

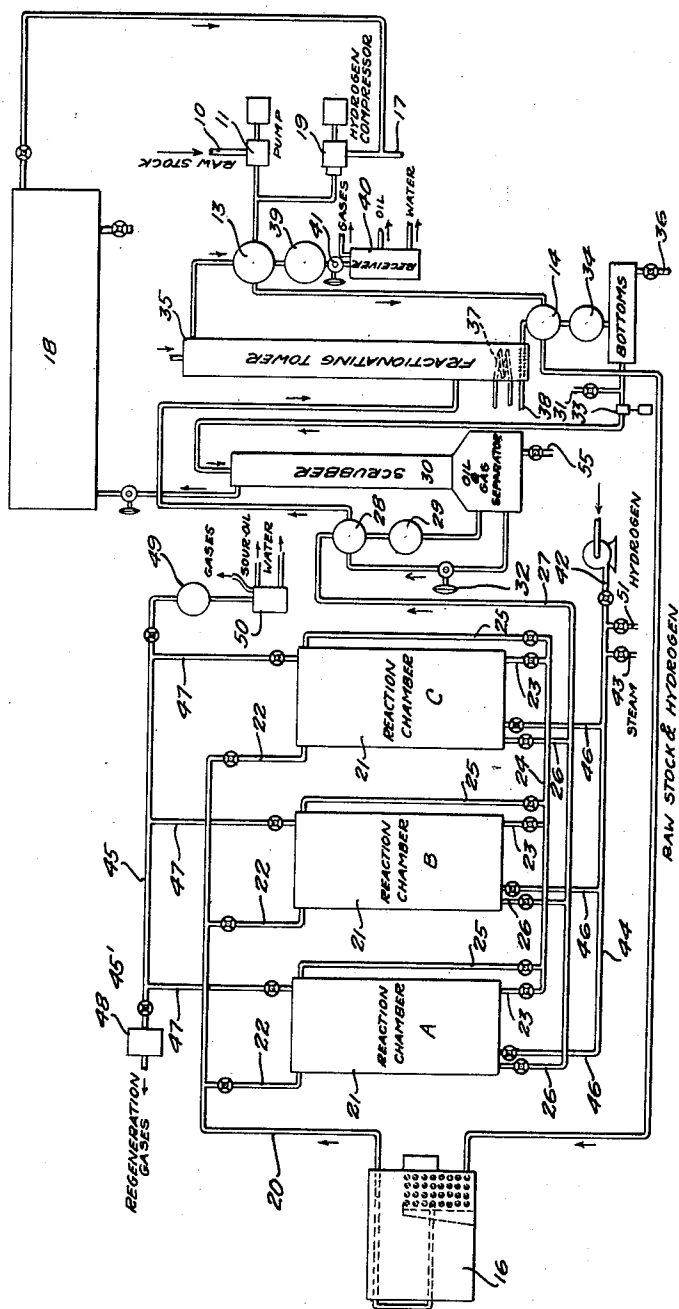
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A. SZAYNA

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TREATMENT OF HYDROCARBONS

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INVENTOR
ANTONI SZAYNA

BY *[Signature]*
ATTORNEYS

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TREATMENT OF HYDROCARBONS

Antoni Szayna, Brooklyn, N. Y., assignor to
Albert C. Travis, New York, N. Y.

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10 Claims. (Cl. 196—24)

This invention relates to a treatment of hydrocarbon, particularly those hydrocarbon oils which can be treated in vapor phase, and to the use and re-use of special contact materials in said process. More particularly, the invention relates to a method of desulfurizing oils and controlling other concomitant reactions by a contact mass, the surface of which is adapted to absorb sulfur from sulfur compounds present in the oil, to a cyclic process in which the contact mass is periodically regenerated and reemployed in the process.

The presence of sulfur or compounds of sulfur in petroleum coal tar and similar products has long been known, and its removal has long been recognized as a problem of great practical importance. In fact a large portion of the crude petroleum which is available at the present time is too high in sulfur content to be available for the production of high grade motor fuel without special desulfurizing treatment. One object of my invention is directed especially toward this problem; namely to provide a process for desulfurizing by which the value and quality of such sulfur bearing materials can be improved, although, as will be apparent from the following description, other advantages are attained by the novel treatment according to my invention which are not necessarily related to desulfurization.

Another object of the present invention is to desulfurize hydrocarbon oils, e. g., gasoline, while at the same time controlling other accompanying reactions to avoid deterioration of the product in other respects.

Another object of the invention is to produce a hydrocarbon product which is "doctor" sweet, non-corrosive, stable, of good color, and substantially free from tendency to form gums upon storage.

Another object of the invention is to produce a motor fuel with improved properties, including improved lead susceptibility, low gum content and gum formation, high octance rating, etc.

Another object of my invention is to produce a motor fuel of such improved properties in high yield and substantially without objectionable by-products.

Another object of the invention is to provide a cyclic process with regeneration of a contact material used in the process, and especially one in which any activity which it might otherwise have to deteriorate the product is largely inhibited in the regenerated material.

The invention comprises controlling the conditions, such as selection and treatment, including regeneration of the contact material, amount of contact material, velocity of flow of oil, amount of hydrogen, pressure, temperature and the various other factors which influence the reactions, to obtain the desired sulfur absorption, selective hydrogenation, etc.

A typical process according to my invention consists briefly, in vaporizing a high sulfur content gasoline and superheating the vapors, mixing them with a relatively small amount of hydrogen, and passing this mixture, advantageously under pressure, through a desulfurizing contactor of controlled activity, with the time of contact, depending upon the length of the contactor and the velocity of gas travel, sufficient to effect the required desulfurization. The treated vapors together with unconsumed hydrogen are treated for recovery of the finished product and separation of the unused hydrogen, which may be recirculated in further operation of the process. After a period of such operation the sulfur absorbing contact material would become more or less saturated with sulfur to the extent that sulfur would begin to appear in the product as hydrogen sulfide. Since more than a trace of hydrogen sulfide in the liquid product is undesirable, I withdraw from the contactor, from time to time, before it is entirely saturated with sulfur, at least the most saturated portion of the contactor and replace or renew this portion so as to sustain the sulfur absorbing quality of the contactor as a whole.

