

May 26, 1942.

L. U. FRANKLIN ET AL

2,284,272

PROCESS FOR SWEETENING LIGHT PETROLEUM DISTILLATES

Filed July 12, 1939

2 Sheets-Sheet 1

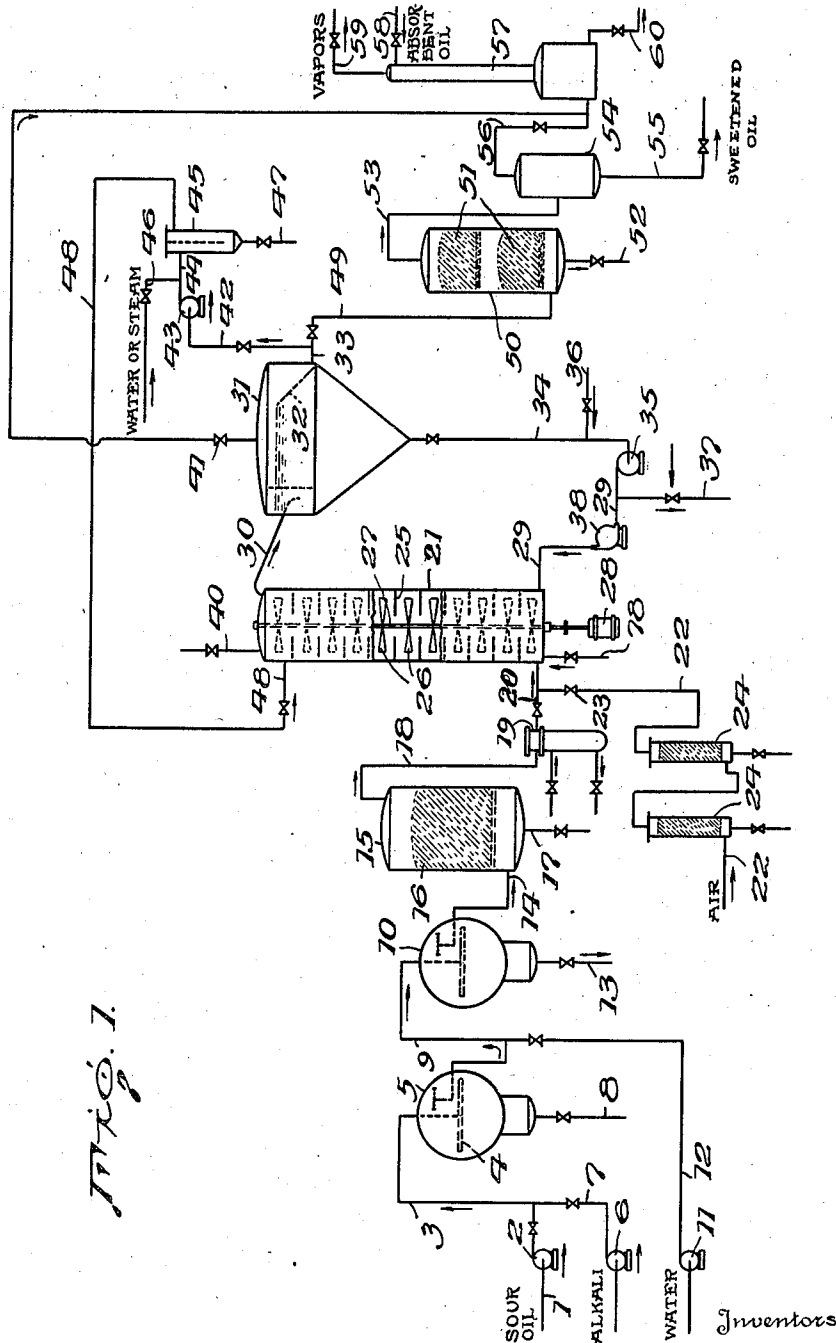


Fig. 1.

LESLE U. FRANKLIN  
WALTER H. WEEKS  
JACK W. HARRIS

By *G. M. Hough*  
their Attorney



# UNITED STATES PATENT OFFICE

2,284,272

## PROCESS FOR SWEETENING LIGHT PETRO- LEUM DISTILLATES

Leslie U. Franklin, Walter H. Weeks, and Jack W. Harris, Port Arthur, Tex., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

Application July 12, 1939, Serial No. 284,117

12 Claims. (Cl. 196—29)

Our invention relates to sweetening sour hydrocarbon oils, more particularly light petroleum distillates such as gasolines, naphthas, kerosenes, furnace oils and the like, that is to say, to processes for treating oils of the character indicated, containing "sour" and malodorous sulfur impurities, such as mercaptans, to convert such impurities into sulfur compounds of less objectionable character, whereby the treated oils are rendered sweet to the "doctor" test and free from disagreeable odor.

More particularly, our invention relates to improvements in what is known in the petroleum art as "copper sweetening," i. e., a process in which sour oil to be treated is contacted with a treating agent comprising a compound or mixture of compounds capable of ionizing to form cupric and chloride ions, for example, cupric chloride, together with a substantially inert solid carrying agent.

The earliest proponents of copper-sweetening processes referred, in the main, to two general types of processes, i. e., those in which solutions of copper salts were used as the treating agents, and those in which solid copper salts, frequently distributed on adsorbents, such as clay, fuller's earth or the like, were used.

In processes wherein the oil is treated while in the liquid phase, it is now generally conceded that sufficient moisture must be present to permit ionization. Naturally, ionization is not a problem in those types of processes in which definite solutions, as distinguished from slurries or solid contact masses are used. However, the solution-type processes involve serious corrosion problems.

For various reasons, the so-called "percolation-type" processes have not proved commercially successful in the treatment of cracked distillates and other oils containing substantial amounts of potential gum- and color-forming constituents. The oxygen stabilities of such oils tend to be seriously reduced after sweetening by this type of process and the treated oils rapidly develop gum and color upon storage. Nor has this type of process been successful with respect to oils containing relatively high amounts of mercaptans, regardless of whether such oils are cracked or straight-run distillates.

