

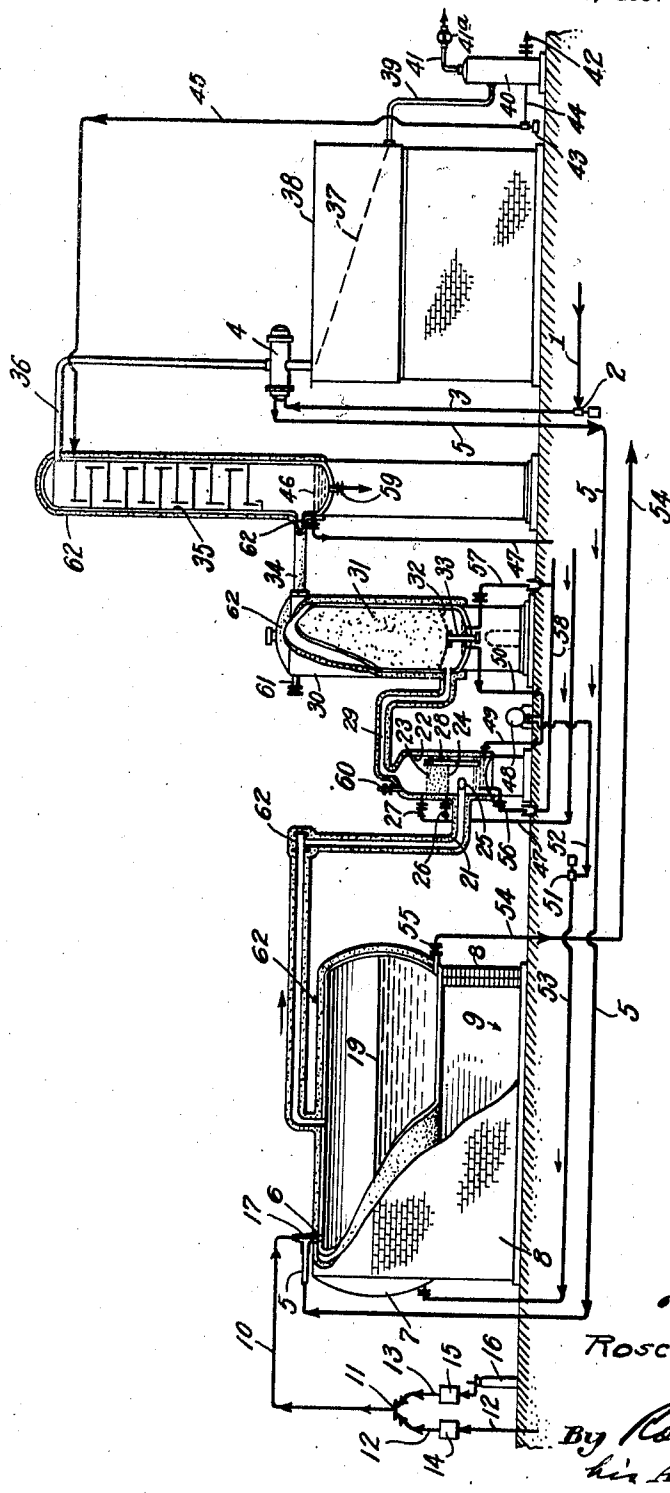
Jan. 11, 1944.

R. D. HOWARD

2,338,941

PROCESS OF REFINING MINERAL OILS

Original Filed Oct. 22, 1937



Inventor.

Roscoe D. Howard

By *Roy A. Kernal*
his Attorney.

UNITED STATES PATENT OFFICE

2,338,941

PROCESS OF REFINING MINERAL OILS

Roscoe D. Howard, Tulsa, Okla., assignor, by
mesne assignments, to Petroleum Research
Corporation, Chicago, Ill., a corporation of
Delaware

Original application October 22, 1937, Serial No.
170,452. Divided and this application June 22,
1940, Serial No. 341,946

2 Claims. (Cl. 196—28)

This invention relates to processes of refining mineral oils. Although the invention is applicable to the refining of mineral oil products generally that are susceptible of being treated in the manner hereinafter disclosed, it is of particular utility in treating crude or raw mineral oil distillates that are relatively low-boiling such, for example, as crude distillates of the motor fuel type, which require further refining in order to produce marketable products. Such raw distillates, whether resulting from the cracking of a mineral oil such as crude petroleum or from straight run distillation of crude petroleum, contain varying proportions of deleterious contaminants including sulphur compounds that are highly objectionable.