The portion of the contactor which is withdrawn may be regenerated, in this typical process, by burning off most of the sulfur therefrom, but leaving enough sulfur thereon to effect the desired chemical inhibition, and then reducing with hydrogen so far as to form a renewed contact material for reuse in the process.

Contactor

I have mentioned in this process the contact material (which I sometimes refer to for convenience as the "contactor"). This is a material which chemically extracts and binds to itself the sulfur from the oil, including sulfur in hydrogen sulfide and in organic compounds, as well as any free sulfur which may be present. This contactor is in a physical form with extended surface such as would be adapted to act as a surface catalyst, and ordinarily its surface will be largely composed of a catalytically active metal, but its activities are so controlled as to avoid undesirable catalysis which otherwise would deteriorate the product during the contact and at the temperatures necessary for the desired efficient desulfurization.

I have found nickel to be the most advantageous metal to use for the contact surface; but I have found that nickel alone, e. g., in the form of metal wool or chips tends to become brittle and to disintegrate in the course of regeneration; I, therefore, prefer to utilize a nickel surface on a porous inert carrier of good mechanical strength and other properties. Such carriers are already well known in the art of catalysis;

among them I may mention as particularly suitable for my reaction, pumice, bauxite, unglazed porcelain, kieselguhr, silica gel, porous carborundum. To these may be added small amounts of difficultly reducible oxides, e. g., oxides of aluminum, chromium, thorium, magnesium, and/or materials for strengthening the carrier, e. g., small amounts of alkali metal compound such as sodium hydroxide or carbonate, when a silicious carrier is used, or water glass, when a non-silicious carrier is used. Materials which also act as catalysts may be used where the reactions which they favor are desired. Active clays will ordinarily be avoided, unless it is desired to catalyze polymerization.

Inhibitor

I may utilize various methods of controlling catalytic activity, in order to inhibit to the desired extent, according to my invention, the undesired reactions, while keeping the surface of the contactor in a form to give rapid and efficient reaction with the sulfur in the flow of gases or vapors to which it is exposed.

The method which, in general, I have found to be most satisfactory is the addition to the contactor of a chemical inhibiting agent, such as a catalytic poison, which may be relied upon to reduce the catalytic activities without a corresponding reduction of the desulfurizing activity; and thus with the inhibited material a much greater desulfurization can be effected without serious deterioration of the product by catalytic reactions. It is important to have this inhibition effective all over the bed of the contact material, i. e., without zones which are fully active.

The control of the activity of the contact material may at the same time reduce its capacity as a desulfurizing agent; but, because the catalytic activities are decreased proportionally much more, the actual desulfurization by my process is more complete, rapid and efficient than by use of highly active catalytic desulfurizing materials, as is made more clear below.

Although, according to my invention, the catalytic activities of the contact mass are intentionally inhibited, e. g., by poisoning, they need not be completely destroyed. It is an important advantage of my invention that it provides a control for catalysis of high temperature reactions in an oil by which a limited and selective hydrogenation and/or dehydrogenation may be utilized to improve the quality of the product as well as to facilitate the desulfurization. This limited and selective hydrogenation activity is retained, according to my invention, while the harmful phenomenon of decomposing hydrocarbons into the elements, hydrogen and carbon, is inhibited entirely or to the point of insignificance, even well above 650° F.

The chemical inhibitor which I have found most satisfactory and most advantageous is the very sulfur which it is the purpose of the contact material to remove from the oil. Other materials which have an inhibiting effect such as chlorine, bromine, iodine, selenium and/or tellurium may be used in small amounts with a somewhat similar effect. The criterion of value of such inhibitors for use in my invention is in the difference in the degree to which they depress or suppress undesired reactions disproportionately more than the desulfurizing activity or capacity. These inhibiting materials may be retained, at least partially, on the catalytic mass during and throughout its regeneration; and insofar as they may be eliminated they are inexpensive to re-

place. Mercury and lead, and in general any metal which forms an alloy with the contactor, will reduce the catalytic activity; such metals, however, tend to reduce the desulfurizing activity more strongly and are, therefore, less desirable than the inhibitors previously mentioned above.

A most advantageous process according to my invention is one in which sulfur is used as the inhibitor; and the contact material, when it has become more or less saturated with sulfur, is not regenerated to a fully active catalyst, but instead is regenerated by a treatment controlled to leave a sufficient amount of sulfur in all parts of the regenerated mass to still inhibit the catalytic activities when the regenerated contactor is again put into service.

The amount of sulfur or other inhibiting agent is not sharply critical. With increasing small amounts of sulfur distributed in the contact surface, the catalytic activity of the contactor is rapidly decreased while the desulfurizing activity decreases only very little. Later, as the surface approaches saturation with sulfur, the desulfurizing activity drops more rapidly while the catalytic activity decreases very little more. This differential is utilized according to my invention by operating between a minimum sulfur content, at which the catalytic activity, especially for decomposition, is already substantially below that of the pure metal, and a maximum content, at which hydrogen sulfide would begin to form. It is important in this process that no substantial part of the contact mass contain less than said minimum sulfur content during its use in the high temperature sulfur absorbing treatment. In practice, however, parts of the contactor may be allowed to reach or exceed the maximum so long as subsequently contacted parts of the mass are well below the maximum so as to remove any hydrogen sulfide which might be formed in the sulfur saturated zone of the contactor.

The amount of sulfur necessary to produce the inhibition which will protect the product against deterioration will depend very much upon the uniformity of distribution of the inhibiting agent in the contact surface, and upon the depth of the sulphur absorbing metal below the exposed surfaces. With a contactor such as is described below in the preferred embodiment, I have found that a most economical effect occurs with a sulfur content in the neighborhood of 15%, based on the weight of the nickel, but if the sulfur is uniformly distributed an amount as low as 5% or even 3% will give substantial protection. Preferably the sulfur content should be reduced to, at the least, about 20% at each regeneration. With heavier coating of nickel on the carrier or especially if nickel is used without inert carrier the percentages of sulfur would be lower, since it is primarily the surface which is concerned in this process.

Within the general limits specified, the precise extent to which sulfur is present in the contactor when its use is begun will ordinarily depend upon cost considerations. Since the uniformity of sulfur distribution becomes more important as the minimum sulfur content is approached, the cost of precautions necessary to assure uniformity will offset to some extent the savings which would otherwise result from longer operating periods made possible by lesser sulfur retention.

