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METHOD OF REFINING HYDROCARBON DISTILLATES

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Fig. 1.

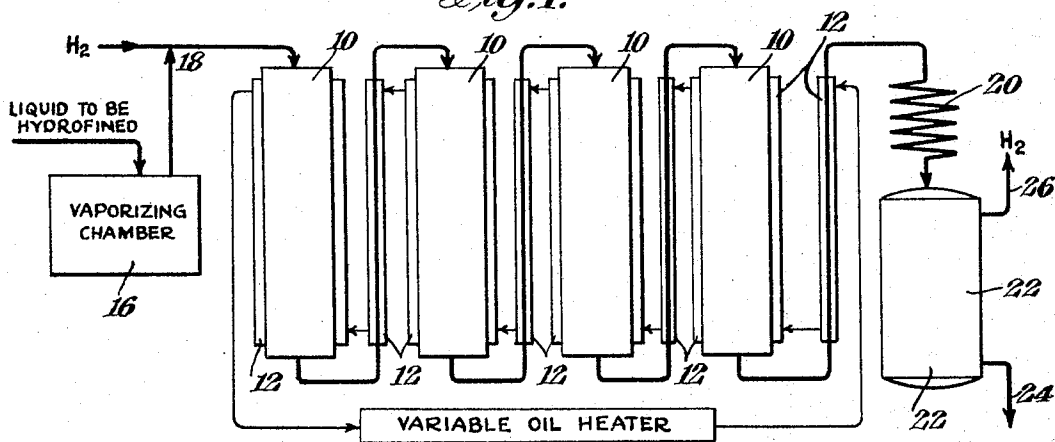


Fig. 2.

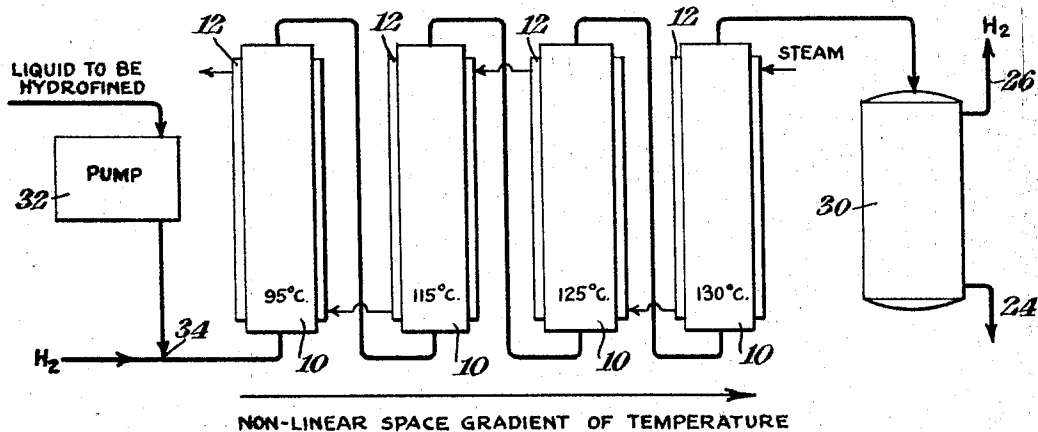
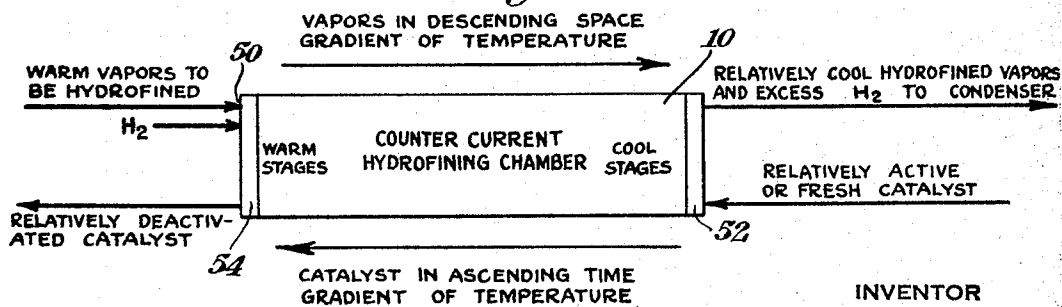


Fig. 3.



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UNITED STATES PATENT OFFICE

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METHOD OF REFINING HYDROCARBON
DISTILLATES

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15 Claims. (Cl. 196—24)

This invention relates to the refining of hydrocarbon distillates, particularly to light petroleum distillates and those free or freed of asphaltic materials; by means of an essentially new method of hydrofining, which may be used alone or in conjunction with the old methods of refining.

The essential feature of this hydrofining is the use of metallic catalysts, such as nickel, together with low pressures and comparatively low temperatures, whereby 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, since it is able to effect the removal of the same types of sulphur compounds, in addition to the hydrogenation of the unsaturates, particularly the diolefines and cyclic compounds with an olefine side chain.

Also contributing to the effectiveness of the invention are a number of other factors; such as the general use of the stationary type of catalyst, making practical the use of the vapor phase as well as enabling practical segregation of the catalyst into several portions, which allows those portions first contacting with the distillate to bear the brunt of "poisoning" actions. The proper selection of catalysts, phase of operation, temperatures, including series of temperatures within the same operation; the division of the hydrofining into two different operations; the separate treatment of fractions within a distillate; the selection of effective non-hydrofining treatments to be used in connection with the hydrofining, although in general these are not necessary; and the use of partially as well as completely reduced catalysts, all are useful in the practice of the invention.