The present application is a division of a co-pending application, Serial No. 170,452, filed October 22, 1937, Patent No. 2,205,411, granted June 25, 1940. The present application is directed especially to the refining of relatively low-boiling crude mineral oil distillates by a procedure which comprises subjecting such a crude distillate in heated vaporous state with air or other appropriate gaseous oxygenating agent admixed therewith in suitable proportion, the mixture also most desirably comprising water vapor, and subjecting the resultant hot vaporous mixture to intimate contacting with a permeable body of contact material comprising metal in oxidized condition, said contact material being adapted to promote sweetening and otherwise to improve the quality of the raw mineral oil distillate or product to be refined; and then cooling and recovering a refined product from the treated vaporous mixture. The aforesaid prior application and patent emphasize more particularly a generally similar process in which, however, chlorine, as well as air, is mixed with the crude distillate vapors in forming the initial reaction mixture. Chlorine is not employed in the process to which the present divisional application is directed.

Raw cracked distillates, produced by high temperature conversion of relatively high-boiling mineral oil material into lower-boiling products for motor fuel of the gasoline type, are commonly characterized by a substantial content of deleterious gums or gum-forming constituents, as well as other objectionable impurities, including sulphur in various states of combination, and are more or less deeply colored and evil-smelling in varying degree depending upon the source and character of the mineral oil material employed as cracking stock. In refining raw distillates of this type the problem is to eliminate these ob-

jectionable characteristics in order to prepare therefrom a finished merchantable product substantially free from gummy or gum-forming constituents, of good color and odor, and sweet to the doctor test (sodium plumbite). Where the raw distillate to be refined is a sour straight run gasoline, the problem is somewhat less complicated because gum-removal is ordinarily not involved to any great extent, but the matter of effecting satisfactory sweetening economically nevertheless presents practical difficulties that are often serious. Moreover, actual reduction of sulphur content is not ordinarily achieved by sweetening treatments heretofore available.

The importance of the problem above referred to is well known to oil refiners and is attested by the numerous methods heretofore proposed, and in some cases employed, in attempting to solve it; but it is also well known that even the best of the refining methods heretofore known falls short of solving it in a completely satisfactory manner, either because of failure to effect the desired refining or purification with the desired completeness or because of operating costs too high to permit profitable operation commercially.

A general object of the present invention is to provide an improved process for purifying or refining mineral oil products derived from petroleum, more particularly relatively low-boiling mineral oil distillates of the type mentioned, for production of refined commercial mineral oil products, especially of the motor fuel or gasoline type. A more specific object of the invention is to enable effective and economical refining of raw cracked mineral oil distillates for removal therefrom of undesirable and contaminating impurities or constituents such as those above referred to, whereby to produce finished commercial products of the required high grade, especially gasoline that is substantially gum-free, doctor sweet, and of good color, odor and stability. A further and still more specific object of the invention is to enable the refining of relatively low-boiling raw straight-run petroleum distillates, especially raw gasoline distillates, in a remarkably simple and economical manner, with production of refined distillates that are doctor sweet, and otherwise of excellent quality or grade.

In applying the process of the invention to production of a merchantable gasoline from a crude cracked gasoline distillate which, therefore, not only is sour but also contains unstable and gum-forming constituents, a suitable proportion of air, or other appropriate gaseous oxygenating agent, that is substantial but yet relatively small,

is mixed with hot vapors of the raw distillate from whatever source derived. Most desirably, a small proportion of water vapor, e. g., steam, is also mixed with the distillate vapors; addition of water vapor being of particular advantage as will more fully hereinafter appear, although not an indispensable feature of the invention in its broader aspects, especially where the crude distillate already contains some moisture. Moisture is not regarded as an active reagent at this stage of the process. Opportunity having been given for the initiation and going forward to a greater or less extent of the desired reactions whereby the gum-forming and unstabilizing constituents, including complex sulphur-containing hydrocarbons, tend to polymerize, the mixture is then subjected, still in vapor phase and sufficiently hot, to suitable treatment to promote completion of said reactions, together with deposition and removal of the resultant gummy and tarry products, and also to accomplish sweetening. In the present example, this part of the process is most desirably carried out in a plurality of successive stages, because thereby it becomes feasible to employ, more or less separately, measures respectively best adapted for gum-removal and for sweetening, with resultant exceptionally economic operation. Thus, gum-removal can be effected, at least for the most part, in an early stage of the treatment, while sweetening can be accomplished at least largely at a later stage with an effectiveness and economy that is enhanced by the prior removal of the heavy or high-boiling polymers aforesaid, or the main bulk of them.

It is an essential feature of the invention that, in effecting the sweetening of the distillate vapors and reduction of their sulphur content, the aforesaid vapor mixture be subjected to the action of a suitable contact material or materials, including metal in oxidized condition, such material also being effective to promote deposition and removal of heavy polymer products from the distillate vapors undergoing treatment. Although the practice of the invention in its broader aspects is not confined to the employment of a contact material comprising any one particular metal oxide having sweetening action on the vapors, the various available oxidation products of zinc are found to afford marked advantages for the purpose.