Regeneration with sulfur retention

If air by which the sulfur is burned from the

contactor is passed through the contactor continuously from one side thereof toward the other and without careful temperature control, the part of the contactor nearest the air inlet may be completely deprived of its sulfur, while the part near the exit of the gases may still retain a substantial part of its sulfur. If such a contactor were put into use in a high temperature desulfurizing treatment, such as is described below, the sulfur-free part of the catalyst would produce objectionable reactions, e. g., of decomposition into hydrogen and carbon and excessive hydrogenation.

In my preferred process, I assure the retention of the necessary small amounts of sulfur throughout the contactor, by the simple step of removal of the sulfur from the contactor under carefully regulated conditions, especially of heat dissipation, such that the reaction can proceed as a self-sustaining reaction at the given temperature only so long as the concentration of sulfur remains above that desired in the regenerated contactor. Thus, as soon as any part of the contactor has its sulfur concentration reduced to the desired extent, the heat balance at its surface will be such as to terminate the reaction; and a residuum of poisoning sulfur will be retained upon that part of the contactor regardless of how long it may be necessary to continue the passage of air and/or other oxidizing gas through the contactor for burning excess sulfur from other parts thereof.

It is important, moreover, that during this treatment the temperature of the contact surface should not be allowed to increase excessively and that the temperature should advantageously be kept below about 1000° F. as measured by a thermocouple embedded in the contactor. Above about 1000° F. the physical or chemical condition of the nickel or other sulfur absorbing material at the surface may be altered so that it is less active for desulfurization.

Both the control of sulfur retention and the control of maximum temperature, I have found can be most effectively secured by supplying to the contactor a regulated mixture of air and steam at temperatures substantially below that at which the reaction with sulfur of the contactor mass would occur and continue spontaneously after the sulfur is reduced to the concentration in which it is to be retained for the purpose of inhibition. The temperature of these gases ordinarily should be well below 600° F.; and in practice I find it advantageous to supply air at room temperature mixed with steam at a temperature as low as is practicable while avoiding undesirable condensation, e. g., about 250° F. The use of steam I have found to have great advantage over any other gases known to me; and, although the nature of its action has not been conclusively determined, I believe that the reason is that the steam serves both as a chemical cooling agent and as an oxygen containing agent for conversion of the sulfide to the oxide, and perhaps has an action also as a catalyst or promoter—at least it causes the reaction to proceed more rapidly at the relatively low temperatures used.

The reaction by which the oxygen of the air reacts with the sulfide, with formation of the metal oxide and sulfur dioxide, is an exothermic one—that is to say, it releases large amounts of heat—and since this release of heat is concentrated on the thin surface layer, the physical condition of which is most important to the

activity of the contactor, the problem of controlling local overheating is a peculiarly difficult one. On the other hand, the reaction by which the water vapor transfers its oxygen to the metal of the sulfide and removes the sulfur as hydrogen sulfide is an endothermic reaction—that is to say, it can proceed only if heat or equivalent energy is supplied from the outside. In the process according to my invention this latter reaction also proceeds directly upon the surface of the contactor; and since this surface tends to adsorb the water vapor, it will proceed whenever the necessary energy is available. Thus, according to my invention, the presence of the water on the surface serves as an automatic control for the temperature of the surface: as soon as the direct oxidizing reaction with air makes energy available, which ordinarily would be released in the form of objectionable heat, the water on the contactor surface, according to my invention, immediately utilizes that energy in its endothermic reaction, so that this energy may be transferred and consumed directly as chemical energy without any serious danger of overheating the surface of the contactor.

The hydrogen sulfide formed in this reaction is, of course, a combustible gas, and to some extent at least it may burn in the excess air or react with SO₂ with further release of heat. I have found, however, that the heat thus released in the gases is relatively harmless, being largely carried off with the exhaust gases, and only being slowly transferred, if at all, to the contactor surfaces, whereas heat released in reactions occurring on the contactor surface may easily overheat and damage that surface. Any excess steam will serve by dilution to slow down such burning of hydrogen sulfide.

The action of the steam thus serves to keep the temperatures of the contactor in a range near the lower limit at which the reaction with air proceeds spontaneously, and consequently, as soon as the concentration of the sulfur on the surface is suitably reduced there will at first be less and less energy available for the reaction with water; and finally, the rate of heat generation in the reaction will fall below the rate of heat dissipation from the contactor surface, after which the surface will soon be cooled below the temperature limit at which the reaction ceases, and the residual sulfur will remain in the contactor surface to serve as a catalysis inhibitor notwithstanding that the passage of air and steam is continued for the burning of other portions of the contactor surface which at first were receiving mostly the sulfur bearing gases from the preceding parts of the contactor and had had as yet no chance to react.

It is possible to effect a similar but less perfect control by diluting the oxygen with inert gases. This method of control, however, will involve a longer reaction time. It is possible to attain sufficient uniformity of sulfur retention merely by controlling the flow of the regenerating gases, especially by reversing the flow or changing its course as certain parts of the contactor approach a given sulfur content. If adequate distribution is maintained, the sulfur content may be controlled merely by stopping the regeneration at the proper moment.

The process of preparation and regeneration of the contactor with control of sulfur removal, and especially by temperature control through control of chemical reactions, is claimed in a

companion application Serial No. 117,673, filed December 24, 1936.

The product of the oxidation treatment is reduced with hydrogen, and this should occur at a moderate temperature to avoid reduction of desulfurizing activity. I prefer to carry this out between 600° and 800° F.

Another important feature which is made possible by my invention is the close temperature maintenance throughout the cyclic process whereby the contact mass, substantially throughout its use and regeneration is maintained within a temperature range of, at most, a very few hundred degrees. I have found that in this way the output of the apparatus required can be very greatly increased and that the activity of the contactor can also be maintained over a much longer useful life.

Temperature of oil treatment

The use of relatively high temperatures during the desulfurization of the gasoline is another important feature of my invention; and when such high temperatures are used the control of catalytic activity, according to my invention, is especially important. The use of such high temperatures will greatly increase the rapidity of desulfurization and the efficiency of utilization of the contactor so that with a given amount of contactor a much larger volume of hydrocarbon oil can be treated and more sulfur can be absorbed from the oil by a given amount of the contactor.