It has been proposed to desulphurize certain petroleum distillates with reducible metals and their oxides in the absence of hydrogen. With one exception where it is used in conjunction with hydrogenation, all the catalytic treatments in this invention are hydrofining, which explicitly or implicitly means hydrogenating and/or desulphurizing in the presence of hydrogen. The effectiveness of the metals and oxides is thereby increased; their usefulness extended beyond straight run distillates, and the method of sulphur removal is changed. Polymerization of the olefinic compounds and consequent blocking of the catalyst is inhibited.

Where the substantial removal of labile, reactive or sour sulphur is desired, partially or completely reduced metals have secondary usefulness,

especially in the "skunk" type of straight run distillates, provided that the effectiveness of such catalysts may be extended greatly by increasing the surface, together with some simple method for operation in the vapor phase. A metal base catalyst with a large surface activation such as obtained with anodic oxidation well answers such a purpose.

It has been proposed to hydrogenate hydrocarbon distillates with completely reduced nickel catalysts in the liquid phase in a single reaction chamber and at temperatures substantially constant. Such a procedure is greatly improved by the use of stationary catalysts and/or a series of temperatures, the vapor phase, and several reaction chambers.

The use of non-reducing hydrogenating catalysts has been proposed, especially the molybdc type. The temperatures of the molybdc catalysis are characteristically in the range of hydrocarbon pyrolysis leading to extensive changes in the character of the product, other than those of simple hydrogenation. Hydrofining with non-reducing catalysts are characteristically liquid phase pyrolytic processes requiring high pressures. On the other hand metallic hydrofining is characteristically non-pyrolytic and is preferably in the vapor phase and at pressures not greatly in excess of atmospheric, under these non-pyrolytic conditions the ring of heterocyclic compounds including thiophene may be opened, and low grade light distillates with much heavy ends and color and doctor sour sulphur are stabilized and sweetened. This metallic hydrofining is more truly a refining process than the high pressure-temperature operations. Kerosene and transformer oils are economically and highly stabilized by metallic hydrofining.

It has been generally thought that the distinct sulphur content of most hydrocarbon distillates constituted an effective barrier against the use of high activity catalysts, such as the metals. The high activity of metallic catalysts and their so termed sulphur susceptibility is a characteristic feature of this invention. This action is much more positive than with the molybdc catalysts, which depend to a large extent on the high temperatures necessary to their action to initially crack the sulphur compounds to hydrogen sulphide before their saturating action is exerted. Their lack of poisoning by sulphur compounds is due primarily to their inability to strongly adsorb them. Moreover, at these high temperatures hydrogen sulphide tends to re-

combine with unsaturated hydrocarbons to form highly resistant forms of thio-compounds.

The "poisoning" or deactivation of the metallic catalysts in past experiments has generally been ascribed to sulphur compounds. Not only do such compounds vary greatly in their inhibitory action, but asphaltic substances, peroxides and other products of oxidation in small quantities are more disturbing to this type of catalyst than sulphur compounds. For practical hydrofining with readily reducible catalysts, especially in the liquid phase, it is necessary to limit the distillates to those which are practically 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. The unsaturates themselves or the reaction prematurely deactivate a metallic catalyst susceptible to sulphur poisoning unless contacted as later described, particularly with gradual raising of the temperature in such a manner as to maintain uniform hydrofining.

Sulphuric acid has long been the principal mode of refining hydrocarbon distillates. It is remarkable that metallic or low pressure hydrofining so parallels and yet is so opposite in its effects. The sludge loss of acid treatment is offset by the gain of valuable new constituents. The distillation range and specific gravity is lowered, not raised, although this is not necessarily true of a product distilled after acid treatment. Instead of containing unstable acid esters, the hydrofined product has been selectively rid of its most unstable constituents. With the advent of cracking, especially in the vapor phase, refining difficulties of such pyrolyzed distillates have been greatly accentuated, yet the more heavily cracked, the greater the advantage to metallic hydrofining. The compounds so highly reactive with acid have valuable solvent and anti-knock properties, which are substantially preserved by selective hydrogenation. Most of these compounds are part of the lighter fractions, at present the most desirable portions in gasoline manufacture.

In practical methods of application, metallic hydrofining is complementary to acid treatment; the former is simplest applied to distillates high in unsaturates and low in organic sulphur, the latter is well applied to those low in unsaturates and high in organic sulphur. In other ways these two processes are highly complementary, for instance an incompletely metallic hydrofined distillate is well adapted for an acid treatment, since the rate of the final portion of a complete metallic hydrofining may be slow compared to the beginning, and since the hydrocarbons of greatest unsaturation are first hydrogenated when the metallic hydrofining is properly conducted.

If for reasons of economy, minor quantities of gum forming unsaturates remain after metallic hydrofining, these may be polymerized by acid, earth contact or other treatments, which may or may not remove the polymers. Generally the content of unsaturates and sulphur in the metallic hydrofined product as in many uncracked light distillates warrants nothing more than a treatment with fuller's earth, activated clay, silica gel or other micro-porous siliceous preparation. If the hydrofining is in the vapor

phase, the siliceous contact is preferably also in the vapor phase; and the same applies to liquid phase refining. The contact with liquid caustics and the addition of antioxidants are also useful after-treatments to metallic hydrofining.

By acid treatment is not only meant fuming and anhydrous sulphuric acid, but sulphuric acid mono- and dihydrate, and acids even somewhat more dilute; also sulphuric acid weakened or "spaced" with various phosphoric acids, glacial acetic acid or ammonia. Phosphoric acid, the liquid and acidic chlorides, instill reagent and earth impregnated with sulphuric acid are also to be considered as acid treatments.