The deposition and removal of heavy polymers can be largely effected at an earlier stage of the treatment, that is, prior to the final sweetening stage, by means other than metal-oxide-containing contact material such as that just referred to, as will presently appear.

Where the process of the invention is applied to the refining of a sour straight-run gasoline, for example, there is sometimes no need to make special provision for removal of heavy gummy and other polymers, since such a gasoline seldom contains more than a relatively small proportion of gum-forming constituents, if any. In such cases, therefore, the treatment of the gasoline vapors and air to effect the desired removal of impurities need consist only in passing the mixture through the metal-oxide-containing contact material to accomplish sweetening.

An important characteristic of the novel process in its best embodiments is that it is continuous in its operation, thus making for simplicity and smoothness of operation or procedure with consequent economy in operating costs as well as uniformity of final product.

Other important features and advantages of the invention will appear from the further detailed description to be given hereinafter for the purpose of affording a more complete understanding of the essential underlying principles of the novel process. In order that these underlying principles may be the more readily made apparent, certain particularly desirable practical embodiments of the invention will be referred to in giving said detailed description, but it is to be understood that this is merely by way of concrete illustrative example explanatory of the general principles involved and is not to be construed as in any way limiting the scope of the invention defined in the appended claims.

In a typical practical embodiment of the invention, the process is applied to the production of a finished gasoline of high grade from a raw motor fuel distillate obtained by cracking relatively heavy and high-boiling mineral oil by any known or suitable cracking process for conversion of such heavy oil into lighter and lower boiling products. Such raw distillate is strongly colored, ranging from light yellow to dark brown, and is characterized by an odor that is unpleasant and often very foul. It also shows a high gum content by the copper dish test, and its sulphur content is ordinarily much higher than is permissible in finished gasoline, a large part of this sulphur content being in complex combination with hydrocarbons in a form rendering the distillate very "sour." In this typical example, it will be assumed that the raw distillate to be treated is supplied initially in the form of a substantially cold liquid condensate requiring heating and vaporization at the commencement of the process; although obviously the raw distillate may be in the form of hot, uncondensed hydrocarbon vapors coming direct from a cracking plant, or it may flow in hot liquid condition from a stabilizer wherein it has undergone treatment for elimination of certain very light hydrocarbon components in the nature of fixed gases, and hydrogen sulphide.

The process can be carried out in apparatus plants or installations varying widely in structural details and arrangement. One type of such plant, the use of which will be assumed in the present illustrative example, is shown more or less diagrammatically in the accompanying side-elevational drawing and will be referred to for the sake of convenience and clarity of explanation in the following detailed description of how the invention may be applied to the refining of a raw cracked distillate of the character above mentioned.

Referring to the drawing, raw cracked gasoline distillate enters the system through line 1 and is forced by charging pump 2 through line 3 and vapor-liquid heat exchanger 4, where the cold charge picks up heat from the hot vapors of the refined gasoline, thereby having its temperature raised, say, from 80° F. to around 240° F., for example. The raw charge thus preheated and partially (e. g., about 50%) vaporized is then conducted through line 5, the liquid-vapor mixture of hydrocarbons being discharged at 6 into vaporizer 7, which in this instance is shown as an ordinary horizontal shell still suitably supported as by brick setting 8 over fire-box 9 heated by burner means (not shown) in the usual manner. This shell still vaporizer may be 30 feet long and 10 feet in diameter, in a typical instance.

Through line 10, a mixture of air and steam

also enters the vapor space of the still at 6, in company with the liquid-vapor mixture of hydrocarbons. The air-steam mixture is formed at the junction 11 of lines 12 and 13, through which air and steam are respectively supplied in quantity and proportion controllable by air control and meter assembly 14, and steam control and meter assembly 15. At 16 is represented a source of steam supply.

The inlet assembly 17, through which the mixture of raw gasoline, air and steam enter the vapor space of the still at 6, may take any convenient form. Most desirably it should be adapted to deliver the air-steam mixture at high velocity into the liquid-vapor stream of hydrocarbons before the latter enters the vaporizer, thus effecting a preliminary commingling of the air and steam with the hydrocarbons. Since the vapor space above the liquid level 19 normally maintained in the vaporizer is relatively large, ample further opportunity is therein afforded for the desired intimate and uniform commingling of the air and steam with hot hydrocarbon vapors and for the desired polymerizing or other action on the hydrocarbons to be initiated.

Next, the vaporous mixture passes from the vapor space of the vaporizer through line 21. In case it is desired further to promote thorough and uniform commingling of the cracked distillate vapors with the air and water vapor prior to exit of the vapor mixture from the vaporizer, baffle means (not shown) may be provided in the vapor space, in such arrangement relative to the inlet 6 and outlet to vapor line 21 as to compel all the components of the mixture to travel together by a circuitous path before reaching said outlet, thus also somewhat prolonging the period of pre-treatment.