I have found also that a number of the more refractory sulfur compounds which occur in the hydrocarbon oils may be readily and substantially completely removed by my contactor at temperatures above 700° F. and especially above 750° F., without the occurrence of other undesirable reactions which might be expected at such temperatures in the presence of a surface active contactor.

The most serious reaction which comes into prominence at these higher temperatures in the presence of the ordinary highly active catalysts is that of decomposition of hydrocarbons into the elements carbon and hydrogen. Although this decomposition is often overlooked or confused with cracking, it is quite a different phenomenon, and one which needs to be carefully avoided. It is bad, not merely because of the waste of those hydrocarbons which would be destroyed by the decomposition, but also, and even more important, because of the fact that products of the decomposition would be deposited upon and blanket the surface of the contact material so as to seriously impair or even to destroy its ability to perform effectively further desulfurization of the oil.

The metals nickel, cobalt and iron which are most desirable for use in the desulfurizing contactor are also most active in catalyzing this decomposition reaction at temperatures above about 600° F.

Such reactions as cracking, polymerization, hydrogenation and dehydrogenation may, of course, proceed to some extent at these temperatures, and more rapidly with increasing temperatures, even in the absence of catalysts; and these reactions may even be stimulated to some extent by the contactor used in my invention. It is in fact an important advantage of my process that, by use of the inhibited catalyst, such reactions may be promoted selectively and limited as desired. Thus, for example, one may

have selective hydrogenation of objectionable, e. g., gum forming, constituents and of the carbon linkages released by sulfur removal, substantially without hydrogenation of desirable, e. g., aromatic, hydrocarbons. Operating conditions may be chosen to favor desired products in accordance with well understood laws of chemical reaction. Thus, an increase in the amount of hydrogen present with the hydrocarbons during treatment or an increase in pressure with sufficient hydrogen will tend to increase hydrogenation. A high temperature without added hydrogen or with very little hydrogen favors dehydrogenation and polymerization. Lower pressure favors simple dehydrogenation, whereas higher pressure favors polymerization. The conditions of high temperature and low pressure will bring into prominence the reactions of dehydrogenation over those of hydrogenation. In the temperature range above 850° F. the cracking reactions are strongly favored by temperature increase.

Hydrogen

The use of hydrogen is important in my invention though not entirely essential. Without hydrogen or with too little the product may be to some degree unstable, of high gum content and subject to serious polymerization; and moreover, the desulfurization will proceed more slowly and in many cases will be less complete if hydrogen is not added. The presence of hydrogen apparently serves, as already described above, to satisfy the carbon linkages in the compounds from which the sulfur is removed, and thus at once to facilitate the desulfurizing reaction and to avoid the formation of unstable unsaturated products.

At higher temperatures such that considerable cracking occurs more hydrogen will be consumed, and unless a highly unsaturated product is desired, more hydrogen should be supplied. (Such cracking in the presence of my novel contactor is more particularly described and claimed in my companion application Serial No. 231,298, filed September 23, 1938.) The amount of hydrogen used is not sharply critical, but depends upon the raw stock being treated and the products desired. In general, straight run and highly paraffinic oils require less hydrogen than cracked or other highly unsaturated oils; and treatment during which cracking or reforming is combined with the desulfurizing will require more hydrogen.

When treating oils for Diesel fuels by my process a relatively high concentration of hydrogen is favorable.

I have found that the use of a large excess of hydrogen tends to stimulate hydrogenation reactions which are undesirable in treating gasoline, and which cause an uneconomic consumption of hydrogen in such treatment, but which may be desirable, e. g., for Diesel fuel. Such excess of hydrogen tends also to form hydrogen sulfide with high sulfur stocks, even with a contactor which is still capable of satisfactory use with a more suitable proportion of hydrogen. Ordinarily, for the average high sulfur raw stock, an addition of 1% of hydrogen, based upon the weight of the oil mixed therewith during the treatment, will be adequate, and in general the amount of hydrogen introduced with the raw stock will be increased with increase of the amount of sulfur which is required to be removed, e. g., 0.25% to 2.0% of hydrogen, but even

five times this amount may be used without serious objection.

Even when an adequate amount of hydrogen is used there may occur simultaneously both hydrogenation of undesirable and gum forming constituents and dehydrogenation of other compounds, e. g., naphthenes. The presence of hydrogen serves to shift the equilibrium between hydrogenation and dehydrogenation, but does not necessarily prevent the latter. When I refer herein to "consumption" of hydrogen I mean the net consumption, i. e., the difference between the amount supplied and the amount remaining after the treatment.

The hydrogen used need not be of high purity.

Specific examples

In the accompanying drawing I have shown also a diagrammatic arrangement of apparatus serving also as a process flow sheet, illustrating a preferred embodiment of my invention. It should be understood that the drawing and the description given herewith and the various alternative structures and procedures suggested herein are not intended to be exhaustive nor limiting of the invention, but on the contrary, are chosen for purposes of illustration and explanation in order that others skilled in the art may so fully understand the invention and the principles thereof and the manner in which it is applied in practice that they will be able to vary and modify it in numerous ways and to embody it in numerous forms each as may be best suited to the conditions and requirements of a particular use.

Referring to the drawing, the raw stock is supplied through the pipe line 10, the pump 11, the heat exchangers 13 and 14, and the tube heater and still 16. The hydrogen, either from the supply line 17 or from the recirculating tank 18 is compressed to pressure required in the system by the compressor 19 and then passed into the raw stock supply line, where it is mixed with the raw stock and with it passed through the heat exchangers 13 and 14 and into the tube heater 16.

The mixture of raw stock and hydrogen passes from the tube heater through the pipe 20 into one of the three reaction chambers 21 A, B or C. These reaction chambers are substantially identical, and each is filled with a contact mass which may consist in this preferred example of a pumice carrier, e. g., in pieces averaging about $\frac{1}{8}$ to $\frac{1}{2}$ inch in diameter. A pumice stone having about 0.38 apparent specific gravity is suitable for this purpose, but the numerous other carriers already known in catalytic work may be used likewise. The pumice grains are impregnated to cover the surfaces with nickel to the extent of about 10% of nickel based on the total weight of the contact mass; and about 1% of aluminum oxide may be added. The aluminum oxide helps to prevent recrystallization of the nickel during regeneration, which would reduce the sulfur absorbing surface, and permits higher regeneration temperatures. It also absorbs water so as to supply it locally during regeneration to offset the exothermic effect of the regeneration reaction. The nickel and aluminum may be applied to the pumice as sulfate solution which is subsequently precipitated, e. g., with sodium carbonate, and/or dried, or as fused salts, e. g., fused nitrates; in either case the deposited salts may be roasted carefully to the oxides and the nickel oxide reduced to metallic nickel at a temperature low enough to assure high surface activity, e. g., below 650° F.