The sulphuric acid treatment is often preceded by one or more accessory operations. Almost the same ones are most effective as pre-metallic hydrofining treatments. Sodium plumbite solution when followed by vaporization; high temperature-pressure non-metallic hydrofining; extraction with liquids such as sulphur dioxide; washing with liquid alkalies like caustic soda, or with liquid metals such as sodium or other alkali metals, unmixed or mixed with alkaline earth metals; all as pretreatments in the wellknown manner, often extend the effectiveness of reducible catalysts.

Diagrammatically shown in the drawing, are three forms of apparatus and control by means of a series of similar stages, adapted for use with the invention.

Fig. 1 represents a four-stage vapor phase treatment.

Fig. 2 represents a four-stage liquid phase treatment.

Fig. 3 represents a countercurrent polystage vapor phase treatment in which the stages are not segregated as in the preceding two figures.

Except in the case where only slight hydrofining is needed, the effective life or cycle of activity of these reducible catalysts is substantially extended by dividing that portion of the equipment in which the reaction takes place into several chambers, especially for liquid phase work. Where the catalyst is in a non-stationary form, each of these chambers should be supplied with agitation. Not only is this not necessary when the distillates and gas are flowed over stationary catalysts, but separation of the catalyst and re-mixing with fresh portions of oil is not required. This stationary or preferred catalyst may be segregated in portions, the first portions inhibiting deactivation of the latter portions. Moreover, the different portions may be of different components, for instance copper in the fore chambers and nickel in the hind. By bringing reserve portions of catalyst into action, the most deactivated old portions may be bypassed for activation.

Also in certain of the stationary catalysts, it has been quite simple to reactivate certain metallic catalysts anodically by procedures such as the anodic oxidation described in U. S. Patent 1,519,035, in which the metal in an ordinary form is a base for the activated metal. However, other indifferent substances, preferably of rough surface, may constitute a stationary base, such as small lumps of carborundum, fuller's earth, or roughened wire.

In general, the activity of a given catalyst falls during the operation, leading to a fall in production. The fall is not uniform, being predominantly the greatest in those catalysts or that portion of the catalyst which first and longest contacts with the distillates, unless the tempera-

tures of these portions are kept lower than the latter portions.

With stationary catalysts, these fore portions may be segregated for a reactivation generally before their production ceases. However, catalyst essentially spent when used at temperatures low in the reduction temperatures of the oxide of the catalytic metal with hydrogen, may be actively desulphurizing at the higher or sulphide reduction temperatures.

Generally it is preferable to introduce reserve or fresh catalyst at the rear portions, especially when operating at low temperatures, comprising relatively countercurrent operation with either continuous or discontinuous introduction of the catalyst.

To obtain a maximum of hydrofining with a minimum change of knock rating, solvency and color, it is essential that the temperature of each portion of the catalyst be adjusted to its activity and amount of hydrofining. Where the different portions of the catalyst are of the same active component, this is ordinarily accomplished by a series of temperatures, which is herein termed a space gradient, in distinction to a time gradient which represents the increase of average temperature of the space gradient with increasing deactivation of the catalyst as a whole, and which is an ascending gradient. The space gradient is ascending and/or descending. The usual gradient is ascending, but in the vapor phase desulphurizing type of hydrofining, and when reserve catalyst is introduced at the last portion of the contact, a descending gradient is useful, especially for the duration of that relatively countercurrent contact with the new catalyst.

The space gradient is an essentially instantaneous gradient, consisting of a series of temperatures which a molecule of the distillate undergoes during its short period of catalyst contact. This gradient is generally of the greater 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.

By using a great excess of catalyst and equipment, it is possible to accomplish the same hydrofining obtained from the space gradient, yet using a constant temperature. However, this is in the lower ranges of that gradient. In such cases the action in the last tubes tends to become sporadic and non-uniform. Likewise it is possible to use a constant temperature in the high ranges of that gradient by using catalyst of very low activity in the first portion of the equipment and catalyst of medium activity at the mid portions. Such low active catalyst may consist of long used catalyst, catalyst reduced at very high temperatures, or catalyst composed of less active elements.

Such an ascending gradient of activity accomplishes the same results, although in a less effective manner, as a corresponding gradient of temperature, namely the approximate equalization of the hydrofining during the different stages of catalytic contact. The two modes may be combined in practice, for in spite of a tendency of the space gradient to equalize the deactivation of the catalyst, the catalyst contacting first with the distillate tends to deactivate more rapidly. This is correctable by shortening the space gradi-

ent with the advance of the time gradient, that is raising the temperatures during deactivation faster at the fore portion than at the hind, in effect utilizing activity as well as thermal gradients.

Likewise the time gradient may be minimized, or even completely eliminated by starting with a partially deactivated catalyst. Such a partially spent catalyst may well result from hydrofining at lower temperatures, especially in the oxide reduction range and in the liquid phase. As in the space gradient, partial deactivation previous to any hydrofining may be accomplished by unusual high temperature reduction, which however is a waste of catalytic efficiency.

The acceleration of such gradients is nearly always negative, especially when the range of the gradient is wide, as with the space gradient in liquid phase hydrofining. Generally when the range of the space gradient is wide, the time gradient is narrow, and vice versa. However, by introducing fresh catalyst during a vapor phase operation, both the space and time gradients may be very wide in range.

The range of the gradients is quite variable, in an unusual case requiring 700 cubic feet of hydrogen per barrel and using a nickel catalyst in the liquid phase, the temperatures begin near 70° C. and end near 160° C., a space gradient of 90° C. range. Where less hydrogen is required, the range is decreased, as is also the case when working in the vapor phase, or with less active metallic catalysts. The range is quite short or even absent when working with temperatures above the reduction temperatures of the oxide of the catalytic metal with hydrogen. Hydrogen sulphide is continually formed under such conditions, to be scrubbed out of the recirculating hydrogen.

