals are black. Hydrated ferric oxide has a higher activity than magnetite.

The moderately reducible oxides such as magnetite and ferric hydrate as a group have activities below unity. These oxides are not reduced to the metallic state during my hydrofining. The sulphides formed are generally oxysulphides. I

may use the more active members of this group.

An alumina comprising catalyst is useful in roasted catalysts.

I prefer that the catalyst base and surface be foraminous and deep in order that the catalyst concentration be relatively large. By catalyst, I particularly refer to the truly catalytic surface portions. The depth of the surface is probably as important a factor as the superficial area of surface. Roasting to convert a sulphided metal catalyst to the oxide little affects the area, but generally diminishes the depth and hence the catalyst concentration. The prior art of regenerating sulphided surfaces ordinarily consists of no other chemical treatment than roasting.

I prefer to carry the reactivation far beyond ordinary roasting, for instance to further oxidize at lower temperatures, thereby producing a darker and deeper surface layer. Such a treatment I have described in my copending applications, e. g., in Serial Number 117,515, the oxidizing reagent is aqueous. Or I may expose the roasted surfaces to the vapors of nitric acid at a liquid phase temperature of the acid, below about the boiling point of the acid. When sufficient acid has been used to give the surface the characteristic color of the nitrate, I may gently roast at a lower temperature than that of the sulphide roasting step to decompose most of the nitrate of the catalytic metal. This surface is deeper than the sulphide roasted surface and generally darker. The decomposed nitrate vapors may be recovered and reconverted to nitric acid, and used again. Other oxidizing or oxidizable reagents may be used, particularly aqueous reagents.

In general I may use in my catalytic surfaces those elements or metals whose precipitated sulphides are black, particularly if they also readily form black oxide surfaces. This includes the noble metals, but their scarcity generally prevents their use.

The catalytic surface generally used comprises nickel or copper, which may be prepared in the many ways known to the art. The catalytic surface may also comprise one or more accessory metallic elements, such as cobalt, chromium, molybdenum. Of lesser total hydrofining capacity, but more inclined to desulphurization as compared to hydrogenation is activated copper. Copper is able to open oxygen heterocycles, especially in the vapor phase. Nickel, the most active, is adjacent in atomic number to the next two most active, namely copper and cobalt, and I prefer these three hydrogenating metals which together with their readily reducible oxygen compounds are essential to practical hydrofining accompanied by substantial hydrogenating. Iron, particularly when promoted with nickel, may be used.

The reduction temperatures of the metallic oxides with hydrogen constitute an index to their activity and effective hydrofining range. When a plurality of catalytic components are mixed together, the reduction temperatures are generally lower than the arithmetic average, although under such circumstances the less active metal may not become fully reduced, which may often be advantageous.

In the vapor phase with an excess of hydrogen, unreduced catalyst may be in a process of reduction while hydrofining.

Deactivation tends to be selective on the most active centers, although my gradient operation apparently minimizes the effect. If oxides or readily reducible oxygen compounds such as the carbonate or formate are present during the deactivation, their gradual reduction constitutes a reserve source of such centers. The oxides themselves possess desulphurizing power, and the black hydrated oxides appear to possess hydrogenating power.

Advantage is taken of the partial sulphiding and other deactivation of nickel and like catalyst to inhibit the complete hydrogenation of compounds such as diolefines and aromatic compounds with olefinic side chains, and to minimize hydrogen addition to non-cyclic mono olefines in the case of motor fuels and solvents. The copper and cobalt catalysts, particularly the copper, promote this type of hydrogenation without being deactivated. Apparently this is true of low pressure hydrogenations where the catalyst activity is below 1.5.

The catalytic surface is preferably a readily reducible oxygen compound of a catalytic and/or hydrogenating metal. When the carbonaceous vapor contains sulphur, this oxygen compound of the catalytic metal is preferably converted to a sulphide. The oxygen compound may be reduced to the metal or a lower oxide concurrently with the hydrogenation and desulphurizing, particularly when the hydrogenation is substantial. The hydrogenation and the reduction, generally highly exothermic, appear to assist the desulphurizing.