A third type of process, known as the "slurry-type" process, has also been proposed, in which the sour gasoline is mixed with the treating agent in more or less dry form, usually in the presence of a finely-divided adsorbent material, such as fuller's earth, adsorbent clay or the like, and the

sweetened gasoline is finally separated and removed. A limited amount of moisture must be present, but processes of this type do not give rise to serious corrosion problems; there is no independent aqueous phase.

The prior art "slurry-type" processes have resulted in little or no commercial adoption, except possibly with respect to certain oils presenting little or no sweetening difficulties. Among the factors contributing to this, we believe, were the following:

(1) Bad effects on oxygen stabilities of the oils tested; caused by operation in such manner as to leave oil-soluble copper in the oil, plus the difficulty of removing the same in many cases. (Process features which make it possible to overcome this difficulty are set forth and claimed in the copending application of Leslie U. Franklin and Walter H. Weeks, Serial No. 284,116, filed concurrently herewith.)

(2) The use of highly adsorbent solid carrying agents, such as fuller's earth, clays and the like. (The use of non-adsorbent, but absorbent, non-polymerizing, finely divided asbestos in this type of process is highly advantageous, as set forth and claimed in the copending application of Leslie U. Franklin, Serial No. 285,636, filed July 20, 1939.)

(3) Improper regulation and control of moisture content and "texture" of the solid sweetening agent.

We have discovered that certain hitherto unknown considerations affecting factor (3) above are of the utmost importance in maintaining efficient and uniform operation.

Thus, in one prior art process, the moisture content of the treating agent is initially low, but gradually increases to around 9 per cent, followed by removal of the agent, re-drying it and re-use as before.

We have discovered that operation in this manner does not produce satisfactory results, for a number of reasons, and that variation in water content of the chemical treating agent (other conditions such as the nature of the oil treated, the character of the carrying agent, the type of apparatus used and the like remaining the same) must be held within far narrower limits during normal operation in order to achieve satisfactory results.

In a system wherein the moisture content continuously varies over a wide range, high efficiency is attained only at relatively infrequent intervals and for brief periods. Moreover, the difficulty tends to be cumulative in effect, because, when

a low state of efficiency is reached, the difficulties of regeneration are vastly increased, as is always the case in this type of process whenever regeneration is permitted to lag behind sweetening to such extent as to "overwork" the treating agent, even for brief intervals of time.

In accordance with our invention, such disadvantages are overcome, and more satisfactory operation is achieved than has heretofore been realized.

Operating in all cases within the limits of from 0.5 per cent to 9.0 per cent moisture content, or in the case of asbestos as a carrying agent, between limits of from 0.5 per cent to 7.0 per cent H<sub>2</sub>O, we do not allow the moisture content of the treating agent to vary over this entire range, but confine it as far as possible to an extremely limited range. More specifically, we never permit the maximum and minimum moisture contents at any times during regular continuous operation to vary over more than a 2:1 ratio.

The moisture contents referred to herein represent percentages of H<sub>2</sub>O by weight, on a basis of the entire mass of solid treating agent (including the carrier).

Thus, we have found that in most full-sized commercial apparatus, with certain exceptions referred to hereinbelow, it is necessary to maintain the moisture content at a very low point. In many actual instances, variation of moisture content over a range wider than from 0.5 per cent to 1.0 per cent results in a serious loss of efficiency; the stage at which the desired "texture" of the solid treating agent is destroyed is rapidly reached in such cases if the variation in moisture content is allowed to exceed the range noted, especially on the high side. In other cases, a range of from 1.0 to 2.0 per cent, or from 3.0 to 6.0 per cent, can be maintained without impairing sweetening and regenerating efficiencies. These figures relate more particularly to cases wherein asbestos is used as the carrying agent. With fuller's earth or other highly adsorbent solid as the carrying agent, somewhat higher ranges (still within the 2:1 ratio) are called for, i. e., the exact location of the range on the moisture percentage scale varies somewhat as between individual carrying agents.

Referring again to the instances mentioned, it may be observed that in many cases the more difficult it is to oxidize the mercaptan content of the oil, the lower will be the actual moisture content carried.

Regulation of the moisture content is accomplished by maintaining the system at such a temperature as will prevent undue accumulation of moisture, and by controlled addition of moisture when and as necessary.

It must not be inferred, however, that we deliberately try to vary the moisture content up and down within the narrow range noted. On the contrary, we maintain as uniform a moisture content as possible, at some point within the range desired, as for example, at about 0.75 or 0.8 per cent. Some variation is bound to occur, however, but we do not permit it to exceed the 2:1 ratio indicated. The fact that an average moisture content of, say, 1 per cent is desirable in one case, and a moisture content of 3 per cent is desirable in another, does not mean that in the first case the moisture content can be permitted to vary up to or beyond 3 per cent at times. In any given operating instance, the

range of moisture variation should be carefully controlled for good results.

Moisture is, of course, added when and as necessary. Strikingly enough, such moisture addition is often necessary even when operating both at temperatures high enough to remove moisture as formed and at lower temperatures; temperature alone does not entirely govern the tendency of the treating agent to gain or lose in moisture content, respectively.