As will be noted in the examples, the time gradient range for this work is preferably more than 100° C. with nickel catalyst, though relatively less with the lower activity catalyst. Fresh nickel will actively desulphurize distillate vapors below 200° C. and will be useful at 300° C. and greater when near spent. On the other hand, the time gradient range with the previous example in the liquid phase is ordinarily of much lower magnitude, 10 or 20° C. Greater increases lead to discoloration; rather than these increases it is better to put reserve catalyst into action at the hind portion of the operation, or to convert the whole unit to vapor phase hydrofining.

An ascending space gradient of negative acceleration in the liquid phase and with a nickel catalyst constitutes a most 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.

When using such a high activity catalyst, the trend of selective hydrogenation of diolefines to olefines, and cyclic olefines to cyclic paraffins, in the presence of minor amounts of sulphur, such as .03%, is increased by lowering temperatures and pressures. Hence the practical problem in refining distillates lighter than the usual burning or kerosene type of distillate is to find the maximum temperatures and pressures compatible with a high degree of selectivity and its corresponding minimum decrease of knock rating and solvent power. Such a range of temperatures is found to be near 80-160° C. averaging near 130° C. with

nickel catalysts, and this is substantially within the oxide reduction temperatures of nickel. Although this is not a normal condition found in these distillates, this selective liquid phase hydrofining may frequently be used subsequent to more

harsh and desulphurizing treatments to be described later.

It is very convenient to maintain the major portion of the temperature control by passing the heating fluid countercurrent to the oil flow, that is the fluid may be introduced into the jacket of the last or nearly the last chamber, the jackets being series connected. A good plan is to connect the heating fluid inlet to the end chamber, and when reserve catalyst is brought into action without bypassing the spent chambers, to allow the fluid to flow two ways, the major stream forward in the old channel, the minor one concurrent with the distillate hydrogen mixture. This will yield a steadily rising temperature in all but the reserve chamber or chambers. However, for the best effects each needs to be separately fitted with a secondary line.

The catalyst generally used is activated nickel, which may be prepared in the many ways known to the art. By nickel catalyst is also meant nickel along with minor quantities of accessory components such as those containing copper, cobalt, chromium or 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. By copper catalyst is also meant copper along with minor quantities of components such as those containing cobalt, nickel, silver, chromium, molybdenum, or cadmium. By cobalt catalyst is also meant cobalt along with minor quantities of components such as those containing nickel, copper, iron, chromium, molybdenum, manganese, cadmium, zinc, or tin. The cobalt catalyst is less sensitive to sulphur deactivation than the nickel catalyst and hence is useful where it is desirable to hydrogenate unsaturates, especially diolefines to olefines in the presence of moderate but permissible amounts of sulphur. It is a striking fact that copper, nickel, cobalt, as well as iron make up an unbroken series of elements from atomic number 29 down to number 25, and further that most of their salts are isomorphous. Nickel, the most active, is adjacent to the next two most active, namely copper and cobalt, and these are the three metals which together with their oxides and sulphides are absolutely essential to the economic progress of this invention. Iron may be useful as a high temperature low pressure hydrofining catalyst for low grade and heavy distillates especially in the vapor phase. Cobalt is unusual in that it may act as an effective promoter with any of the other three metals, especially copper.

There are several other possible metals whose oxides are reducible by hydrogen, such as zinc, cadmium, tin, which are able to hydrogenate, but are of little use on account of their low activity and low melting point. Such metals along with lead, mercury, the alkali and alkaline earth metals, when contacted liquid with crude distillate may be of secondary usefulness as accessory treatments, for instance as pretreatments on high boiling distillates to metallic hydrofining with nickel or even an adjacent element.

The oxides of silver, palladium, gold and platinum are reducible either by hydrogen or heat alone. Principally on account of their scarcity,

these noble metals have strictly limited use, such as that of promoters to nickel or an adjacent element, or for the complete hydrofining of high premium distillates.

Before reduction, the oxides should be as nearly free of alkali as practical. A short treatment of the oxides with dilute chromic or molybdic trioxide solutions before reduction can assist in ridding of free alkali, and in other respects.

The reduction temperatures of the metallic oxides with hydrogen constitute an index to their activity and effective hydrofining range, especially when considered together with the sulphide reduction temperatures. For instance, the following table gives the approximate reduction temperatures with hydrogen in degrees centigrade:

Element	Incipient oxide	Normal oxide in the presence of the element or material of high heat conductivity	Normal oxide by precipitation, i. e. in the absence of metal or material of high heat conductivity
Copper.....	75	175	225
Nickel.....	75	200	325
Cobalt.....	175	310	425
Iron.....	350	425	500

With the exception of copper and nickel, the last two columns also approximately represent the incipient sulphide reduction temperatures. With copper and nickel these sulphide reduction temperatures are more than 100° C. higher. With this in mind the range between the first two columns may be termed the oxide reduction temperatures, and between the last two the sulphide reduction temperatures.

When a plurality of metallic catalytic components are mixed together, the reduction temperatures are generally lower than the arithmetic average, although under such circumstances the less activity metal may not be fully reduced. However, this is often of advantage, as constituting a reserve of slowly reducing fresh catalyst during the operation.

The type of metallic hydrofining characterized by much hydrogenation along with adsorption rather than destructive decomposition of sulphur compounds is in the oxide reduction temperatures. On the other hand, the type of hydrofining, generally vapor phase, with comparatively little hydrogenation and much decomposition of sulphur compounds, and formation of hydrogen sulphide, is in the sulphide reduction temperatures. The former method generally uses a series of temperatures, while the latter will operate well at a constant temperature. In the vapor phase with an excess of hydrogen, unreduced catalyst may be in a process of reduction while hydrofining. A high temperature treatment, followed by separation of the distillate and perhaps caustic washing if containing much dissolved hydrogen sulphide or phenolic compounds, and then rehydrofining with the low temperature conditions constitutes an important method of treating these distillates.