The following is a sample reaction when using catalytic surfaces comprising nickel on cracked motor fuel distillate as described in the countercurrent example. The surfaces function here both as a catalyst and reagent:

$$Ni_3O_4.4H_2O+3RS+nR+(7+n)H_2\rightarrow 3NiS+(3+n)RH_2+8H_2O$$

where R is mono or diolefinic and where n is an integer which may be varied and depending upon several factors such as the refractory nature of the distillate and the pressure of the treatment, and the catalyst activity. 3 is an example of a value for n. With similar vapors and pressures, diminished values of catalyst activity, fresh or partially deactivated, result in rapid decreases in the value of n.

Thus when operating the stationary form of my invention at constant pressure, the value of n, at first relatively high, progressively falls, and when the catalytic surfaces are nearly spent the value may even be negative, indicating dehydrogenation. Thus, in hydrofining the vapors of motor fuel distillate, the hydrogenation decreases much more rapidly than the desulphurization as the catalyst becomes spent when using constant pressure. By substantially increasing the pressures as shown in the stationary example, particularly when also decreasing the hydrogen excess, the ratio of hydrogenation to desulphurization is substantially maintained.

I prefer to hydrofine at pressures below about 100 atmospheres and on motor fuel distillates between about 1 and 20 atmospheres. On higher boiling distillates, the upper preferred limit is lower still than 20 atmospheres because hydrogen is useful up to a certain excess, beyond which it is detrimental. More than 10 or 20 volumes of hydrogen excessively dilute, and as a result retard the hydrofining. For motor fuel hydrofining I prefer an excess below the reaction optimum, particularly in the hotter stages so as

to minimize the heat requirements in excess of those for the cooler stages.

The amount of hydrogen needed for the hydrofining varies; in general an excess is used, and in practice the lower the temperature, the greater this excess.

The following proportion is an example of the excess of hydrogen and differential variations or gradients thereof, which may be used with motor fuel distillates:

$$\frac{\text{Minimum desirable volume } H_2}{\text{Volume hydrocarbon vapors}} = \frac{G^{1/4}}{0.01T - y}$$

where G is the Cu dish gum of the unhydrofined distillate in mg. per 100 ml., and where T is the absolute Kelvin temperature, and where y is the fresh catalyst activity.

Indeed my invention may be operated without any added hydrogen or hydrogen excess during the hotter or warmer stage contacts when the catalyst is highly deactivated, particularly when relatively large quantities of labile sulphur compounds and relatively small quantities of diolefines and olefines are present. However it is preferable to have hydrogen present, the atom of removed sulphur is best replaced by a molecule of hydrogen.

Hydrogen may be generated during hydrofining and render it unnecessary to add other hydrogen. Relatively crude or impure hydrogens may be used in the practice of my invention, since the hydrogen is in a process of refinement concurrent with that of carbonaceous vapors. In sulphur sensitive catalysis, the excess hydrogen undergoes continual purification. In sulphur immune catalysis, the hydrogen undergoes continual contamination. Crude hydrogen may be purified independently by my invention, particularly with temperature gradients.

Stationary example

In Fig. 2 is diagrammatically shown a vertical stationary catalyst form of the invention.

Refractionated liquid motor fuel distillate is pumped by pump 11 through a pipe coil in a variable heat furnace 13, into a vaporizing tower 15. Here the distillate is vaporized and meets a regulated excess of hydrogen 17, preferably preheated. The regulation takes place at the valve device 19. Heavy ends may be withdrawn from the vaporizing tower at 21 or 23. The vapor-hydrogen mixture leaves 15 at outlet 25 and passes into the top of the hydrofining chamber 10 at the inlet 27. The chamber 10 contains the catalyst. The chamber is supplied with open steam inlet 29 and steam outlet 31. The hydrofined vapors plus any possible condensate then pass through exchanger 18, through condenser 20 into the receiver-separator 33. The bulk of the water of reduction is withdrawn at outlet 24. The residual moisture is separated from the hydrofined liquid in dehydrator 36. Gum inhibiting antioxidants in solution may be pumped by proportionator 40 into the pump 38, where they are mixed with hydrofined motor fuel and pumped to storage 41. Meanwhile the excess hydrogen separated in 29 is returned to the tower 15 via recirculator 42 through exchanger 18 in heat exchange with vapor-hydrogen mixture.