Thus, we have found that if the solid treating agent is efficiently ground as it recirculates in the system, a higher average moisture content, with correspondingly lower operating temperatures, can be carried and is in fact desirable. The same oil, which without efficient grinding requires an average moisture content in the treating agent of around 0.8 per cent, and maintenance of operating temperatures above about 100° F., can be sweetened at an even greater efficiency and lower cost at a temperature below 100° F. and with a sweetening agent maintained at an average water content of from 3 to 6 per cent, when highly efficient grinding means are provided in the cycle. In one specific case, for example, we found that under these conditions (using asbestos as the carrying agent) the permissible variation, at least after an initial or "conditioning" period to be referred to hereinbelow, was from 3 to 6 per cent. Drier material resulted in poor regeneration, with a greatly augmented tendency to leave oil-soluble, insufficiently regenerated cuprous compounds in the final gasoline product. Higher moisture content resulted in impairment of the "texture" of the sweetening agent, which in this case was maintained in a highly effective and highly flocculent condition. It may be noted at this point that we always aim to maintain the agent in a flocculent or semi-flocculent condition, as we have found that best results are secured only when this condition is reached or approached. With excessive variation in moisture content, it is impossible to achieve this highly desirable and important result.

The exact causes underlying this particular necessity are not so fully understood as would justify us in predicating our invention upon any particular chemical or physico-chemical theory, and it is unnecessary for us to do so. We may state, however, that we have discovered that a high state of operating efficiency can only be obtained when the chemical treating agent is maintained throughout in a proper physical condition, or "texture," i. e. in a flocculent or semi-flocculent condition, and that, while the average moisture content effective to give the optimum texture will vary considerably in different cases, too wide a variation of moisture content in any individual case will make it impossible to maintain the desired texture over commercially satisfactory periods of time.

We have referred hereinabove to an initial operating period or "conditioning" period. During such period the moisture content may sometimes increase from a point considerably below the minimum moisture content subsequently maintained, or it may decrease from a point considerably above the desired maximum. This fact is intimately connected with another feature of our invention, which we shall now proceed to set forth.

We have observed that the treating agents of the prior art were strongly hygroscopic in character, and that it was very difficult to maintain

the desired uniformity of moisture content when they were used. We have discovered, however, that a highly advantageous and effective and less inherently hygroscopic sweetening agent may be prepared by mixing cupric sulfate, NaCl or NH<sub>4</sub>Cl and finely divided asbestos, aging the mixture in the presence of some moisture, and then drying the mixture down to around 0.5 to 1.0 per cent H<sub>2</sub>O content at a temperature of about 95° to 100° F. or higher. Drying at temperatures substantially below 90° F. is not so effective. When the treating agent has once been treated in this manner, it is, for some reason not fully understood, far less hygroscopic in subsequent operation; that is to say, it does not possess the strong tendency to accumulate moisture in the system that has been characteristic of prior art materials. Hence, such "pre-conditioned" material aids in carrying out our process, in which excessive variation in moisture content is avoided.

Here again, we do not wish to limit ourselves to any particular theory of operation. The following facts may, however, be significant:

(1) This feature of our invention relates only to mixtures containing Na<sub>2</sub>SO<sub>4</sub> and NaCl;

(2) The decomposition point of Na<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O is around 65° F.; that of the higher hydrate, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, is around 92° F.; and

(3) The addition of anhydrous Na<sub>2</sub>SO<sub>4</sub> to a treating agent comprising fairly dry Na<sub>2</sub>SO<sub>4</sub> and NaCl (enough water being present to form hydrates) tends to have a strongly dehydrating effect.

It may therefore be that the absence of both the hepta- and deca-hydrates, or the presence of anhydrous Na<sub>2</sub>SO<sub>4</sub>, exerts a marked depressing effect upon the water-accumulating or hygroscopic tendency of the sweetening agent, and this in turn may account for the fact that drying at temperatures below 90°-100° F. has not been found effective, while drying at higher temperatures has. But, whatever the theory, this pre-conditioning step is definitely of value.

When temperatures of 100° F. or more are maintained in the system, it is not absolutely essential that the treating agent be dried prior to use in the process. Such drying or pre-conditioning takes place reading in the system itself, under such conditions. Moisture should not be added, however, until the moisture content of the agent is down to 0.5 to 1.0 per cent; thereafter moisture is added, when and as necessary to maintain the uniformity referred to above.

Where lower temperatures are used (or even where higher temperatures are used, if desired) the partial drying step may be carried out prior to adding the chemical agent to the system, and preferably after aging the mixed chemicals and absorbent at a relatively high moisture content, as for example in a humid atmosphere. Such aging is useful in order to complete the reaction forming CuCl<sub>2</sub>; the presence of moisture accelerates the rate at which the reaction approaches its equilibrium. Aging is therefore best effected prior to drying, whether such drying takes place in the system or outside it. Addition of HCl also increases the amount and rate of CuCl<sub>2</sub> formation.

In those cases where the average moisture content to be maintained in the system is above 1 per cent, for example, in the instance mentioned above where variation outside a range of from 3 to 6 per cent moisture content is to be avoided during continuous operation, the moisture content of the treating agent may be

increased to some extent (after the partial dehydration step set forth above) prior to putting it into the system, as for example by exposure to humid atmosphere, by steam treatment, or by spraying it with water. The amount of moisture so added need only be such as to bring the moisture content of the treating agent to a point lying within the desired range.

If desired, however, the partially dried agent may be simply put into the system, moisture being added in somewhat larger amounts than are necessary later, until the moisture content of the treating agent in the system is within the desired range.

Thus, where a low average moisture content (below 2 per cent) is to be maintained in the operation, we may follow any of the following procedures:

(1) Dry the sweetening material—at a temperature of 100° F. or higher—down to a moisture content of from 0.5 to 1.0 per cent prior to putting it into the system;

(2) Introduce the aged material into the system without pre-drying it, and effect the drying step in the presence of sweet oil, prior to charging sour oil to be sweetened;

(3) Introduce the aged material into the system without pre-drying it, and reduce the moisture content down to 0.5 to 1.0 per cent in the presence of the sour oil being charged; or

(4) A combination of (2) and (3) above, i. e. drying part of the way with sweet oil and the rest of the way in the presence of the sour oil to be sweetened.