The contact mass should be suitably treated for inhibition of catalytic activity before regular use. This could be done, e. g., by passing gases or oil containing hydrogen sulfide through the mass.

The contact chambers 21 are connected to the supply line 20 by valved branch pipes 22; and a manifold 24 is provided for connecting the top of any chamber with the bottom of any other chamber through the valved connections 23 and 25 respectively. Any of the chambers A, B or C may be connected through the valved connections 26 to an off-take manifold 27. From the off-take manifold 27 the treated vapors pass to a suitable oil separating and recovery system.

As one example of the use of this apparatus for the process of my invention, I have taken as raw stock a naphtha from a high sulfur Mexican crude. This naphtha contained about 0.67% sulfur, had a boiling range from about 160° F. to 450° F. This raw stock was fed into the system by the pump 11. Hydrogen at a rate slightly below 1% (by weight) that of the raw stock was supplied by the compressor 19. The pressure was maintained in the system and especially in the reaction chambers about 200 lbs. per square inch.

The mixture was preheated to a temperature of about 830° F. by the heat exchangers 13 and 14 and the tube heater 16. Assuming that the reaction chambers A and B are operating in series, and C is being regenerated, the valved connection 22 to the reaction chamber A will be open and the corresponding connections 22 to the chambers B and C will be closed. Likewise, the connection 23 for chamber A will be open while the connections 23 for the chambers B and C will be closed, and the connections 25 and 26 in the chambers A and C will be closed, whereas in the chamber B the connections 25 and 26 will be opened. Thus, the mixture of vapors and hydrogen passes into the top of the chamber A and through the contactor therein, which will be at a temperature a little above 800° F., and out through the connection 23 and the manifold 24 into the connection 25 of the chamber B and thus into the top of the second reaction chamber B, from which the treated product passes off through 26 and 27 for cooling, separation and further treatment.

The rate of flow is regulated to give a contact period in the two chambers A and B sufficient to effect the desired desulfurization.

In the reaction chamber A the vapors have encountered a contactor relatively high in sulfur content. In the chamber B the vapors encounter the most recently regenerated contactor and one, therefore, which although inhibited by its retained sulfur content, is more active as a desulfurizing agent. Thus, when the vapors have passed through the second chamber B the desired chemical treatment is completed.

By suitable insulation of the reaction chambers and connections the heat of the vapors is conserved and no other heating is required. However, if less insulation is used or if the fresh or freshly regenerated contactor in the second reaction chamber is at lower temperature when first put into service, the temperature in a part or all of the second chamber may be much lower. There is no objection to this except that the effectiveness of the cooler contact mass is reduced.

The vapors which leave the reaction chamber B through the connection 26 and 27 are com-

pletely treated so far as chemical reactions are concerned; and are then cooled and condensed and any residual hydrogen separated therefrom. This is accomplished in the present case by passing the effluent from the reaction chambers through a heat exchanger 28 and a water cooler 29 into the gas separator and scrubber 30 where condensible and soluble hydrocarbons are removed from residual hydrogen and the residual hydrogen bled off and collected in the tank 18 for recycling in the process.

With such recycling, in the particular example mentioned, about 0.18% of hydrogen (based on the weight of the oil) is consumed, including losses in the operation and must be supplied from outside sources when residual hydrogen is recycled.

The oil passing from the gas separator and scrubber 30 is again heated by the heat-exchanger 28 and passes from thence with reduction of pressure by the valve 32 into the fractionating tower 35 where any heavier hydrocarbons are separated and collected in the bottom of the fractionating column, from which they are recirculated by a pump 33 to the scrubber 30, passing first through the heat exchanger 14 and the water cooled heat-exchanger 34. If there should be an excess of bottoms it may be drawn off to storage through the line 36.

A steam heating coil 37 may be provided in the bottom of the fractionating column for indirect heating, and live steam may be supplied through the pipe 38.

The desired product comes from the fractionating column 35, passes through the heat exchanger 13, where it serves to preheat the raw stock and hydrogen, and advantageously through a final cooler 39 and a pressure release valve 41 to a gas separator and receiver 40 and finally into a gasoline storage tank (not shown). Tail gases and water separated from the gasoline are drawn off from the separator 40 through the connections shown.

The following comparison of the same stock used in the example just described, i. e., naphtha from high sulfur Mexican crude, treated by ordinary methods and by my process as just described will illustrate the advantage of my process:

	Raw stock	My product	Acid treated 10 lbs./bbl.	Acid treated 20 lbs./bbl.
Chemical treatment.	No treatment.	Vapor phase contact described above.	Acid caustic doctor.	Acid caustic doctor.
Treatment loss.	None.	1%.	12.7%.	12.2%.
Gravity.	50.4.	51.3.	50.1.	49.1.
Color (Saybolt).	+17.	+30.	+23.	+28.
Doctor.	Sour.	Sweet.	Sweet.	Sweet.
Sulfur.	0.67%.	0.020%.	0.442%.	0.230%.
Gum (ASTM).	Not tested.	0.2 mg.	0.4 mg.	0.3 mg.
Initial boiling point.	100°.	142°.	172°.	220°.
10%.	228°.	220°.	244°.	260°.
50%.	312°.	308°.	314°.	320°.
90%.	380°.	385°.	379°.	390°.
End point.	446°.	444°.	438°.	442°.

The sample of my product tested was a composite blend of ten samples taken at equal intervals during the entire period of operation of one pair of reaction chambers until one was ready for regeneration.