As an example of how the stationary catalyst form of my invention may be practiced, the hydrofining chamber 10 is filled with stationary unreduced nickel catalyst prepared as described in my copending application Serial Number 86,741. Steam is passed in at 29 while outlet 31 is partially open. When the temperature of the chamber has reached 120° C. 29 and 31 are shut off. Meanwhile a cross-cracked California motor fuel distillate may be pumped at a substantially constant rate through 13 into the vaporizing tower 15. The vapor along with 3 volumes of hydrogen at a temperature of 110° C. may be passed into the hydrofining chamber 10 at 27.

The temperature of the vapor-hydrogen mixture may be steadily increased by increasing the heat in furnace 13 and in accordance with a schedule as indicated in Fig. 1, intermediate to curves 5 and 6, corresponding to a parabolic exponent of about 2.7 and a catalyst activity of 1.7 in the fresh state. The unit time is about 30 hours corresponding to a total time of about 48 or 50 hours. The pressures may also be increased and the relative hydrogen volume and excess decreased according to the following schedule. The changes may be stepwise or continuous:

Hours	Temperature	Hydrogen	Pressure
	°C.	*Volume*	*Atmospheres*
0	115	3	1
8	181	2.5	1.5
16	203	2	2
24	210	1.8	3
32	228	1.6	4
40	265	1.3	6
48		1	10

After this, the operation may be shut down and hydrogen alone passed for a while, then the catalyst may be steamed via inlet 29 and outlet 31, and hydrocarbons recovered from the steam by condensation.

Results of the hydrofining on the different samples:

	Before hydrofining	After hydrofining
Sulphur percent (average)	0.76	0.13.
Color	Orange	Water white.
Doctor test	Positive	Negative.
Silicotungstic acid test	Positive	Negative.

The same operation was run without changes in the hydrogen excess or pressure, but as previously noted the adsorption and product lacked uniformity. In a run in a similar apparatus but without pressure increases, the octane number on the average product both before and after hydrofining was tested at 62 in spite of considerable hydrogenation. The average sulphur after the hydrofining was 0.18%, but the adsorption and various samples were not uniform. The same operation on a highly cracked Venezuela motor fuel distillate of 0.40% sulphur was hydrofined to 0.11% overage sulphur content. Increases of pressure would result in an average sulphur content of below 0.09%. All samples in all these runs were doctor sweet, all water white up to about 240° C. at 1 atmosphere.

All samples represent a steady state, obtained without restriction on the output per weight of catalyst.

The hydrogen consumption in the 1 atmosphere runs was approximated at less than 2 or 3 cubic feet per gallon.

Inspection of the cross-cracked California distillate before hydrofining:

Gravity, °A. P. I.	51
Gum Cu dish	500
Sulphur, per cent	0.76
A. S. T. M. distillation °F.:	
I. B. P.	136
50% off	289
90% off	408
E. P.	449

Sulphur distribution:

Fraction	Percent sulphur
0-10	
10-20	0.050
20-30	0.425
30-40	0.575
40-50	0.650
50-60	0.695
60-70	0.730
70-80	0.750
80-90	0.725
90-100	0.510

Countercurrent example

In Fig. 3 is diagrammatically shown a vertical countercurrent form of my invention in detail. This may be operated strictly continuously, and at atmospheric pressure, to produce a uniform stable product highly responsive to antiknock and antioxidant reagents.

Refractionated motor fuel vapor mixed with hydrogen is fed into the vertical countercurrent hydrofining chamber 10 at the inlet 12. The vapor mixture may enter as shown at 280° C. and as it passes upward may be cooled by passing cold or somewhat preheated hydrogen into the mixture through graduated openings in the concentric pipe 14 running the length of chamber 10. The hydrofined vapor mixture may leave the chamber 10 at the outlet 16 near the top, any may then pass in heat exchange with the recirculating hydrogen through the exchanger 18, thence through the condenser 20 into the separator 22. Any water may be drawn off at the outet 24. The liquid hydrofined motor fuel is stripped of its dissolved hydrogen in the hydrogen stripping tower 26 with steam inlet 28, and outlet 30. Inlet 28 may be shut or throttled and a vacuum applied at outlet 30. The stripped liquid passes thence into receiver 32. Further water may be drawn off at outlet 24. The hydrofined liquid passes thence through the hydrofined liquid outlet 34 through the dehydrator 36 into the pump 38 where it may be mixed with a gum inhibiting antioxidant in solution from the inhibitor proportionator 40. The inhibited hydrofined liquid may then pass to finished storage 41.