When higher average moisture contents (above 2 per cent) are to be maintained in the system, we may use any of the following procedures:

(5) Follow (1) above, and then raise the moisture content to the desired point before introducing the material into the system;

(6) Follow (1) above, but raise the moisture content after introducing the material to the system, in the presence of sweet oil, prior to charging some oil to be sweetened;

(7) Follow (1) above, but raise the moisture content in the presence of sour oil being sweetened;

(8) A combination of (6) and (7) above;

(9) Follow (2) above, and raise the moisture content either (a) in the presence of sweet oil or (b) in the presence of the sour oil to be sweetened; or

(10) Follow (3) above, and then adjust the moisture content as the sweetening operation proceeds.

Each of these procedures has its own advantages in certain cases.

In every case, however, it is important for best results that at some time prior to or during the initial phases of operation, in the moisture content of the sweetening material be at least temporarily reduced to from 0.5 to 1.0 per cent, by drying at a temperature of about 100° F. or higher.

It will be obvious that some of the procedures set forth above involve a preliminary sweetening or "conditioning" stage. Unfavorable results do not, however, occur during this period, if not unduly prolonged, for reasons which we shall now explain as fully as possible.

We have stated hereinabove that, when the range is, say, from 3 to 6 per cent moisture content, then, in the later stages of the operation, reduction of the water content below 3 per cent tends to cause retention of oil-soluble copper in

the gasoline; that much water is required, under these conditions, for effective regeneration of the spent or cuprous copper back to active or cupric copper. But, in such latter stages (i. e. after said initial period) a large part or all of the agent may not actually be present as  $\text{CuCl}_2$ ; there is a gradual tendency in operation for the  $\text{CuCl}_2$  initially added to be converted to some other cupric compound, possibly an oxychloride.  $\text{CuCl}_2$ , under nearly all conditions, is a far more active sweetening agent. On the other hand, the cupric compound formed on regeneration, other than  $\text{CuCl}_2$ , may actually be the effective sweetening agent itself in the later stages, though somewhat less rapid in action than  $\text{CuCl}_2$  in most cases. But, during the initial or "conditioning" period following introduction of the sweetening agent into the system, even when some gasoline is being charged to the system during this period, the concentration of  $\text{CuCl}_2$  in the agent is relatively high, and the agent is therefore in a highly active condition. Consequently, variation in moisture content is not as harmful at this time as it is later on.

Various methods of supplying moisture to the system, when and as required, may be employed. Thus, it may be introduced directly to the treating zone, or in the air or oil supplied to the system.

HCl may also be added. We have found, however, that addition of HCl (the purpose of which is to maintain the copper compound largely in the form of  $\text{CuCl}_2$ ), is rendered more difficult when the operating temperatures are high, as for example at 100° F. or higher. At lower operating temperatures, of, say, 60° to 70° F., and in the presence of relatively larger amounts of water, HCl is more easily added, and the amount of  $\text{CuCl}_2$  in the system may be maintained at a relatively high point.

From several standpoints, there are advantages in maintaining a relatively high average moisture content and a relatively high  $\text{CuCl}_2$  content in the treating agent. But it must be emphasized that mere addition of water will not necessarily produce the desired results. On the contrary, in many cases attempts to maintain high average moisture content result most unfavorably. The explanation of this lies in part in the necessity for maintaining the solid treating agent in a proper physical condition or "texture." Prior workers in this field do not appear to have recognized the sensitivity and narrow range of texture permissible, nor to have suggested adequate means or steps for maintaining it.

From time to time, fresh sweetening material may be added to the system, to replace that lost mechanically or otherwise. We prefer to add fresh sweetening material in relatively small quantities at frequent intervals, approaching continuous addition, rather than to add it in large quantities at infrequent periods. In this way, we avoid excessive variation of conditions in the system which would be incident to the addition of large quantities at any one time. It should not be inferred, however, that it is necessary to add fresh treating chemicals in an amount anywhere near that amount required to react stoichiometrically with the amount of mercaptans present in the oil charged.

It will be apparent from the above that our process is capable of being embodied in two fairly distinct types of operations. On the one hand, low moisture contents ranging from 0.5 to 1.5 per

cent and treating temperatures usually ranging from 100° F. to 150° F., or even somewhat higher, are carried. In this type of operation the amount of cupric chloride ( $\text{CuCl}_2$ ) actually maintained in the system, except at the start, and for brief periods following the addition of any large amount of fresh chemical, is normally very low. On the other hand, we have operations in which lower treating temperatures of, for example, from 60° to 70° F., or in any event below 100° F., are carried, and the average moisture content of the treating agent is maintained at a relatively high point, for example, from 3 to 6 per cent. In this type of process the amount of  $\text{CuCl}_2$  present as such is considerably higher.

Naturally, many operations will lie intermediate between the two types of operations just referred to. Whether the operation requires relatively high temperatures and low average moisture content, or relatively low temperatures and relatively high average moisture content, is largely determined in each case by the "texture" of the solid treating agent, and, for that reason, by the presence or absence of mechanical conditioning means. But, except for relatively brief periods following initial introduction of the solid treating agent into the system (where the moisture content of the agent, as added, must be adjusted to that desired to be maintained in the system), the limited range of moisture variation referred to above must be maintained throughout.

By controlling and regulating the moisture content of the solid treating agent, as set forth above, conditions are so maintained as to favor maintenance of the treating agent in a proper physical condition or texture, that is to say, in a flocculent or semi-flocculent state. But, in almost all cases, it will be necessary, in order to achieve low-temperature operation and relatively high moisture content, to provide means for mechanically conditioning the solid treating agent in the system. Mere agitation or mere passage of the slurry through a recirculating pump is not enough. This does not mean that our process requires more than mere agitation or pumping for good results; it does mean that with such expedients alone we have found it necessary in almost all cases to maintain the treating agent at a low moisture content, not exceeding 2 per cent at the most.