The advantage as to octane rating and lead susceptibility is shown by tests made on blends

of these same products with casing head gasoline:

	My product	Acid treated 10 lbs./bbl.	Acid treated 25 lbs./bbl.
Casing head gasoline added.....percent..	21	21	23
Octane No.	66.7	63.2	62.7
Octane No. with 0.5 cc. tetra ethyl lead/gal.	72.5	67.3	68.0
Octane No. with 1.0 cc. tetra ethyl lead/gal.	77.3	70.0	70.3
Octane No. with 2.0 cc. tetra lead/gal.	Over 79.7	72.4	73.8

The influence of the temperature is shown below in a series of experiments with separate samples of the same California cracked distillate using the same contactor as was used with the Mexican naphtha above referred to. The amount of nickel was 2.5% based on the oil, and 1.06% hydrogen was introduced, the time of reaction being about 12 minutes in each case:

		Temperature, °F.			
		Raw stock	690°	760°	820°
Yield by weight.....percent..	100	98.5	98.9	98.8	
Gravity A.P.I. at 60°.....degrees..	49.7	50.5	51.1	51.9	
Sulfur.....percent..	0.66	0.31	0.19	0.07	

The influence of the amount of contactor relative to the oil is shown below in a series of experiments in a batch operation with the same raw stock; the amount of hydrogen introduced and time of contact being as shown above, and the temperature of reaction being about 820° F.:

Metallic nickel..	2.5%	1.4%	Raw stock
Sulfur.....	0.07%	0.19%	0.66%

Another example follows in which cracked California heavy naphtha was treated at high temperature in the reaction chambers for production of low sulfur gasoline:

Condition of treatment

Contact material: Regenerated nickel contactor with residual sulfur poisoning
Temperature of treatment: 780°-905° F.
Time of contact: 17 minutes
Pressure: 500 lbs. per sq. in.

Hydrogen introduced: 1.6% weight

Hydrogen consumed: 0.8% weight

Total liquid yield: 97.4% by volume of treated semi-product. This semi-product was washed with 1 lb. of acid per barrel to remove remaining nitrogen bases and phenols, caustic washed and then rerun for gasoline.

Gasoline yield: 60.0% by volume of 420° end point gasoline of high octane number.

The analysis of these stocks is given below:

	Raw stock	Semiproduct	Finished gasoline
Gravity.....	37.0°	43.2°	49.2°
Color.....	Very dark.	Yellow.	+30.
Doctor.....	Sour.	Sweet.	Sweet.
Sulfur.....	0.956%	0.037%	0.018%.
Corrosion.....	Corrosive.	Not corrosive.	Not corrosive.
Copper-dish gum.			0.8 mg.
Initial boiling point.	337° F.	100° F.	100° F.
End boiling point.	500° F.	617° F.	420° F.
Octane No.	30.	49.	70.

The lead susceptibility of this product (like all products resulting from my process) was greatly improved as compared with that of the raw stock,

and as compared with products of ordinary reforming and acid treating.

No acid treatment is necessary in my process unless the raw stock treated has nitrogen bases or phenols. These compounds are only partly attacked by the desulfurization treatment according to my invention, and for their complete elimination a small amount of diluted acid, e. g., 80% strength may be used and followed by a caustic wash.

The chemical treatment of the semi-product in the example just given requires that the oil from the separator 30 should be drawn off to the treating tanks (not shown) before passing on to the fractionator 35. It is also advisable in this case to use a separate scrubber for the gases from the separator, because these gases contain a much larger proportion of hydrocarbon gases as a result of the cracking and require, therefore, a larger amount of scrubbing oil which it is not desirable to mix with the condensed product. Instead of the oil scrubber, active charcoal can be used.

Two additional examples are given below in parallel columns:

Treatment of contact material

Regeneration medium.....	Air and steam	air and steam
Regeneration temperature.....	760°-800° F.	700°-810° F.
Reduction medium.....	Hydrogen	Hydrogen of 85% purity
Reduction temperature.....	450°-800° F.	400°-780° F.

	California cracked distillate	Coal tar light crude oil
Raw stock:		
Gravity A. P. I. at 60° F	57.7°	31.1°
Color.....	Brown.....	Yellow.
Doctor.....	Sour.....	Sour.
Sulfur.....	1.15%.....	0.96%.
Corrosion.....	Corrosive.....	Corrosive.
Initial boiling point.....	106° F.....	151° F.
50% boiling point.....	268° F.....	203° F.
End boiling point.....	428° F.....	390° F.
Conditions of treatment:		
Temperature.....	750°-840° F.....	760°-835° F.
Pressure.....	200 lbs. sq. in.....	200 lbs. sq. in.
Percent hydrogen by weight introduced.....	1.3%.....	1.6%.
Percent hydrogen by weight consumed.....	0.3%.....	0.4%.
Product:		
Gravity A. P. I. at 60° F	58.2°	33.4°
Color.....	+30.....	+30.
Sulfur.....	0.050%.....	0.081%.
Corrosion.....	Not corrosive.....	Not corrosive.
End boiling point.....	427° F.....	390° F.

Aromatics in both cases remained unchanged within limits of analytical error.

As an example of heavier raw stock, Mexican (Panuco Field) kerosene was treated under conditions similar to those described in the first example with Mexican naphtha, but at somewhat lower temperatures (730°-810° F.). 0.21% by weight hydrogen was consumed. Results are given below:

	Raw stock	My process
Gravity.....degrees..	44.2	44.6
Color Saybolt.....	+15	+30
Doctor.....	NG	OK
Sulfur.....percent..	0.57	0.026

All other tests (including burning tests) classed my product as premium kerosene.

The raw stock ordinarily need not be distilled and fractionated before the desulfurization treatment; but such treatment is advisable with weathered and asphaltic oils in order to remove gummy and tarry constituents which might de-

posit on the contactor and impair its desulfurizing ability.

If more sulfur can be tolerated it may be more economical to operate with more rapid flow, or shorter path of travel through the contactor or with less hydrogen.

During the desulfurizing operation the third reaction chamber C may be undergoing a process of regeneration. Assuming that the reaction chamber C has previously been utilized in the desulfurizing series and has just been segregated from the flow of vapors, its contact mass will be at a temperature in the neighborhood of 800° F., and its reaction mass will be largely converted to sulfide.

As a preliminary to the regeneration it is ordinarily desirable to clean out the reaction chamber by closing the valved connections 22, 23, 25 and 26 and opening the valved connections 46 and 47 and then admitting steam from the line 43 through the manifold 44. The effluent from this cleaning treatment may pass off with the waste gases through the valved connection 47, the manifold 45, and condenser 49, to the separator 50 designed to separate the hydrocarbons from the condensed water. Since these hydrocarbons contain hydrogen sulfide formed by action of the steam on the contactor they are not mixed with the treated product, but they may be mixed with the raw stock if desired.