Said vapor line 21 delivers the vapor-gas mixture into the lower part of a preliminary treating tower 22, wherein it intimately contacts a body 23 of contact material, in this instance metallic zinc in the form known as "mossy zinc," of such character as to promote precipitation or deposition of gummy and tarry polymers. This contact material is supported on perforated plate 24 located somewhere above the point where the vapor-gas mixture enters the tower on a tangent, as indicated at 25. In a typical instance, this tower, which serves as a "knock-out" box or separator for removal of most of the heavy polymers from the vapor-gas mixture prior to its further treatment, may be 3 feet in diameter and 8 feet high, and the body of mossy zinc supported on perforated plate 24 may be approximately 3 feet thick vertically.

A certain amount of relatively heavy reflux oil, derived from a later stage of the process as will be presently explained, is introduced into tower 22 in such manner as to contact with the vapors as they pass through the mass of mossy zinc, and thus to aid the action of the zinc in causing a major portion of the heavy polymer tars and gums carried by the gasoline vapors to drop out. Such heavy reflux oil may enter the tower either through line 26 discharging just above the plate 24, or through line 27 discharging above the surface of the zinc mass 23, or through both these lines, each of which is suitably valved to afford the necessary control and adjustment. In any case, the number and size of the apertures in plate 24 are so correlated to the volume of vapors passing upwardly through the plate that practically none of the reflux oil introduced into the

tower is permitted to drop through the apertures or perforations in the plate. The hot heavy reflux oil dissolves and continuously removes from the zinc mass the tars, gums and other relatively heavy, high-boiling impurities deposited therein, which are then carried out with the heavy reflux oils through overflow pipe 28 which conducts them down into the lower section of the tower below plate 24. Especially effective action of the reflux oil is attained in dissolving the aforesaid impurities and keeping clean and active the zinc surfaces of the contact mass in tower 22, if all or most of said reflux oil is introduced thereto through the lower inlet 26. Reflux oil thus introduced is carried upwardly through the entire mass of contact material, in a state of extreme agitation and turbulence, by the rapid upflow of vapors through apertured plate 24.

The vapors, freed in large part, at least, of gummy and tarry polymers, pass from tower 22 through line 29 into the lower part of a second treating tower 30, containing a body 31 of contact material comprising zinc in oxidized condition. This mass of oxidized zinc material accomplishes final treating of the hydrocarbon vapors insofar as concerns de-gumming, de-colorizing, sulphur reduction and sweetening. The second tower, and the body of contact material contained therein, are desirably much larger than the preliminary treating tower 22 and body 23 of contact material therein contained. In a typical instance, tower 30 may have an inside diameter of 6 feet and vertical length of 26 feet. The mass of oxidized zinc material therein may be 16 to 20 feet in depth, and is supported on a perforated plate or false bottom 32 located above the point of entry of vapor line 29 and spaced 3 feet or so above the tower bottom proper. These figures merely illustrate typical good practice and are in no sense restrictive. A clean-out or discharge opening 33 is provided for removal of the contact material from tower 30 when this becomes necessary or desirable.

After passing upwardly through mass 31 of oxidized zinc material in tower 30, the vapors leave this tower through line 34 and enter the lower part of tower or column 35 which constitutes an after-fractionator and is for the purpose of making final separation of any residual relatively heavy constituents, and controlling the final end point of the finished gasoline as may be desired by the refiner. This tower 35 may take the form, for example, of a fractionating column of the bubble tray type; but any type of column suitable for effecting the desired fractionation may be employed.

Refined and fractionated gasoline vapors leaving the upper part of the column 35 through vapor line 36, give up heat to incoming raw gasoline charge in heat exchanger 4, and are then condensed in condenser coils, indicated diagrammatically at 37, contained in condenser box 38. The refined gasoline condensate passes, together with uncondensed gas and vapor, through condensate line 39 into separator 40. From this separator, uncondensable gases are vented from the system through line 41 containing regulator 41^a which maintains a predetermined back pressure upon the treating system. The refined liquid gasoline constituting the finished product is conducted from the separator through line 42 to storage tanks. A small pump 43 is provided to take some finished gasoline from separator 40 through line 44 and to pump the same through

line 45 to the top of the fractionating column 35 to provide reflux for said column.