As noted before, the second catalyst may be used for the first, and this is not the only manner in which these two methods supplement each other. The high temperature vapor phase method is best adapted to distillates whose ratio of sulphur to unsaturates is high, while the low temperature method is best when this ratio is low. The former method is a low pressure operation

generally above but near atmospheric pressure, ordinarily between one-half and twenty atmospheres; while the latter is a higher pressure operation preferably near ten but under 100 atmospheres.

There is a third important and intermediate method, the most typical of metallic hydrofining, partaking of the advantages and characteristics of each of the above methods and making an excellent single operation hydrofining method, especially for the reduction of moderate sulphur contents. It operates in the vapor phase at low pressures, without much or any hydrogen sulphide formation and essentially in the oxide reduction range. Its thermal space gradient is nearer that of the sulphide vapor operation.

It is possible to combine this method with the other two, making it the middle of three treatments, or as more likely, combining it with only one of the others either separately or in a single operation. Likewise the same operation may combine two effects by using different catalytic components. The more inactive catalyst may be placed in the hind portion of equipment and operated at higher temperatures, especially on distillates which have not undergone pyrolysis.

If not containing dissolved hydrogen sulphide, all these hydrofining methods yield doctor sweet products, although those treated at lower temperatures and in the liquid phase are the more stable.

Deactivation is selective on the most active centers; without which 50° C. or higher temperatures must be reached to attain vigorous hydrogenation. If oxides are present during the deactivation, their gradual reduction constitutes a reserve source of such centers. The oxides themselves, especially copper and such oxides, possess desulphurizing power. Oxide reduction during hydrogenation is particularly applicable in practice to vapor phase hydrofining.

Advantage is taken of the partial deactivation of nickel 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 olefines in the case of motor fuels and solvents. The copper and cobalt catalysts promote this type of hydrogenation without being deactivated.

The highest selective pressure corresponding to the low liquid phase temperatures is experimentally determined as near the point where the increases of the reaction rate are proportional to the half power of the pressure. The reaction is very highly selective at lower pressures, where the rate is proportional to powers of the pressure greater than unity. The range of selective pressure is best defined as those pressures at which the differential of the reaction rate with respect to pressure is greater than one-half. Ordinarily such pressures are below twenty atmospheres, but may be extended much higher, even above 100 atmospheres when agitation is near to cessation; when much inert gas dilutes the hydrogen; when temperatures are lower than necessary; or when catalyst activities are low. A better way of correcting this last deficiency is to raise the temperatures 10-20° C. A pressure that gives just uniform or non-sporadic hydrofining is near the optimum for selectivity.

Twenty atmospheres represents the usual limit of pressure operation, pressures above that being chiefly useful in the liquid phase hydrogenation of distillates which it is desired to completely

hydrogenate, such as kerosene and transformer oil.

It is difficult to evaluate total hydrofining in terms of simple hydrogenation, since desulphurization involves such diverse compounds and methods. With the vapor phase and cobalt, the removal of one atom of sulphur may almost equal the addition of one molecule of hydrogen. With the vapor phase and copper or nickel one atom of sulphur removed may be equivalent to several molecules of added hydrogen, while in the liquid phase the increase may be again much greater. Where the sulphur content is very low, and the content of unsaturates high, it becomes very easy to control the approximate equalization of hydrofining, so desirable in the forward portion of the operation. Samples may be withdrawn and the decrease in refractive index from chamber to chamber followed. Where the hydrogen absorbed is 90 cubic feet per barrel and the number of reaction chambers ten, the drop in refractive index in each of the first eight tubes averages .0002, in the last two .0001. The sacrifice of production in the last two chambers is in the interest of completeness of hydrogenation.

All of the metal hydrofining is in the presence of hydrogen, by which is meant in hydrogen bearing gases whose non-hydrogen component is substantially inert to the particular catalyst used. No gas has been found completely inert, and it is preferable to keep such components quite low, lest they build up to unknown quantities during recirculation. In general, increase of temperatures allows some relaxation of purity standards of hydrogen. Hydrogen itself does not necessarily have to be added, but materials yielding hydrogen must, such as ammonia which may be used in high temperature vapor phase work, when even portions of the distillates themselves may be dehydrogenated especially when the original olefinic content is low, although such methods have little to recommend them. 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.

Likewise, reduction of the catalyst does not necessarily require hydrogen. Vaporous compounds with hydrogen in a combined state are much more readily used than with hydrofining. Also carbon monoxide or water gas may be the reducing agents, especially for the sulphide reduction range hydrofining and for cobalt and iron, performing the reduction of these at considerably lower temperatures than hydrogen. The application of thermal gradients to the reduction of these metallic catalysts either before or during hydrofining, especially when on metallic bases, contributes to their effectiveness, especially for liquid phase hydrofining.

Air may be used to reactivate an old catalyst after removal of the adhering hydrocarbons, and before reduction.