As soon as the hydrocarbons and any other vaporizable materials are sufficiently cleaned out of the reaction chamber the exhaust is diverted through the outlet 45'. At the same time the steam flow through the valved connection 43 is decreased and at the same time air is blown in from the air line 42 through the manifold 44 and the valved connection 46. Since at this stage the contact mass within the chamber C is still at a temperature at which energetic oxidation of the sulfide (which I sometimes refer to as combustion) occurs spontaneously, such reaction will begin to take place at once. By a suitable control of the proportion of steam supplied from the line 43 the temperature within the reaction chamber C may be suitably controlled.

More steam than air is ordinarily to be used at the start and less steam or even air alone may be used near the end of this regenerating step.

If the steam and air are properly proportioned, the reaction will terminate automatically as soon as the desired degree of desulfurization has occurred. As soon as the temperature drops, e. g., to about 650° F., the oxidation treatment may be considered completed for my purpose. The temperature in some zones may drop considerably lower, e. g., to about 500° F. or lower and this condition can be improved by reversing the flow of steam, and/or air or hydrogen or other gas used during regeneration; and also this part of the mass may be heated by the oil vapors when put into service.

Limited preheating of regenerating air by the exhaust gases, e. g., in the heat-exchanger 48, may also be used to avoid excessive cooling.

When the oxidation is complete to the desired extent, the connections to the air line 42 and the steam line 43 are shut off, preferably allowing the steam to continue long enough to sweep the air out of the system. Hydrogen is then admitted through the connection 51, and the flow of hydrogen thus continued until the desired reduction is attained.

It is not essential that the reduction in this

stage should be complete, and in fact the oxidized material may be reduced by turning the flow of hydrocarbon vapors and hydrogen directly into the oxidized contact mass. This latter procedure, however, is not recommended, since it consumes hydrogen which should be available for reaction with the oil; and if it is adopted a much larger amount of hydrogen should be supplied to care for the reduction of the oxide. Even with this additional hydrogen, however, the oxide may cause a temporary deficiency of hydrogen in parts of the vapors so that the results may be unsatisfactory with respect to polymerization, stability and gums. It is for this reason especially that the reduction is recommended.

When the desired reduction has been effected the reaction chamber C is ready for use in the process; and it may, therefore, be cut into the series once more by closing its valved connections 46 and 47 and opening the valved connections 25 and 26. At the same time the chamber B will be changed from the second in series to the first in series by closing its valved connections 25 and 26 and opening its valved connections 22 and 23, and the reaction chamber A will then be segregated from the flow of vapors by closing its valved connections 22 and 23 and its contact mass regenerated as already described in connection with the chamber C.

Thus, each chamber in turn when regenerated serves first as the second chamber of the series, then as the first chamber of the series and during a third period is segregated from the flow of vapors and its contact mass regenerated; while the flow of vapors is treated continuously in an initial contactor which is partially exhausted, and finally in a freshly regenerated but at least partially inhibited contactor.

During the period of treating the oil the heating of the contact mass is assured by the hot vapors coming from the pipe still until at the end of this period the contact mass is above about 800° F. sometimes even considerably higher, e. g. 950° F.

During the steaming out treatment the temperature drops somewhat lower, but with the admission of air a further heating occurs which is controlled by the regulated addition of steam to carry the temperature up to about 900° F.

Upon termination of the reaction, the air and steam lower the temperature of the mass again, e. g., to a temperature of about 700° F.; and during the reduction treatment the temperature ordinarily is not very greatly changed.

The pressure chosen may be maintained throughout the desulfurizing operation without change, the burning of the sulfide may with advantage be at atmospheric pressure, and in that case the pressure may be gradually brought back to the operating pressure by the hydrogen used during the reducing step.

Although I have used for these examples pressures of 200 lbs. and 500 lbs. per square inch and I have found pressures from 100-1000 lbs. per square inch most suitable for the treatment of these particular oils; nevertheless, a wide range of pressure is permissible without departing from my invention.

Although I have shown in each of my examples, three reaction chambers, it will be understood, of course, that the number will be determined primarily by engineering considerations. The flow of gases in the chambers may, of course, be upward or downward.

Hydrogen, which in the example is added to

the liquid oil, may with some advantages be added to the vapors, e. g., in the line 20, or at other point or points in the line of flow.

Although I have specified in each of the examples the regeneration of the contact mass by treatment with air and steam and subsequent reduction with hydrogen, my invention is not limited to this particular type of treatment and in general I may use any of the methods available for regenerating catalysts provided that they are controlled to retain a small amount of poisoning, or that the regenerated contactor is otherwise treated to control its catalytic activity.

These various alternatives have been mentioned to illustrate the numerous variations which can be made without departing from the scope of my invention, and it will be understood that these are only a few of the variations which are possible.

This application is a continuation-in-part of the prior copending applications Serial Nos. 231,298, filed September 23, 1938; 117,673, filed December 24, 1936; 94,578, filed August 6, 1936; and 60,466, filed January 23, 1936.

What I claim is:

1. A process of desulfurizing sulfur-bearing hydrocarbon oils which comprises passing such oil thru a porous contact mass having an extended surface comprising free metal of the class consisting of nickel, cobalt and iron, and having sulfur distributed substantially throughout said surface acting as an inhibitor of its catalytic activity, segregating at least a part of said mass from the oil flow after it has taken up a substantial amount of additional sulfur from the oil, removing such additional sulfur by oxidation at temperature sufficiently low to avoid substantial impairment of desulfurizing activity, terminating the oxidation reaction in each part of the mass while sufficient sulfur remains in said mass to substantially poison its catalytic activity, substantially reducing the oxide formed in the oxidation step, and again in a repetition of the process utilizing the contact mass thus reformed.

2. A process of desulfurizing sulfur-bearing hydrocarbon oils which comprises passing such oil thru a porous contact mass having an extended surface of a metal of the class consisting of nickel, cobalt and iron, which contact mass contains at least about 15% of sulfur, based on the weight of said metal, segregating at least a part of said mass from the oil flow after it has taken up a substantial amount of additional sulfur from the oil, removing such additional sulfur by oxidation at a temperature sufficiently low to avoid substantial impairment of desulfurizing activity, terminating the oxidation reaction while at least about 15% of sulfur based on the weight of said metal remains in said mass to substantially poison its catalytic activity, reducing the oxide formed in the oxidation step while substantially retaining said sulfur, and again utilizing in a repetition of the process the contact mass thus reformed.