Meanwhile the excess hydrogen separated in separator 22 is pumped by the hydrogen recirculator 42 through exchanger 18 into the pipe 14 and/or into the reboiler section 44 of the motor fuel fractionator 46 at inlet 48. New hydrogen from the hydrogen producer not shown is also passed into the reboiler section 44 at inlet 50. The hydrogen-refractionated vapor mixture passes from the reboiler section 44 through outlet 52 and on into the hydrofining chamber 10. Meanwhile the hot spent catalytic surfaces pass at constant intervals into the lock 60 and thence via the catalyst conveyor 62 into the countercurrent steaming chamber 64 where the hot catalyst passing downward meets upflowing steam, entering chamber 64 at opening 63. The steam-motor fuel vapor mixture passes out at orifice 61, is condensed and separated and the upper layer passed back into the reboiler section 44. The catalytic surfaces pass thence into the roasting chamber 66 via lock 60. The sulphided surfaces pass downward and meet an upflowing current of hot air from inlet 67. The air-sulphur dioxide mixture passes out at orifice 65.

The sulphur dioxide may be recovered, for instance as liquid sulphur dioxide or made into sulphuric acid. The sulphided catalytic surfaces are substantially converted into an oxide in 66, and pass out at the bottom of 66 into the lock 60 to conveyor 62 and on into chambers 68 and 70, where the oxide surfaces are countercurrently further oxidized to deeper and preferably black surfaces. The reactivated catalytic surfaces pass out of the chamber 70 through the bottom lock 60 into conveyor 62 and into the top lock 60 of the hydrofining chamber 10, to complete the cycle. Where substantial sulphur is removed from the distillate, the cycle or "turnover" of the catalytic surfaces may require 1 to 3 days. Usually cracked distillate passes from furnace coils to a soaking drum to the primary fractionator. The motor fuel distillate therefrom usually contains excessive quantities of propane, butane, isobutane and butylene and isobutylene. These are separated as overhead through 47 in the refractionator 46. The "debutanized" distillate may then be reboiled, mixed with hydrogen in 44, and passed out via 52 and 12 into the hydrofining chamber 10 just above the lock 60. I prefer to "debutanize" or "stabilize" in the refractionator somewhat more deeply than usual since desulphurizing and/or hydrogenating lowers the boiling point of these compounds. Each of the locks 60 are alternately opened and closed by a mechanical device not shown, allowing the catalytic surfaces to alternately fill and discharge. The locks of chamber 10 may also be provided with means for intermittently charging with hydrogen or inert gas. Two or more pipes may be substituted for pipe 14 to allow the introduction of cooling hydrogen at two or more temperatures. The chamber 10 contains devices 39 for distributing the catalyst and alleviating the head pressure thereof.

Twelve stages of different temperatures as shown divide the hydrofining chamber 10. One to four more such stages may be inserted at the bottom to extend the temperatures up to 350° C. or up to the temperature at which substantial pyrolysis occurs, particularly if the additional heat is available. Or one or two stages might be eliminated if insufficient heat is at hand. The temperatures shown are merely exemplary of the more active and hydrogenating catalytic surfaces such as those which comprise an element selected from the group which consists of copper, nickel and cobalt, or from the group which consists of nickel and copper.

The countercurrent form of my invention may be practiced for example using the same distillate as in the stationary form.

The catalytic surfaces may be prepared by immersing small lumps of an abrasive and refractory form of alumina in molten nickel nitrate hexahydrate, draining, drying, and gently roasting the impregnated lumps to decompose most of the nitrate. The hydrofining chamber 10 may be filled with this material and warmed with open steam or hydrogen. The California cracked distillate in substantially constant feed may then

be mixed with 3 volumes of hydrogen in the reboiler section 44, and the vapor mixture fed into 10 at inlet 12 at a temperature of about 130° C. The mixture is cooled to about 110° C. with hydrogen before it emerges from 10 at outlet 16. The temperatures in 10 are gradually raised to the schedule shown to the right of the chamber 10 in Fig. 3. The period should require at least a day and preferably three days. During that day or so, fresh catalyst is fed in through the top lock 60 of chamber 10 at an average of about one-half the usual rate once the operation is established. The catalyst feed should start from about nothing and progressively increase to the full feed as the temperatures reach the 280° C.-cooled-to-150° C. schedule as shown. Concurrent with these increases of temperature and catalyst feed during that day or so, the volume of hydrogen fed into 44 is gradually decreased to about one-half volumes or less, when it may remain constant.