As an example of how this invention is to be carried out in practice, a highly pyrolyzed Pan-handle distillate is hydrofined as follows:

A closed vessel is divided into four chambers holding separate catalyst units, composed of 90% nickel and 10% cobalt. The chambers are connected in series and jacket heated with oil. The jacket connections are series connected and the oil flows backward or countercurrent to the flow of the mixture of equal volumes hydrocarbon vapors and hydrogen. The catalyst is prepared by the anodic oxidation with sodium carbonate

electrolyte as described in U. S. Patent, 1,519,035. Liquid is continuously pumped into a hot (200° C.) vaporizing chamber. At the outlet of this chamber, the vapors are mixed with an excess of hydrogen, the total pressure being 2 atmospheres, and the mixtures led down over the first catalyst at 160° C., the second at 170° C., the third at 175° C. and the fourth at 180° C., a non-linear space gradient of 20° C. range. During the first few hours the temperatures are rapidly raised and from then on quite slowly, at the same time shortening the space gradient. Near 300° C. these temperatures are 280, 285, 288, and 290° C. respectively. However, the hydrofining then takes place to little disadvantage at constant temperature. When the rise of temperature yields considerable discoloration or other evidence of pyrolysis and no increase of hydrofining, further passage of vapors is not warranted. The pumping is stopped and hydrogen alone passed for awhile. The catalysts are then reactivated.

In Fig. 1 the catalyst chambers 10, having jackets 12 are shown connected together, the first chamber being connected with a vaporizing chamber 16 into which the liquid distillate or like material to be treated is passed. At the outlet 18 of the vaporizing chamber the vapors are mixed with hydrogen and the mixture lead down through the catalyst chambers 10. Oil is used for heating the chambers and connecting lines as shown in the drawing, and the oil enters the jacket 12 of the last connecting line so that the oil flows in a direction opposite to the direction of the vapors being treated. The vapors are thereby subjected to an ascending non-linear space gradient. Later on as the catalyst becomes deactivated, the oil is progressively heated by a variable oil heater 14 capable of raising the catalyst temperatures as a whole in a time gradient through a range preferably of about 200° C. and below the temperature at which substantial discoloration or pyrolysis occurs with said distillate or like material. A condenser 20 is used to condense the hydrofined vapor and the condensate is collected in a receiver 22, with liquid drawoff 24 and exit 26 whereby the excess hydrogen is returned to the system. By means of the variable oil heater 14, the catalyst in the catalyst chamber 10 may be subjected to a series of temperatures comprising a polystage time gradient.

The yield from this operation is more than 99.5%, and the product is radically improved as noted in the table of tests following. It may then be treated with a few pounds of sulphuric acid per barrel or given another hydrofining treatment in the liquid phase at much lower temperatures, constituting an essentially complete stabilization.

The liquid phase operation is carried out much as is the vapor phase, but the temperatures are much lower and steam is effectively used as a heating medium. The same component catalyst may be used, although the cobalt here is less effective. A cooler and separating chamber for the hydrogen excess, but not a condenser, are needed at the outlet. The liquid is fed with a proportionating pump into the first reaction chamber with hydrogen gas under 12 atmospheres pressure. The successive chambers are 95, 115, 125, 130° C. These temperatures are raised 15° C. or more as the catalyst becomes deactivated with age. The catalyst may then be used for the first vapor phase treatment. It is to be expressly understood that the pressures and temperatures, especially the pressures, given in the examples are not to be taken as invariable.

The apparatus shown in Fig. 2 for carrying out the four-stage operation is similar to the one shown for the four-stage vapor apparatus in that both are jacketed and countercurrently heated. However, a condenser is not required and a cooler and separating chamber 30 is used. Also a proportionating pump 32 is used for feeding the liquid distillate and like material together with hydrogen at the outlet 34 into the first stage or catalyst chamber. Steam instead of oil is passed through the jackets 12 as the heating medium. The temperatures shown in the four chambers or stages are 95° C. in the first stage, 115° C. in the second, 125° C. in the third, and 130° C. in the fourth. This is a non-linear ascending space gradient having a range of 35° C. The direction of liquid and hydrogen flow is the same as that of said ascending space gradient, as shown by the arrow at the bottom of Fig. 2. The apparatus and relative flows shown in Fig. 3 is a polystage countercurrent method of carrying out a vapor state hydrofining. This differs from the apparatus in Fig. 1 in that the vapors are subjected to progressively decreasing temperatures comprising a descending space gradient, whereas the gradients in the apparatus shown in Fig. 1 are ascending. The countercurrent hydrofining or reaction chamber 10 contains means of contacting the vapors and hydrogen and the catalyst, means of continuously or discontinuously moving the catalyst, and means of heat control which are not shown. In Fig. 3 the warm vapors to be hydrogenated enter 10 at the inlet 50. The vapors mixed with hydrogen contact the catalyst first in a relatively heated and deactivated condition, then in a progressively cooler and more active condition, passing in a hydrofined condition together with an excess of hydrogen to a condenser 20 not shown. Relatively active catalyst is continuously or discontinuously supplied at the inlet 52. The relatively deactivated or spent catalyst leaves the apparatus at the orifice 54 and may then be reactivated and reenter at 52. The vapors and catalyst pass through the apparatus not only countercurrently but at different rates, resulting in two opposed gradients or series of stages, as shown in the arrows above and below the hydrofining chamber 10.

There are other effective methods of hydrofining. With distillate that has undergone pyrolysis, a succession of catalysts of relatively increasing activity and of temperatures decreasing, is in general the best method. Straight run distillates rarely require such vigorous treatments, but when they do, the succession may be with catalysts of decreasing activity. Two treatments may be combined in one as when such a straight run light

Test	Original Panhandle distillate	After vapor phase hydrofining	After vapor and liquid phase hydrofining
Doctor.....	Positive	Negative	Negative
Corrosion (copper strip).....	Positive	Negative	Negative
Sulphur %.....	.23	.09	.04
Unsaturation %.....	23	11	
Gum (porcelain dish) milligrams per 100 mls.....	170	9	1
Specific gravity at 15.5° C.....	.801		.794
Distillation:			
First drop ° C.....	40	39	40
50% over ° C.....	145		140
End point ° C.....	225	220	220
Knock rating:			
Octane No. fresh.....	75	73	73
Octane No. after 1 week in light and air.....	66	72	73

distillate is vaporized and passed with hydrogen over a nickel, copper or cobalt catalyst under conditions producing very minor quantities of hydrogen sulphide by using temperatures in the oxide reduction range; and finally without any condensation or separation of hydrogen, passing the whole over nickel at 290° C., when most of the desulphurizing occurs as liberated hydrogen sulphide which does not then have the opportunity of contaminating the forward catalysts. Fixation of sulphur in cyclic compounds is also minimized. Using such a procedure the sulphur content of uncracked Lima type naptha may be reduced from .4% to less than .1%, and the solvency by the Kauri-butanol test less than one point. The treatment is also applicable to pyrolyzed distillate.