3. A process of desulfurizing sulfur-bearing hydrocarbon oils which comprises passing such oil thru a porous contact mass having an extended surface of a metal of the class consisting of nickel, cobalt and iron, which contact mass contains at least about 5% of sulfur based on the weight of said metal distributed throughout substantially all parts of the mass, segregating at least a part of said mass from the oil flow after it has taken up a substantial amount of

additional sulfur from the oil, removing such additional sulfur by oxidization at a temperature sufficiently low to avoid substantial impairment of desulfurizing activity, terminating the oxidation reaction while at least about 5% of sulfur based on the weight of said metal remains in every part of said mass to substantially poison its catalytic activity, reducing the oxide formed in the oxidation step while retaining sulfur therein, and again utilizing the contact mass thus reformed in a repetition of the process.

4. A process of desulfurizing sulfur-bearing hydrocarbon oils which comprises passing such oil thru a porous contact mass having an extended surface of nickel, which contact mass contains at least about 3% of sulfur based on the weight of said metal, segregating at least a part of said mass from the oil flow after it has taken up a substantial amount of additional sulfur from the oil, removing such additional sulfur by oxidization at a temperature sufficiently low to avoid substantial impairment of desulfurizing activity, terminating the oxidation reaction while at least about 3% of sulfur based on the weight of said metal remains in said mass to substantially poison its catalytic activity, reducing the oxide formed in the oxidation step but retaining at least about 3% sulfur base on the weight of said metal, and again utilizing the contact mass thus reformed in a repetition of the process.

5. A process of desulfurizing sulfur-bearing hydrocarbon oils which comprises vaporizing such oil and superheating its vapors, passing said vapors through a porous mass of contact material having an extended surface of a metal of the class consisting of nickel, cobalt and iron and having an inhibitor distributed substantially throughout said surface, continuing such passage until at least a part of the contact mass is substantially converted to sulfide by sulfur taken up from the oil, segregating from the oil at least a part of the contact mass which has been thus converted to sulfide, passing through the contact mass an oxygen-containing gas adapted to convert said sulfide to oxide, passing through said mass a reducing gas adapted to reduce said oxide to the metal, and again utilizing the reduced mass for desulfurization by passing the oil vapors therethrough, which process is characterized by the fact that the temperature of the contact mass during each of said steps of the entire cycle is within a range between approximately 600° F. and 1000° F., and said material is at all times maintained in its extended surface condition, and an inhibitor is at all times maintained in and distributed throughout said material sufficient to avoid catalytic decomposition of the oil and blanketing of the catalyst with carbon formed thereby.

6. A process of desulfurizing sulfur-bearing hydrocarbon oils which comprises vaporizing such oil and superheating its vapors, passing said vapors through a porous mass of contact material having an extended surface of nickel poisoned with sulfur in substantially every part of the mass, continuing such passage until at least a part of the contact mass is substantially converted to sulfide by sulfur taken up from the oil, segregating from the oil at least a part of the contact mass which has been thus converted to sulfide, passing through the contact mass an oxygen containing gas adapted to convert said sulfide to oxide, passing through said mass a reducing gas adapted to reduce said oxide to the

metal, and again utilizing the reduced mass for desulfurization by passing the oil vapors therethrough, which process is characterized by the fact that the temperature of the contact mass during each of said steps of the entire cycle is within a range between approximately 700° F. and 900° F. and said material is at all times maintained in its extended surface condition and sulfur poisoning is at all times maintained in substantially every part of the mass sufficient to avoid catalytic decomposition of the oil and blanketing of the catalyst with carbon formed thereby.

7. The process as defined in claim 5, in which the passage of the oil through the contact mass is continued until at least the part of the contact mass which is to be segregated is so far converted to sulfide that it can be oxidized spontaneously by air at room temperature and without otherwise raising its own temperature, air is supplied to said mass for oxidation of the sulfide, and the temperature of the contact mass during said oxidation is kept within said range and overheating is prevented by a regulated supply of steam thereto during said oxidation.

8. The process as defined in claim 5, in which the passage of the oil through the contact mass is continued until at least the part of said contact mass which is to be segregated is so far converted to sulfide that it can be oxidized spontaneously by air supplied at room temperature, and, without otherwise raising its own temperature, air is supplied to said mass at a temperature lower than that at which spontaneous combustion of the sulfide, and the temperature of the mass during the oxidation is kept sufficiently low that the reaction stops spontaneously by decrease of the sulfide concentration before the sulfur poisoning of the catalytic activity of the mass is eliminated.

9. The process of treating petroleum oils for production of improved motor fuels which comprises passing the oil at temperature above 700° F., at which catalytic decomposition of hydrocarbons into elements could occur, and in the presence of hydrogen, over and in intimate contact with a free metal selected from the class consisting of nickel, cobalt and iron in extended-surface condition, said metal at all times during said treatment having a catalytic-inhibiting substance distributed over substantially its entire surface in amount sufficient to substantially avoid the decomposition of hydrocarbons into elements, which would otherwise occur and at least some of said free metal remaining exposed to the oil at all times during said treatment.

10. The process of producing doctor-sweet products of reduced sulfur content from sulfur containing hydrocarbon oil which comprises passing such oil in vapor phase with addition of hydrogen at temperature above 700° F. at which catalytic decomposition of hydrocarbons into elements could occur and through a contact mass comprising a porous carrier having free metal selected from the class consisting of nickel, cobalt and iron extended on its surface in physical condition adapted to give it high surface activity but at all times during said treatment having sulfur distributed substantially throughout said surface as an inhibitor for the catalytic activity thereof and at least some of said free metal remaining exposed to the oil at all times during said treatment.

ANTONI SZAYNA.

CERTIFICATE OF CORRECTION.

Patent No. 2,273,299.

February 17, 1942.

ANTONI SZAYNA.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 6, first column, lines 51 to 54, in the heading to the table, for "Acid treated 20 lbs. acid/bbl." read --Acid treated 25 lbs. acid/bbl.--; page 9, first column, line 28, claim 4, for "base" read --based--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 21st day of April, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.