There are advantages in maintaining a somewhat higher average moisture content, when this can be done without destroying the desired texture of the treating agent—one is the fact that the  $\text{CuCl}_2$  content of the treating agent can be maintained at a somewhat higher point. To do this, however, we have found it necessary to provide grinding means located at some point in the system, through which the solid treating agent is repeatedly caused to pass during the operation. Various types of grinding means, such as ball mills, tube mills, disc grinders, impact grinders and roller grinders, may be employed.

Strikingly, the more efficient the grinding means the more truly flocculent will be the condition of the solid treating agent. It might be expected that passing a suspension of asbestos and the solid chemical or chemicals used, in oil, through an efficient grinder would tend to produce a very finely divided material and thereby to destroy whatever flocculent character the suspension possessed. The reverse is actually true in copper-sweetening processes of the slurry type. The more efficient the grinding means,

the more flocculent is the character of the suspension, and the more moisture the suspension can tolerate without losing its flocculent character or texture. Thus, low-temperature, high-average-moisture-content operations normally require and to a large extent depend upon the use of highly efficient grinding means; with less efficient grinding means, it is usually necessary to hold the moisture content at a relatively low point, with the temperature correspondingly high.

This may be due in part to the fact that very efficient grinding tends to exert a mechanical dehydrating effect upon the solid treating agent. Also, grinding tends to prevent accumulation of gummy or resinous matter on the individual suspended particles. Whatever be the reason, grinding does assist greatly in maintaining the desired flocculent or semi-flocculent texture referred to, especially in the presence of more than 1 per cent moisture.

When all factors are such as to permit the use of relatively high average moisture content and relatively low operating temperatures, the most efficient and advantageous results are secured. In this type of operation the content of cupric chloride in the treating agent tends to remain fairly high, with consequent improvement in operating efficiency; regeneration is improved and made more thorough, the tendency toward retention of oil-soluble copper in the treated oil is reduced, and the consumption of chemicals over extended operating periods is also reduced. Sweetening takes place more quickly and regeneration is also improved.

The grinding means may be located at various points in the system, as, for example, in the treating zone itself or in the recirculation line which conveys the regenerated treating agent from the separating zone back to the initial treating zone, or both.

We have also found that if the treating zone is so constituted as to secure a turbulent, cyclic flow of oil and suspended treating agent within the treating zone itself, highly efficient sweetening and regeneration are secured, and apparatus providing for such turbulent, cyclic flow is described hereinbelow.

In any event, the process is carried out by commingling the solid treating agent with a flowing stream of sour oil to be treated, in the presence of oxygen (supplied as such or in air or other oxygen-containing gas), and permitting the mixture thus formed to flow in essentially concurrent fashion through a treating zone, wherein sweetening and regeneration of the treating agent proceed more or less simultaneously and concurrently. The mixture is then transferred to a separating zone where the flow is sufficiently quiescent to permit the separation and withdrawal of the treated oil, free or substantially free from suspended treating agent. The latter, still in suspension in oil, but as a far more concentrated suspension or slurry, is then re-circulated back to the initial contact zone.

As set forth and claimed in the copending application of Leslie U. Franklin and Walter H. Weeks, Serial No. 284,116, filed concurrently herewith, it is important not to effect separation of the treated oil from the suspended treating agent at or immediately after that point in the system where the oil first shows itself sweet to the "doctor" test, but to maintain the oil undergoing treatment and the suspended treating agent undergoing regeneration in contact through a sweetening zone and a subsequent stabilizing

zone until the oil is free from cuprous chloride and cuprous mercaptides, and contains not more than a slight trace of copper in any form.

With regard to the composition of the treating material itself, we have found that the best results are secured by forming a mixture as follows:

	Parts by weight
CuSO <sub>4</sub> .5H <sub>2</sub> O	1
NaCl	2 to 4 (preferably 3)
Asbestos	0.5 to 1

As disclosed in U. S. Patent No. 744,720, the chemicals employed in the sweetening mixture may comprise iron sulfate in addition to cupric sulfate and sodium chloride, the presence of iron sulfate (either ferric, ferrous or both) being beneficial.

As pointed out in application Serial No. 285,636, filed July 20, 1939, increasing the amount of asbestos in the mixture above about 20 per cent is neither necessary nor particularly effective. Amounts of asbestos in excess of about 20 per cent simply represent an unnecessary excess of asbestos above and beyond that amount necessary to serve as an effective carrying or supporting agent.

The same conditions apply to mixtures containing fuller's earth or the like in the place of asbestos, except that asbestos is preferable from many standpoints and requires the presence of somewhat less moisture than when highly adsorbent carrying agents are used.

As aforesaid, the treating agent, after being initially prepared by mixing the above ingredients in the proportions noted, should be preconditioned, either before or after adding it to the system, by partial dehydration, preferably after permitting the mixture to age for some time.

By operating in accordance with our invention, we have been able to secure successful continuous operation on a full commercial scale over extended periods of time, sweetening a wide variety of distillates, including both straight-run and cracked gasolines, of varying degrees of "sourness." Apparatus and processing costs have been reduced, and the finished oils have been of good quality.

In addition to the objects and advantages specifically referred to hereinabove, our invention has for further objects such additional operative advantages and improvements as may hereinafter be found to obtain.

In order that our invention may be fully set forth and understood, we now describe, with reference to the drawings accompanying and forming a part of this specification, various preferred forms and manners in which our invention may be practiced and embodied, without however limiting our invention to the details of such exemplifications as are described hereinbelow, except as in the claims hereinafter made. In these drawings,

Fig. 1 is a more or less diagrammatic elevational view of apparatus for sweetening sour petroleum distillate in accordance with our invention; and

Fig. 2 is a similar view of an alternative form of a portion of the apparatus illustrated in Fig. 1.

Similar reference numerals designate similar or corresponding parts in both figures.