In column 35, a relatively heavy fraction in the nature of a light gas oil is separated and accumulates in the bottom of the tower as indicated at 46, which is suitable to serve as the "heavy reflux oil" hereinabove referred to for providing reflux liquid in the preliminary knock-out box or tower 22. This hot fraction collecting in the base of tower 35, or such portion of it as may be desirable to use for the purpose, is accordingly conducted through line 47 and continuously delivered, still hot, to tower 22 through inlet 26, or through both inlets 26 and 27, as hereinabove described. Any surplus not required for use as a reflux or washing medium in tower 22 may be conducted by suitable piping connection (not shown) directly into surge tank 43, into which are also conducted heavy polymer fractions and heavy bottom fractions from towers 22 and 30 through lines 49 and 50, respectively. From the surge tank, pump 51 picks up these relatively heavy fractions or residues through line 52 and delivers them through line 53 back into the vaporizer 7 where they are denuded of any gasoline naphthas which they may carry. Accumulation of heavy bottoms in the vaporizer may be continuously or intermittently withdrawn therefrom through residuum line 54, valved at 55, and delivered to fuel storage or otherwise disposed of. The large body of relatively heavy and high-boiling bottoms or residuum thus accumulated and continuously maintained in the vaporizer, substantially half-filling the same, provides a large-capacity storage medium for heat units supplied thereto by the heating furnace therebelow. The temperature of this large body of residuum can easily be held substantially constant, thus ensuring substantially constant or uniform rate of vaporization of the liquid portion of the raw distillate charged to the vaporizer, and a substantially constant supply of cracked distillate vapors for a given rate of feed of such raw distillate into the vaporizer at inlet 6. This is obviously an important advantage because it greatly facilitates achieving smoothly continuous operation of the process as a whole.

Towers 22 and 30 are also provided with valved bottom drain connections 56 and 57, respectively, for discharging accumulated heavy liquid matter into sewer or sump 58, when desired. Column 35 may be provided with a clean-out or discharge outlet as indicated at 59.

Towers 22 and 30 are desirably provided in their upper portions with steam inlet connections 60 and 61, respectively, for a purpose which will hereinafter appear.

All the parts of the system, from the vaporizer 7 clear through to and including the heat exchanger 4 are desirably heavily lagged with insulation, indicated at 62, for example, in order to maintain the temperature of the vapors sufficiently above that at which the desired gasoline product will condense, until after the refined vapor-gas mixture has left the top of the after-fractionator column 35.

The amount of air and steam employed in operating as above described may vary considerably depending upon the type, analysis and other characteristics of the particular raw distillate to be refined, the required specifications of the finished gasoline to be produced, and similar practical considerations. Very small proportions of oxygen and of steam are sufficient to produce very noticeable beneficial effects. On

the other hand, it is undesirable to use either oxygen or steam in substantially larger proportion than is necessary to accomplish the desired results. The use of too much oxygen would adversely affect, for example, the color of the finished gasoline; and it is obvious that it should never be employed in such large proportion as to form a combustible mixture with the hydrocarbon vapors. In general, the proportion of oxygen employed may vary from about 0.1 pound, to about 0.4 pound, per 42-gallon barrel of raw mineral oil to be refined, which is equivalent to from about 0.03 to about 0.12 per cent by weight; while the presence of a small percentage of moisture in the vaporous mixture leaving the vaporizer, on the order of 0.1 to 1.0 per cent by weight, represents good practice. These ranges are not to be taken, of course, as rigidly fixed or absolutely limited, but only as indicative of bounds outside of which it is ordinarily unnecessary to go in practicing the invention. It will be observed that even the maximum limits indicated correspond to a relatively very small volume percentage of oxygen and moisture, respectively, in the initial mixture thereof with the vapors of the mineral oil to be refined. It is to be further understood that the oxygen is not necessarily employed in free condition, but that it may be supplied as a compound capable of yielding it or making it available in active form under the conditions of operation. Many such compounds or combinations are known in the art and require no specific description here.

In employing the present process to treat a cracked gasoline distillate of the general type assumed in the specific example above given, the use of 0.176 pound of oxygen (represented by 10 cubic feet of air at 60° F. and atmospheric pressure), per 42-gallon barrel of the raw distillate charged to the still or vaporizer, represents average good practice. Otherwise stated, this means that in the hot initial or pre-treating mixture described in the above specific example, air is present in about 1.1 per cent by volume.

The operating temperatures employed in practicing the process are capable of considerable variation while still realizing in substantial measure the benefits of the invention. They should be high enough, of course, to maintain substantially in vapor phase the desired components of the raw mineral oil product to be refined, until the refining treatment of the vapors has been effected to the extent desired. Thus, in the specific example hereinabove given, the body of relatively heavy liquid substantially half-filling the still or vaporizer 7 to the level indicated at 19 may be maintained at approximately 400° to 425° F.; while the vapor-gas mixture leaving the vaporizer through line 21 may be at a temperature approximating 390° to 400° F., that is, at approximately the normal mean boiling temperature of the raw distillate, or slightly above. The raw cracked distillate, together with the proper proportion of the air-steam mixture, is charged into the vaporizer continuously at a substantially constant rate which may be regulated and controlled as desired by valve means provided in the respective feed lines. Under these conditions, the temperature in the knock-out box or tower 22 is on the order of about 380° to 390° F.; the vapors enter the oxidized zinc contact tower or column 30 at from