However, the succession of catalysts of increasing activity is the rule. The succession does not need to be always metallic. For distillates containing appreciable asphaltic matter and very large amounts of sulphur, a destructive hydrogenation with molybdic oxide at the usual temperatures and pressures (over 100 atmospheres) may be followed by a nickel hydrofining within the reduction temperatures of nickel and at pressures near 10 atmospheres or less. Likewise, an unsaturated stock converted to aromatic compounds over a molybdic catalyst may be finished by a metallic hydrofining.

Since it is general that light petroleum distillate which has undergone pyrolysis contains most of the gum forming unsaturates in the light fractions and most of the sulphur compounds in the heavy, the following example illustrates a further type of two stage hydrofining using an Oklahoma pressure distillate of the usual gasoline boiling range, first drop at 30° C., 50% over at 140° C., end point at 225° C. This is fractionally distilled into three cuts, the first boiling up to 122° C., the second from 122 to 162° C., and the third from 162° C. on. The first needs no hydrofining, the second is hydrogenated under the same conditions as with the liquid phase hydrofining of the Panhandle distillate, but using a little wider space gradient. This treatment reduces the sulphur percentage from .04 to .01% and renders the doctor and corrosion tests negative. The third fraction is treated in the same manner as the first or vaporous hydrofining of Panhandle distillate, thereby reducing the sulphur percentage from .15 to .09%, likewise rendering the doctor and corrosion tests negative. On remixing the three fractions, the boiling range and specific gravity is lowered, the gum is 4 milligrams per 100 cc., and the sulphur content .05% previous to a liquid phase fuller's earth treatment, which is optional. The distillate before fractionation tests .09% sulphur; doctor and corrosion both positive, unsaturation 12%, gum 40 milligrams per 100 cc., and specific gravity .773.

Besides petroleum distillates, the light distillates or gases from other sources, such as those resulting from the pyrolysis of shale oil, primary tars and Berginized oils from coal are refined and even converted to new products by metallic 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 metallic hydrofining. These distillates after the washes above may still contain heterocyclic compounds of oxygen in addition to those of sulphur. Copper hydrofining, especial-

ly in the vapor phase, will convert the oxygen heterocycles to tar acids, and these may then be extracted by alkali and recovered. Other carbonaceous compounds, particularly those containing oxygen, may be subjected to the hydrofining in stages as described herein.

Some of the effects with stationary catalyst can also be obtained with catalyst in the powder form. A plurality or gradient of temperatures in a single chamber may be simply obtained by adding hydrogen and agitation while the distillate and catalyst are still in the process of being heated. If the hydrofining may be repeated with the separated catalyst essentially without change of conditions, the series of stages comprise a space gradient. Continuous operation in the liquid phase with a powder catalyst is obtainable in a plurality of chambers series connected, each preferably fitted with agitation or in its absence with a porous plate at the bottom of each to finely divide the hydrogen bubbles. Each chamber may be kept at a different temperature, but the method does not adapt itself to the use of different catalysts. The stationary catalyst may be used as a batch or discontinuous method of operation in the liquid phase. In the vapor phase the preferred direction of feed is downflow, and there is less advantage to be gained in distributing the catalyst over a series of reaction chambers.

What I claim is:

1. A method of hydrofining hydrocarbon distillates and like materials, which comprises contacting the material in the presence of hydrogen and in a series of similar stages with a catalyst susceptible to sulphur poisoning at a maximum temperature between about 75° C. and the temperature at which substantial pyrolysis occurs with said material, and adjusting the temperature 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 sufficient to sustain uniform hydrofining.

2. A method as described in claim 1, then further hydrofining the material under similar conditions in additional but fewer stages, and with decreasingly less amounts of hydrofining in said additional stages.

3. A method of hydrofining hydrocarbon distillates and like materials, which comprises contacting the material in the presence of hydrogen and in a series of progressive stages with a catalyst susceptible to sulphur poisoning and containing an active metallic element, at a series of elevated and increasing temperatures in the progressive stages but below the temperature at which substantial pyrolysis occurs with said material, the range or difference between the temperature extremes of said series of progressive stages having a lower limit of about 35° C. and an upper limit of about 150° C. to 200° C., and said series of temperatures comprising an ascending non-linear gradient with respect to the series of progressive stages, while maintaining the pressure of each stage sufficient to sustain uniform hydrofining.

4. A method as described in claim 3, in which the catalyst is readily reducible in the freshly activated condition, and in which the temperatures of the ascending non-linear gradient are increased more rapidly in the first stages than in the later stages, the amount of hydrofining in said first stages being relatively equal to the amount in said later stages.