Referring now to Fig. 1, sour oil to be treated enters the system through a pipe 1 and is delivered by a pump 2 through a pipe 3 and a distributor 4 into a vessel 5. A solution of alkali,

such as a 10 per cent aqueous solution of caustic soda is mixed with the oil entering the vessel 5 by means of a pump 6 and a valved line 7. This alkali wash removes H<sub>2</sub>S from the oil, to the extent that the same has not been removed by prior refining steps. In the vessel 5, separation takes place, the spent washing solution being withdrawn through a valved line 8 while the separated oil passes through a valved line 9 into a second treating and separating vessel 10. Water is introduced into the oil passing to the vessel 10 by means of a pump 11 and a valved line 12, the purpose being to remove such quantities of alkali solution as may remain in the oil leaving the vessel 5. After separation in the vessel 10, the wash water is removed through a valved line 13, while the treated oil passes through a line 14 into a drying tower 15. The interior of this tower is provided with a suitably supported bed of drying material, such as rock salt, calcium chloride or the like. Any moisture accumulating in the chamber 15 is removed therefrom from time to time by a valved outlet 17. Obviously other methods of drying the oil to be treated may be employed.

The dry oil then passes through a line 18 into a heater 19, which is provided with suitable connections for introducing and removing a suitable fluid heating medium, such as steam.

The heater 19 may or may not be operated, as desired, depending largely upon the moisture content which it is desired to maintain in the subsequent treating stage. Temperatures above 160° F. are rarely if ever necessary in any event, and the heating should never be carried to such extent as to cause substantial vaporization of the oil under the pressures employed. We prefer to maintain the oil throughout the system under a moderate superatmospheric pressure ranging from, for example, 10 to 60 pounds per square inch. Such pressures assist in maintaining the air or other gaseous oxidizing agent (subsequently added) in solution in the oil throughout the treating and regenerating stage.

The oil leaving the heater 19 passes through a line 20 into the lower part of a treating vessel or tower 21. Dry air is also introduced along with the oil. In the instance shown, such air enters the system, under suitable pressure, through a line 22, having a regulating valve 23 and wherein are located one or more drying towers 24. As is true of the drying chamber 15, these drying towers 24 may be internally provided with beds of rock salt, calcium chloride or other drying agent.

Various forms of treating apparatus may be employed, but that illustrated in Fig. 1 has been found practical and useful. As shown, the tower 21 is provided with a plurality of baffles 25 and with agitating means comprising a plurality of blades or paddles 26 mounted on a vertically disposed shaft 27, which is in turn driven by a motor 28.

The oil to be treated, together with suspended solid treating agent, usually comprising a mixture of the reaction products of copper sulfate and sodium chloride together with finely divided asbestos, or other suitable carrying agent, which is introduced through a line 29 in the form of a relatively concentrated slurry in oil of the same character as that being treated passes upward through the tower 21. During its upward flow through the tower 21, the mixture of oxidizing gas, oil and solid treating agent is subjected to intimate contact and agitation. Sweetening of

the oil, that is to say conversion of the original mercaptans, is first effected. This is followed, and to a large extent accompanied, by stabilization and regeneration of the treating material under the influence of the oxidizing gas. The latter is usually in solution in the oil, as aforesaid.

The mixture reaching the top of the tower 21 then passes through a line 30 into a separating vessel 31, where, by reason of relatively quiescent flow, the solid treating agent is caused to separate by gravity from the main body of oil undergoing treatment. Treated oil, free of suspended solid matter, is removed by means of a weir device 32 and an outlet line 33. The treating agent, in the form of a relatively concentrated slurry in treated oil, is withdrawn from the bottom of separator 31 through a valved outlet line 34 and returned to the bottom of the treating vessel 21 by means of a pump 35. Valved lines 36 and 37 are provided on the suction and pressure sides of the pump 35, respectively, for the purpose of introducing and removing solid treating agent (in slurry form), when and as desired.

In the instance shown, the slurry separated at the bottom of the separator 31 and recirculated into tower 21, is passed, before being reintroduced into the latter, through a suitable grinder 38 located in the line 29. The function and purpose of the grinder 38 have been set forth hereinabove, where it has also been stated that various types of grinders may be employed. It should be emphasized, however, that the desired function of such grinding means is not realized by merely passing the slurry through an agitating or mixing device or through a pump; a definite grinding action is essential for maintenance of the suspended treating agent in the most advantageous physical conditions, i. e., in a flocculent or semi-flocculent state.

Suitable vents 40 and 41 are provided at the tops of the tower 21 and the separator 31, respectively. The vent 40 is normally kept closed but is provided with a safety valve suitably adjusted in accordance with the pressures to be maintained in the system. The vent 41 is provided with a back-pressure-regulating valve, and leads to an absorber (referred to hereinbelow).

Where the addition of moisture in regulated quantities is desired, this may be provided for by withdrawing a portion of the treated oil leaving the separator 31 through a line 42 leading to a pump 43, which in turn delivers it through a line 44 and settling device 45. Water or steam is introduced ahead of the device 45 through a valved line 46.

It is advantageous to introduce such moisture as may be desired in the main treating system in the form of a "foggy" suspension of water in hydrocarbon oil, preferably a sweetened oil of the same character as that undergoing treatment. The specific means illustrated in Fig. 1 for moisture addition is adapted to operate in this manner.

Any excess of water separating out of the oil in the device 45 is withdrawn therefrom through a line 47, while the moisture-containing oil is returned through a line 48 into the treating tower 21. Alternatively, this oil may be commingled with the sour oil prior to its entry into the treating tower 21.

That portion of the treated oil not employed for the purpose of furnishing a carrying medium for introducing moisture into the system, as described, passes through a line 49 to an after-



treater 50. Various types of after-treatment may be employed, but in the instance shown, the after-treater 50 comprises a vessel adapted to contain one or more beds 51 of salt, or a mixture of salt and sand, which may or may not be treated with copper compounds or other copper-removing material prior to use. Moisture accumulating at this point in the system may be removed from time to time as necessary, through a valve line 52.