about 370° to 390° F. and leave the top of the contact bed at from about 340° to 350° F.; while the vapors leaving the after-fractionator 35 are at a temperature approximating 300 F. The foregoing assumes, of course, effective heat insulation of the various parts of the installation referred to. All the temperatures mentioned are of course variable in practice, depending upon the specific characteristics of the raw charging stock to be refined and what end point is desired for the finished gasoline, as well as upon the operating pressure maintained in the system and other practical considerations. The specific temperatures above given therefore merely represent average good practice in a typical instance, assuming operation under a superatmospheric pressure of about 5 pounds per square inch.

In carrying out the process of the invention, it is found desirable to operate the treating system under moderate superatmospheric pressure which, however, need seldom exceed 15 to 20 pounds as a maximum. More usually, when operating on the type of raw distillate and employing the type of apparatus installation described in the above specific example, the operating pressure is on the order of 5 to 10 pounds per square inch above atmospheric, the degree of pressure being capable of close regulation and control through suitable adjustment of a back-pressure control valve, for example, such as that indicated at 41^a. Moderate superatmospheric pressure has the advantage, among others, of apparently rendering more efficient the desired action of the contact materials upon the vapors passed therethrough.

The sweetening of the hydrocarbon vapors and reduction of total sulphur, together with removal of residual small proportions of heavy polymers, is accomplished mainly or almost entirely in the second and larger contact tower 30 which contains contact material comprising oxidized zinc. By first accomplishing most of the heavy polymer removal in knock-out tower 22, so that there is comparatively little deposition of gummy and tarry materials in the oxidized zinc contact mass 31, the operating life of this latter is greatly prolonged, with resultant important economies in operation.

The contact mass 31 employed in the second, and in this instance the final, contacting treatment of the vapor-gas mixture should be metal-liferous, but it is essential that the metal content be present, at least in substantial part, in oxidized condition, since this is found to be indispensably essential to enable effecting the desired sweetening action upon the hydrocarbon vapors which it is a principal function of this contact body 31 to accomplish. The sweetening action of the metal oxide contact material can be prolonged substantially if a small amount of water vapor is present in the initial mixture of hydrocarbon vapors and oxygen. This may be conveniently ensured by saturating with water vapor the air employed as the source of oxygen. Zinc in oxidized form is particularly suitable as the active component of this contact mass and is therefore mentioned in describing the specific example given hereinabove. This contact mass may consist, for instance, of small fragments of a mixture of equal parts by weight of commercial zinc oxide and plaster of Paris with water, which has been allowed to set or harden and has then been crushed and screened to desired size. Typically suitable sizing for such material is such that practically all of it will pass a $\frac{3}{8}$ inch screen

but will be retained on a $\frac{1}{8}$ inch screen. This gives a mass offering more resistance to vapor flow than the vapors encounter in passing through tower 22, and a longer period of time, on the order of several minutes, say two or three minutes in a typical instance, is required for the vapors to pass through it. However, in refining certain types of raw charging material, this contacting period with the mass comprising oxidized zinc can be reduced to one minute or even less with satisfactory results.

Although zinc in oxidized condition is recommended more particularly for use in the second or sweetening contact treatment in tower 30, it is also very effective in removing gummy and tarry polymers and may therefore be employed for this purpose, as well as for sweetening, within the broad scope of the invention. But since it is more difficult to keep contact material consisting largely or mainly of oxidized zinc or other oxidized metal free from the extensive deposits of gums, tars and other heavy carbonaceous polymers etc. which would form thereon if used in the primary or knock-out contact step, considerable advantage is gained by using it primarily for sweetening rather than for de-gumming.

It has been found that if the oxidized zinc content of the contact mass 31 is in the form of one or more of the numerous oxychlorides of zinc, which may also be regarded as zinc oxide-zinc chloride combinations or complexes, exceptionally good results are attainable. Such oxychloride contact material contains water of hydration in proportion varying with the conditions under which it was produced; and in order to maintain it at highest operating efficiency for the maximum period of time, it is therefore found advisable to ensure that the initial vapor-gas mixture leaving vaporizer 1 shall contain a small percentage (e. g., on the order of 0.1 to 1 per cent by weight) of moisture which may be introduced continuously at a proper regulated rate into the vapor space of the vaporizer, along with the air or otherwise as may be most convenient. In some cases, the raw distillate charged into the vaporizer may contain moisture in quantity wholly or partly sufficient for this purpose, and this should of course be duly taken into account. The presence of a small amount of water vapor in the initial vapor-gas mixture appears to exercise a beneficial action tending to maintain an equilibrium among the crystalline compounds comprised in the zinc oxychloride mixture or complex.