After the first two days or so the operation is uniform and as strictly continuous as desired barring mechanical disturbance. A relatively large volume of cooling hydrogen is added in the cooler stages relative to that added in the intermediate stages. Once established, the total cycle including reactivation may be completed in about two days. The time for fresh catalyst at the top of chamber 10 to reach the bottom lock 60 of the chamber is several hours less. The time varies principally with the amount of sulphur removed. Where $S_r\%$ is the percentage of sulphur removed by weight of the distillate, the maximum total cycle including reactivation appears to be between $1S_r\%^{-1/3}$ and $2S_r\%^{-1/3}$ days for either the countercurrent or stationary form of the invention. The resulting countercurrent hydrofined product at one atmosphere may also equal the extent of the hydrofining by the stationary form under ascending gradients of temperature and pressure and a descending gradient of hydrogen excess. When using the same distillate, the same catalytic components and the same means of activation, the two forms compared over extended practice may be expected to yield nearly the same product.

Reactivation of the spent catalytic surfaces from the bottom lock 60 of chamber 10 may be steamed and roasted as in the description of Fig. 3. The further oxidizing may be carried out by the nitric acid vapor treatment and gentle roasting previously described. Or the surfaces may be further oxidized by other means, particularly one of those previously described.

The countercurrent form of my invention may be practiced in a horizontal or slightly inclined hydrofining chamber. Such a chamber with a helical screw within may rotate like a kiln, and use the same type of catalyst described for the Fig. 3 form.

Or a horizontal or vertical chamber may be operated with screen catalyst such as described in form and activation in my copending application Serial Number 86,741.

Where the vapors are accompanied by liquid, the flow of reactants is preferably downward, and the flow of catalytic surface upward.

In the stationary form, it is relatively simple to control the temperature and hydrogen excess in each stage so that relatively equal amounts of hydrofining occur in each stage. The operation is constantly focused on producing a uniform product whatever the condition of the catalyst. In the countercurrent form however the warmest stages are devoted almost entirely to desulphurizing, while hydrogenating is usually the predominant hydrofining reaction in the coldest stages. The ratio of hydrogenation to desulphurization increases with the cooling and hence the comparative total hydrofining in each stage cannot be directly compared with that in the other stages. The comparison may be made indirectly by comparing with similar stationary results. For example samples may be withdrawn at each of the twelve stages in Fig. 3, and comparing them with the twelve successive samples (one every 4 hours say) from a full stationary run at the same pressure, but using the optimum temperatures and hydrogen excesses determined from a previous run at optimum differentially varied temperatures, hydrogen excesses, and pressures.

Ordinary surface transfer cooling may be used instead of, or in conjunction with, hydrogen cooling in my invention.

I may maintain a space gradient as well as a time gradient in the stationary and countercurrent forms of the invention. For instance an ascending space gradient in the stationary form is maintained by conserving the heat of reaction or applying fluid heat countercurrent to the vapor flow, or by progressively mixing relatively warm hydrogen with the vapors.

My invention may be applied to hydrogenations of simpler olefines or aromatics, as for instance using the stationary form with relatively narrow time gradients and a relatively wide space thermal gradient. This unusual space gradient is due to the exothermal heat which may be controlled with narrow reaction chambers, e. g., 4 cm. (1½ inches) diameter cylinders surrounded by a heat exchange fluid. Hydrogen cooling may also be used for this control. The rate of change in the time gradients as well as the ranges thereof are small relative to the desulphurizing type of hydrofining. The reaction is preferably spread over several chambers in series, whereas one single chamber is usually sufficient in the desulphurizing type of hydrofining. The catalyst activity is preferably in excess of about 1.5. The hydrogen excess is regulated preferably so that the vapor mixture is near saturation during hydrofining. Likewise my method may be applied to the conversion of water gas to motor fuel distillate, particularly with the promoted catalysts described in my copending application Serial Number 117,515, and with small diameter reaction tubes. My invention may be likewise applied to the conversion of isooctene, isononene, isodecene, to isooctane, isononane, isodecane respectively.