5. A method as described in claim 3, in which the material is contacted in the liquid state, at a series of temperatures along a series of substantially equal stages comprising an ascending space gradient, the warmest or last stage of which is less than about 80° C. or 90° C. above the first stage, while the temperature of the middle of said series of stages is above the average of the first and last stage temperatures.
6. A method of hydrofining hydrocarbon distillates and like materials comprising destructively derived components, which comprises contacting said material in the presence of hydrogen and in stages with a catalyst susceptible to sulphur poisoning, at a plurality of temperatures above about 75° C. and below the temperature at which substantial pyrolysis or hydrogen sulphide formation occurs with said distillate, the difference between the extremes of said plurality of temperatures having a lower limit of about 20° C. and an upper limit of about 150° C. to 200° C., and effecting said plurality of temperatures by raising catalyst temperatures in an ascending series of temperatures comprising a time gradient and also by subjecting said material to a series of temperatures comprising a space gradient, while maintaining a pressure on each stage between about 1 and 100 atmospheres, and the contact at least until the material is doctor sweet.
7. A method as described in claim 6, in which the material in the vapor state is passed counter-current relative to the catalyst and in which each portion of the vapor is contacted with the catalyst first in a relatively warm and deactivated condition and then in a progressively cooler but more active condition, said series of vapor temperatures comprising a descending space gradient, while maintaining a pressure less than about 20 atmospheres.
8. A method of hydrofining light hydrocarbon distillates and like materials, which comprises the continuous passage of the material in the vapor state in contact with hydrogen and a catalyst susceptible to sulphur poisoning and containing an active metallic element, at a temperature in each stage above about 75° C. but below an upper limit of about 300° C. to 325° C., the different temperatures of the progressive stages comprising an ascending time gradient, the rise of temperature as a whole over a single cycle of active life of the catalyst, while maintaining a pressure on each stage between about 1 and 20 atmospheres and contact at least until the material is doctor sweet.
9. A method as described in claim 8 in which a substantial excess of hydrogen is continuously added to the vapors in the warmer stages and a still larger excess of hydrogen in the cooler stages, the catalyst containing in said cooler stages a readily reducible oxygen compound of the active metal as well as the active metal itself formed by reduction concurrent with the hydrofining.
10. A method of hydrofining light hydrocarbon distillates and like materials, which comprises continuously passing the material in the vapor state with an excess of hydrogen in stages and in contact with a catalyst susceptible to sulphur poisoning and comprising a metal selected from the group which consists of cobalt, nickel and copper, at a temperature between 75° C. and about 160° C., then raising the catalyst temperature in a time gradient at first rapidly then more slowly, and continuing to raise the temperature of the catalyst as a whole until nearly spent at about 300° C. or until substantial hydrogen sulphide formation begins, while maintaining the difference between the temperature extremes of the time gradient greater than about 120° C. and the difference between the temperature extremes of the space gradient substantially less than that of the time gradient, and a pressure on each stage between about 1 and 20 atmospheres and a total time of contact at least until the hydrofined material is doctor sweet.
11. A method as described in claim 10 in which the vapor material consists of the heavier fractions of a pyrolyzed motor fuel distillate, said fractions being relatively high in sulphur content and relatively low in unsaturation, and separately contacting the lighter fractions of said distillate which are relatively low in sulphur and high in unsaturation with hydrogen and a catalyst under conditions of temperature, pressure and time similar to the catalyst and conditions described for the first stages of said time gradient, then mixing substantially all the hydrofined lighter material with said hydrofined heavier material.
12. A method of hydrofining hydrocarbon distillates and like materials, which comprises contacting the material in the liquid state with an excess of hydrogen and in a plurality of stages with a catalyst susceptible to sulphur poisoning and readily reducible, at a series of elevated and increasing temperatures in progressive stages but below the temperature at which substantial quantities of hydrogen sulphide are formed therein, each portion of the liquid material being subjected to said series of temperatures which comprises an ascending space gradient, maintaining the temperature of the last stage of said gradient between about 35° C. and about 90° C. greater than that of the first stage, and a superatmospheric pressure on each stage but less than about 100 atmospheres of hydrogen, then separating the hydrofined liquid and further contacting more untreated liquid material under like conditions but at a generally higher series of space gradient temperatures, said general increase comprising a time gradient, and repeating said separation and further contact of said liquid at still higher temperatures until the total increase in the time gradient measured along corresponding stages of the space gradient is more than about 10° C. but not greatly in excess of about 20° C.
13. A method as described in claim 12 in which the liquid material substantially free of catalyst poisons is continuously passed over a stationary catalyst comprising nickel, and passing the liquid and hydrogen in the same direction as that of the ascending temperatures, the temperature in each stage being between about 75° C. and 200° C.
14. A method of hydrofining hydrocarbon distillates and like material, which comprises the steps of refining the material with hydrogenation catalysts first in the vapor phase, then in a series of similar stages in the liquid phase with a relatively more active catalyst and at a somewhat lower temperature than in the vapor phase, and maintaining a pressure in each stage and step between about 1 and 100 atmospheres, said liquid refining comprising contacting the refined condensed material with an excess of hydrogen and a catalyst susceptible to sulphur poisoning and comprising an active metallic element, and subjecting each portion of the refined liquid as it contacts the progressive similar stages to a series of substantially increasing temperatures comprising an ascending space gradient, the temperatures of said liquid phase stages being between

about 75° C. and the temperature at which substantial quantities of hydrogen sulphide form.

15. A method of hydrofining hydrocarbon distillate and like materials, which comprises continuously passing the distillate as a vapor with an excess of hydrogen in contact with sulphur-susceptible catalyst which contains nickel, in a series of space gradient and time gradient stages at a series of increasing temperatures, the temperatures for the first series of stages being between about 160° C. and 180° C., raising the tempera-

tures in all the stages in a time gradient and also raising the temperatures in the first portion of the series of stages more rapidly than the temperatures in the later portion thereof to reduce the temperature range of the space gradient until the catalyst is nearly spent at about 300° C. and maintaining a pressure on each stage above atmospheric pressure and maintaining a time of contact until the hydrofined distillate is doctor sweet.

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