In case it finally becomes necessary to re-vivify the oxidized zinc contact mass, tower 30 may be simply cut out of the system and the flow of the vapor-gas mixture through line 29 diverted through a duplicate or spare tower and contact mass (not shown) of the same character. The method of re-vivifying the spent zinc oxide contact mass, although simple and economical, is very effective and constitutes an important specific feature of the present invention. It is only necessary to introduce steam into the tower through inlet connection 61 and force it through the contact mass therein. In practice, it is found advantageous to use steam at a temperature somewhat higher than 212° F., say 300°-350° F., since this not only speeds up the action and shortens the time required for re-vivifying, but it also leaves a zinc oxychloride mass of such chemical composition and physical structure (finely porous) as to render it particularly effective in using it subsequently for contacting pur-

poses in the oil refining process. Although any heavy liquid polymers adhering to the contact surfaces of the oxidized zinc material of contact mass 31 are also removed to a considerable extent by steaming the mass as described, it becomes increasingly difficult to effect this cleansing and re-vivification as times goes on. However, when the steaming action eventually ceases to be effective due to excessive accumulation of heavy tarry and other carbonaceous deposits, it is feasible to burn these off under carefully controlled conditions in order to re-vivify the contact mass.

Various methods of preparing zinc oxide-zinc chloride combinations or complexes of the oxychloride type are well known to chemists and require no detailed description here. It may be stated that, in general, oxychloride complexes wherein the molecular ratio ranges from $1\text{ZnCl}_2:7\text{ZnO}$ to $1\text{ZnCl}_2:20\text{ZnO}$ have been found particularly effective for use in a contact mass employed in the type of oil refining process herein described; and therefore, for the purposes of this invention, the conditions of its formation are most desirably controlled and regulated to attain a molecular ratio within the range above mentioned. However, the invention is in no sense restricted in this regard since that molecular ratio range can be departed from substantially in oxychloride contact masses of this general character while still realizing the benefits of the invention to a substantial extent.

Although the metallic surfaces of the contact mass contained in the first or primary contact treating tower 22 can be kept substantially free of gums and tars by the washing and dissolving action of the reflux oil employed as described, those surfaces may eventually become coated to a greater or less extent with carbonaceous deposits not soluble in the reflux oil nor easily dislodged therefrom by its washing action. When this occurs to such an extent as to noticeably decrease the efficiency of this contact mass in its de-gumming action, it is advisable to disconnect this tower from the system and to re-vivify the contact mass, meanwhile running the vapors through a spare or duplicate de-gumming contact tower (not shown) connected in parallel with tower 22. By introducing steam into tower 22 through inlet 60 and forcing it through the contact mass therein, in a manner similar to that hereinabove described for tower 30, the surfaces of the mossy zinc metal can be effectively freed of practically all such tenaciously adherent carbonaceous deposits of the character above-mentioned.

The refined gasoline product condensed from the after-fractionator 35, may be optionally subjected to a washing treatment, either with water alone or with a very dilute solution of a suitable alkaline agent, such as caustic soda.

The present process is especially advantageous to employ in cases where the mineral oil product to be refined is free or relatively free of gum-forming constituents and requires merely to be sweetened in order to render it fit for commercial purposes. Thus, in applying the principles of the invention to the refining of a straight run gasoline that is sour, the necessary sweetening may be effected, as well as reduction in total sulphur content, by commingling the sour gasoline vapors in heated condition with a small proportion of oxygen supplied in the form of air and, after allowing a brief reaction period to elapse, then passing the hot vapor-gas mixture through a metal oxide contact mass to

effect the desired sweetening; then subjecting the sweetened vapors to after-fractionation, if desired, before condensing a refined gasoline product therefrom. The metal oxide contact material employed may desirably comprise some oxidized form of zinc, such as zinc oxide or zinc oxychloride, since this, in addition to sweetening, will also function effectively to remove any small proportion of gums that may be incidentally carried by the vapors undergoing treatment. In the case of such a straight run gasoline, because of the absence of any large amount of gum-forming constituents to be removed, it is also feasible to replace the oxidized zinc content of the permeable contact material, either wholly or in large part, by lead oxide which, although relatively ineffective as a de-gumming agent, is very effective as a sweetener.

It is desirable also, in thus refining a sour straight run gasoline, to employ air saturated with moisture for commixture with the gasoline vapors prior to the contact treatment, since this tends to prolong the effective operating life of the metal oxide contact material.