Straight run or cracked petroleum distillate may be separated into fractions high in sulphur, and fractions high in gum but low in sulphur. These may be separately hydrofined and reblended wholly or partially.

Besides natural and synthetic petroleum distillates, the light distillates or gases from other sources, such as those resulting from the pyrolysis of shale oil, primary tars and Bergenized oils from coal are refined and even converted to new products by my hydrofining. Such distillates are apt to contain considerable quantities of organic bases and acids, which are best washed out with acid and alkali solutions respectively, before being subjected to my hydrofining. These distillates after the washes above may still contain heterocyclic compounds of oxygen in addition to those of sulphur. Copper hydrofining especially in the vapor phase will convert the oxygen hetero-

cycles to tar acids, and these may then be extracted by alkali and recovered. Other carbonaceous vapors, particularly those containing oxygen, may be subjected to my hydrofining method.

What I claim is:

1. A method of continuously hydrofining carbonaceous vapors, which comprises continuously contacting the vapor and an excess of hydrogen in a series of time stages with a solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black, at a plurality of temperatures above about 75° C. but below the temperature at which substantial pyrolysis occurs with said vapor, and adjusting the temperature and hydrogen excess of each of the time stages so that relatively equal amounts of hydrofining occur in each of said stages, said plurality of temperatures consisting substantially of an ascending time gradient of temperature, the rise of temperature occurring as the catalytic surface becomes progressively spent, the difference between the extremes of said gradient being between about 20° C. and 200° C., while maintaining the pressure of each stage between about 1 and 100 atmospheres.

2. A method as described in claim 1, then further hydrofining the carbonaceous compound or compounds in additional but fewer stages, and with decreasingly less amounts of hydrofining in said additional stages.

3. A method of continuously hydrofining carbonaceous vapors, which comprises contacting the vapor of motor fuel distillate and an excess of hydrogen in a series of similar stages with a solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black, the temperature in each stage being above about 75° C., but below the temperature at which substantial pyrolysis occurs with said vapor, and adjusting the temperature and hydrogen excess of each of the series of similar stages so that relatively equal amounts of hydrofining occur in each of said stages, while maintaining the pressure of each stage between about 1 and 20 atmospheres, and a time of contact at least until the distillate is doctor sweet but insufficient to completely hydrofine, and after condensing the hydrofined distillate adding a small portion of a gum inhibiting antioxidant sufficient to inhibit formation of gum.

4. A method of continuously hydrofining carbonaceous vapors, which comprises mixing the vapor of cracked and refractionated motor fuel distillate from petroleum together with an excess of hydrogen and in a series of similar stages contacting the mixture with a readily reactivatable solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black, at a plurality of temperatures above about 75° C. but below the temperature at which substantial pyrolysis occurs with said distillate, and adjusting the temperature and hydrogen excess of each of said similar stages so that relatively equal amounts of hydrofining occur in each of said stages, said plurality of temperatures consisting substantially of an ascending time gradient of temperature, the difference between the extremes of said gradient being between about 20° C. and 200° C., while maintaining the pressure of each stage between about 1 and 20 atmospheres and a time of contact at least until the distillate is doctor sweet, then condensing the hydrocarbons and separating the excess hydrogen to produce without further chemical treatment or separations a refined motor fuel which is highly responsive to any subsequent addition of antioxidant or antiknock reagents.