As set forth and claimed in the copending application of L. U. Franklin and W. H. Weeks, Serial No. 284,116, filed concurrently herewith, the operation of the treating unit described is so conducted as to maintain the oil undergoing treatment and the treating agent in contact through a sweetening zone and also through a subsequent stabilizing zone, until regeneration has been effected to an extent indicated by freedom of the oil from cuprous chlorides and cuprous mercaptides. Nevertheless, slight traces of copper compounds, such as copper naphthenates and the like, may persist in the oil leaving the separating zone. The purpose of the after-treater is to remove such traces, inasmuch as amounts of copper compounds as low as one part or even less per million parts of oil are highly deleterious, and also to offset any inadvertent or accidental loss of copper compounds from the heating system, through occasional unavoidable entrainment in the oil leaving the separator 31.

The oil leaving the after-treater 50 passes through a line 53 into an accumulator 54, from which sweetened oil is withdrawn into a valved line 55. Any air and vapors separating at this point are preferably passed through a line 56 into an absorber 57 where they are scrubbed to remove valuable hydrocarbon constituents by means of absorbent oil introduced through a line 58. The vent line 41 also leads to the absorber 57. The scrubbed vapors leave the absorber 57 through a line 59, while the enriched absorbent oil is removed from the system through a line 60.

The desired pressure in the system is regulated by means of the pump 2, and the settings of the valves 40 and 41 and the valves located in the various outlet lines.

In the somewhat modified form of apparatus illustrated in Fig. 2, means are provided for maintaining a continuous cyclic flow in the initial treating zone.

As shown in this instance the treating vessel 21 is provided with an externally disposed pipe or "sweetening tube" 70, communicating at its upper and lower ends with the upper and lower portions of the tower 21 respectively, and provided internally with impelling and agitating means 71 driven by a motor 72. The sour oil enters through the line 20. The slurry recovered from the bottom of the separator 31 is delivered through the pipe 29 to the tower 21, and passes down through the tube 70 with the sour oil, and then upward through the tower 21.

As in Fig. 1, a grinder similar to that shown at 38 therein may be provided in the line 29. However, in the instance illustrated in Fig. 2, the grinder 38 is located elsewhere, as shown. Slurry is removed from the bottom of the treating vessel 21 through a line 75 wherein is located a circulating pump 76 and the grinder 38. After passing through the grinder 38 the slurry thus withdrawn from the tower 21 is returned to the tower 21 through a line 77. Preferably, the pump 76 and grinder 38 are operated continuously

throughout the entire operating period, although it may in some cases be sufficient to operate these units at frequent but intermittent periods.

Referring again to Fig. 1, hydrochloric acid, in any suitable form, may be added, when and if desired, by means of a valved line 78, which is conveniently located at or near the bottom of the treating tower 21.

Operation of the system as described above is conducted in accordance with the disclosure set forth in that portion of this specification immediately preceding the description of the drawings, i. e. to maintain uniformity of moisture content and texture of the solid treating agent within the system, and in accordance with other considerations set forth.

The following specific operating examples will further illustrate the operation and advantages of our process:

#### Example I

In this example, we sweetened a sour, acid-treated re-run gasoline produced by cracking West Texas crude. Analyses of the gasoline, before and after treating in accordance with our invention, were as follows:

	Before treatment	After treatment
Gravity (°API).....	60.4	60.4
Color (Saybolt).....	+29	+29
Color (Saybolt, after 5 hrs. exposure to sunlight).....	+26	+27
Doctor test.....	Sour	Sweet
Copper in gasoline.....	Nil	Nil
Mercaptan sulfur..... percent.....	0.01	Nil
Copper strip test (3 hrs. at 122° F.).....	Bad	Good
Gum (Copper dish), mg. per 100 cc.....	3	3
Oxygen stability..... minutes.....	235	340
Octane number (CFR method).....	68.5	68.5

The solid treating agent used was initially prepared by mixing 416 lbs. of powdered cupric sulfate pentahydrate, 1250 lbs. of powdered sodium chloride, and 334 lbs. of finely divided asbestos. This mixture was allowed to age and react for 48 hours in a humid atmosphere, the moisture content running up in excess of 5 per cent. The aged mixture was then heated on a hot plate for about 6 hours at a temperature of from 175° to 200° F., the moisture content falling to 0.6 per cent. This partially dehydrated material was then introduced into the apparatus, (substantially as illustrated in Fig. 2), together with sweet gasoline, and agitated and recirculated for about three hours at 80° F., to assist in improving the texture of the solid treating agent.

Moisture-containing sweet gasoline was then introduced into the system, until the moisture content of the treating agent reached 1.0 per cent. The actual treating operation was then commenced, sour gasoline being introduced at a temperature of 80° F. at the rate of 400 barrels per hour, and air at the rate of 2000 cubic feet per hour (measured at 60° F. and 14.7 lbs. per square inch). A gauge pressure of 30 lbs. per square inch or a little higher was maintained throughout the run.

Large quantities of gasoline were treated in this run, which extended over a long period, and the results given above are typical and characteristic.

#### Example II

In this example, analyses of the sour gasoline treated and the gasoline after treatment were substantially as shown in Example I above. Apparatus similar to that illustrated in Fig. 1 was used.

The solid treating agent was prepared by mixing the same amounts of ingredients in the same proportions as in Example I, but in this case the aged material was dehydrated from about 6.0 per cent down to 2.0 per cent by agitation in the system in suspension in sweet gasoline at a temperature of 135° F.

Some gasoline was then introduced at a rate of 200 barrels per hour, at a temperature of 135° F., the gauge pressure being 30 lbs. per square inch, together with air in the same relative proportion as in Example I. This initial stage was continued until the moisture content of the treating agent fell to 0.5 per cent. Moisture was then introduced until the moisture content of the treating agent rose to 0.8 per cent, whereupon the oil charging rate was raised to 450 barrels per hour, and the amount of air supplied increased in proportion.