For example, hot raw straight run gasoline vapors may be led directly from the main fractionating column of a straight run gasoline distillation plant of the usual type, the required small amount of air, most desirably saturated with water vapor, may then be mixed with the hot hydrocarbon vapors, and the mixture then passed through a tower containing a permeable contact mass consisting of fragments of a hard, set mixture of lead oxide and plaster of Paris. From the hot vapor mixture leaving this contact tower, a finished gasoline is condensed which is virtually sweet to doctor test and also has a lowered total sulphur content. This mode of procedure entirely obviates the necessity for treating sour straight run gasoline with sodium plumbite solution to effect sweetening, which has been a rather general practice heretofore. The present novel process just described has the advantage of being substantially simpler and more economical.

The sweetening action effected by passage of the vapor-gas mixture through a metal oxide contact mass apparently differs in its chemical mechanism from the sweetening action effected by such well known processes as those involving treatment with sodium plumbite or alkaline hypochlorite. This seems to be evidenced by the fact that the pleasant odor characterizing finished gasoline produced by the present process is different and easily distinguishable from the odor of gasoline that has been sweetened by either the sodium plumbite treatment or hypochlorite treatment. It is generally supposed that by these last-mentioned treatments, certain hydrocarbon sulphur complexes responsible for sourness are converted into compounds of the type represented by the formula $\text{R}-\text{S}-\text{S}-\text{R}$ (R being a hydrocarbon radical) which are negative to the doctor test. It appears possible that, by the present process, the objectionable hydrocarbon-sulphur complexes are converted into compounds of the thioether type represented by the formula $\text{R}-\text{S}-\text{R}$, also negative to the doctor test. Whether or not this is the correct explanation, the fact remains that the present process produces a sweet finished gasoline of distinctive pleasant odor and, moreover, of substantially reduced sulphur content. This reduction in sulphur content, not achieved in ordinary "sweetening" treatments, is

a noteworthy and important feature of the present process.

Although, as pointed out, the practice of the invention is not confined to the employment, in the treatment of the vapor-gas mixture with a metal oxide contact material, of a zinc oxide material for that purpose, a zinc oxide material is nevertheless outstandingly desirable because of its highly effective action both as a sweetening agent and also as a degumming and de-colorizing agent. In its ability to function satisfactorily in these several different capacities, zinc oxide material is found to be superior to other metal oxide materials, as a rule, for employment in the present process. The terms metal oxide material and zinc oxide material are to be understood as employed in a broad sense to include not merely oxides per se but other conditions of oxidation broadly, such as basic or oxy-salts, especially oxychlorides, hydrated oxides, and the like, capable of functioning as described under the conditions herein set forth.

Commercial zinc oxide, commonly containing around 5% of basic lead sulphate as an impurity, is typically satisfactory for use in the practice of the present process, usually in association with a carrier and binder, such as plaster Paris, as in the specific example given hereinabove. Where zinc oxychloride contact material is to be used, an effective way to prepare it is to saturate with zinc chloride solution inert porous material such as brick, tile or the like, and then steam the mass thoroughly to produce the desired labile and sensitive basic chlorides or oxychlorides of zinc so effective in their sweetening action. Oxidized ores of zinc constitute another available form of zinc oxide material suitable for use in practicing the process. Among other types of carriers and binders which may be associated with oxidized zinc in any of its forms to produce satisfactory zinc oxide contact material, are fuller's earth, certain types of cements, clays, and the like, pumice, firebrick, etc. Zinc dust, which commonly contains around 3% of zinc oxide, may be employed

to form contact masses having pronounced sweetening action.

Other metal oxides, in addition to lead oxide, which may also be employed as such or in conjunction with inert carriers, etc., as metal oxide contact material for sweetening, within the scope of the invention in its broader aspects, are the oxides of iron, copper and magnesium, especially in their hydrated forms. However, like lead oxide, these various oxides are not particularly effective as de-gumming or decolorizing agents.

What is claimed is:

1. In the art of refining relatively low-boiling petroleum distillates containing deleterious contaminants including sulphur compounds, the process which comprises subjecting hot vapors of such a distillate to the conjoint action of small proportions of oxygen and water vapor and without adding any other active reagent, separating resultant heavy reaction products from the vapors while passing them in contact with reflux liquid comprising condensed components of such vapors, then passing the vapors, while still hot, through a permeable mass comprising solid contact material containing oxidized metal whereby to effect sweetening, and condensing a refined relatively low-boiling product from the treated vapors.

2. The process of refining a sour crude gasoline distillate which comprises subjecting hot vapors thereof to the conjoint action of relatively small proportions of air and water vapor and without adding any other active reagent, separating resultant heavy reaction products from said vapors while passing them in contact with reflux liquid comprising condensed components of such vapors, then passing the vapors, while still hot, through a permeable mass comprising zinc in oxidized condition to effect sweetening of the vapors and removal therefrom of any residual heavy reaction products, and condensing a refined gasoline from the treated vapors.

ROSCOE D. HOWARD.