5. A method of continuously hydrofining carbonaceous vapors, which comprises contacting the vapor of a motor fuel or like distillate and an excess of hydrogen in a series of similar stages with a solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black, at a plurality of temperatures above about 75° C. but below the temperature at which substantial pyrolysis occurs with said distillate, and adjusting the temperature and hydrogen excess of each of the similar stages so that relatively equal amounts of hydrofining occur in each of said stages, said plurality of temperatures consisting substantially of an ascending time gradient of temperature, the rise of temperature occurring as the catalytic surface becomes progressively spent, said rise being less than 200° C. in extent, while maintaining the pressure of each stage between about 1 and 20 atmospheres and a time of contact at least until the distillate is doctor sweet, then reactivating the deactivated or sulphided catalytic surface by a process comprising steaming to remove any residual carbonaceous material, then roasting to convert the sulphide substantially to an oxide, and afterwards further oxidizing said oxide surface at lower temperatures to form a black and deeper surface, and then recycling said reactivated catalytic surface to the initial and lowest temperature hydrofining stage.

6. A method of continuously hydrofining carbonaceous vapors, which comprises contacting the vapor of a motor fuel or like distillate and an excess of hydrogen in a series of similar stages with a solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black at a plurality of temperatures above about 75° C. but below the temperature at which substantial pyrolysis occurs with said distillate, and adjusting the temperature and hydrogen excess of each of the similar stages so that relatively equal amounts of hydrofining occur in each of said stages, said plurality of temperatures consisting substantially of an ascending time gradient of temperature, the rise of temperature occurring as the catalytic surface becomes progressively spent, said rise being less than 200° C. in extent, while maintaining the pressure of each stage between about 1 and 20 atmospheres, and a time of contact at least until the distillate is doctor sweet but insufficient to completely hydrofine, then reactivating the catalytic surface by a process which comprises roasting to substantially convert the metal sulphide to oxide, and afterwards treating the roasted catalyst with nitric acid vapors, followed by gentle roasting at a temperature lower than that of the sulphide roasting step to decompose most of the nitrate of the catalytic metal, and then recycling said reactivated catalytic surface to the initial and lowest temperature hydrofining stage.

7. A method of continuously hydrofining carbonaceous vapors, which comprises contacting the vapors of motor fuel or like distillate and an excess of hydrogen in a series of stages with a solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black, the hydrogen excess being high and the temperatures being relatively low but above about 75° C. in the stages when the catalytic surface is in a freshly activated condition, and pro-

gressively decreasing the hydrogen excess and increasing the temperature to an upper limit between about 250° C. and the temperature at which substantial pyrolysis occurs with said vapors as the catalyst activity decreases during hydrofining, the total rise in temperature being between about 100° C. and 200° C., and maintaining a pressure in each stage between about 1 and 20 atmospheres and a time of contact at least until the distillate is doctor sweet but insufficient to completely hydrofine, said freshly activated catalytic surface comprising a readily reducible oxygen compound of a sulphur sensitive hydrogenating metal, said catalytic surface being converted to the sulphide of said hydrogenating metal during hydrofining.

8. A method as described in claim 7 in which the temperatures are raised less rapidly in the intermediate than in the extreme stages.

9. A method of continuously hydrofining the vapor of motor fuel or like distillate, which comprises the countercurrent contact of the vapor of distillate with solid sulphur sensitive catalytic surfaces comprising nickel, at a plurality of temperatures above about 75° C. but below the temperatures at which substantial pyrolysis occurs with said vapor, and progressively adding hydrogen in amounts over and above the chemical requirement to cool the vapor or vapor mixture as it contacts progressively fresher catalyst, the total cooling being between 100° and 200° C., while maintaining a substantially constant pressure between about 1 and 20 atmospheres throughout the contact, and a time of contact at least until the distillate is doctor sweet.

10. A method as described in claim 9 in which the flow of catalyst is downward, the flow of vapors upward, and in which the catalytic surfaces in the cooler and fresher catalyst stages comprise an oxgen compound of nickel in the process of partial reduction concurrent with the hydrofining.

11. A method of continuously hydrofining carbonaceous vapors, which comprises contacting the vapors and an excess of hydrogen in a series of similar stages with a solid sulphur sensitive catalytic surface containing a catalytic metal whose precipitated sulphide is black, and decreasing the hydrogen excess and increasing the temperature in the time stages of said series as the catalytic surface becomes progressively spent during hydrofining, said temperature increase not to exceed 200° C., the temperatures in each stage being above about 75° C. but below the temperature at which substantial pyrolysis occurs with said vapors, while maintaining the pressure of each stage between about 1 and 100 atmospheres.

MARION H. GWYNN.