Throughout the remainder of the run, which continued over a long period of time, moisture was added as necessary to maintain the treating agent at an average moisture content of 0.8 per cent, and to avoid excessive variation therein, in accordance with our invention. Fresh quantities of treating material were added from time to time.

#### Example III

In this example, we treated a sour straight-run gasoline from West Texas crude. Analyses before and after treatment were as follows:

	Before treatment	After treatment
Gravity (°API).....	67.9	67.9
Color, Saybolt.....	+25	+25
Doctor test.....	Sour	Sweet
Copper in gasoline.....	Nil	Nil
Mercaptan sulfur..... per cent.	0.056	Nil
Copper strip test (3 hrs. at 122° F.).....	Good	Good
Gum (copper dish), mg. per 100 cc.....	12	12
Oxygen stability..... minutes.	600+	600+
Octane number (CFR method).....	65.0	65.0

The sweetening agent used was prepared by mixing the following ingredients in the following proportions:

	Parts by weight
Powdered cupric sulfate pentahydrate.....	125
Powdered sodium chloride.....	375
Powdered asbestos.....	100

After ageing for 48 hours in a humid atmosphere the mixture was dehydrated to 0.6 per cent moisture content. It was then suspended in sweet gasoline and impregnated with moisture until the moisture content rose to 5.0 per cent.

The sweetening operation was then started and sour gasoline charged at a temperature of 75° F., at substantially atmospheric pressure, and at a rate equivalent to those shown in the foregoing examples. (In this case, smaller apparatus was used, so that the optimum of oil charged per hour was correspondingly lower). Throughout the run, moisture was added at frequent but intermittent periods to maintain the average moisture content at 5.0 per cent, and the maximum variation within limits of from 3.0 to 6.0 per cent. Some HCl was added at one point to replace that lost from the system. Air was also added, as in Examples I and II.

This experimental run was continued for 365 hours, at the end of which time it was arbitrarily discontinued. The results throughout were entirely satisfactory, and at the end of the run

the solid treating agent was fully active, although no fresh chemical was added at any time.

The highly successful results attained in this relatively small scale run were largely due to the fact that we had available at that time small-scale grinding means far more efficient than the grinding means which we then had available for larger-scale operation. Because of that fact, we were able to maintain the solid treating agent in a highly flocculent and efficient condition, with a high CuCl<sub>2</sub> content, yet at a relatively high average moisture content. But, under these conditions, as under others, regardless of the actual average moisture content maintained, excessive variation in moisture content, beyond the limits referred to hereinabove, has a highly unfavorable effect.

In the claims hereinafter made, the term "oxygen" is intended to denote not merely pure oxygen itself, but also oxygen as existing in air or other oxygen-containing gas.

While we have set forth and described our invention hereinabove with reference to numerous operating details (some of which are in accordance with inventions disclosed in the other copending applications referred to herein), and with reference to specific operating examples, our invention may be variously practiced and embodied within the scope of the claims hereinafter made.

What we claim is:

1. The process of sweetening sour hydrocarbon oils containing mercaptans, which comprises passing a flow of said oil, oxygen and a suspended solid treating agent comprising (1) a substance capable of ionizing to give cupric ions and chloride ions and (2) a solid, substantially inert carrying agent, through a treating and regenerating zone, maintaining the average moisture content of the solid treating agent between 0.5 per cent and 9.0 per cent, and also regulating the amount of moisture present in the system so that the maximum water content of the treating agent at any time is never more than twice the minimum water content of the treating agent at any time.

2. A process as claimed in claim 1, wherein the carrying agent is finely divided asbestos, and the average moisture content of the solid treating agent is maintained between 0.5 per cent and 7.0 per cent.

3. The process of sweetening sour hydrocarbon oils containing mercaptans, which comprises passing a flow of said oil, oxygen and a suspended solid treating agent comprising a substance capable of ionizing to give cupric ions and chloride ions and a solid, substantially inert carrying agent, through a treating and regenerating zone, maintaining the average moisture content of the solid treating agent between 0.5 per cent and 9.0 per cent, and also regulating the amount of moisture present in the system so that the maximum water content of the treating agent at any time is never more than twice the minimum water content of the treating agent at any time, separating treated oil from the solid treating agent, and recycling the latter to the initial contact stage.

4. A process as claimed in claim 1, wherein the supporting material comprises finely divided asbestos, and the solid treating agent is maintained in an at least semi-flocculent condition.

5. A process as claimed in claim 1, wherein the solid treating agent, after separation of treated oil, and in the presence of oil not sep-

arated therefrom, is subjected to grinding prior to recirculation.

6. A process as claimed in claim 1, wherein a cyclic circulation of oil, oxygen and solid treating agent, without separation, is maintained in the contact stage, the mixture being subjected to mechanical grinding during at least a portion of the cycle thus established.

7. A process as claimed in claim 1, wherein the solid treating agent, as added, comprises a mixture of cupric sulfate and a chloride selected from the class consisting of NaCl and NH<sub>4</sub>Cl, together with an absorbent but not highly adsorbent solid supporting material in finely divided form.

8. A process as set forth in claim 1, wherein the oil undergoing treatment is maintained at a temperature not substantially below 100° F., and the average moisture content of the solid treating agent is maintained at from 0.5 to 1.5 per cent.

9. A process as set forth in claim 1, wherein the oil undergoing treatment is maintained at a temperature below 100° F., and the average moisture content of the solid treating agent is maintained at from 3.0 to 6.0 per cent.

10. A process of sweetening sour hydrocarbon oils comprising forming a solid treating agent from cupric sulfate, a chloride selected from the class consisting of NaCl and NH<sub>4</sub>Cl, and a finely divided absorbent but not highly adsorbent solid supporting material, initially drying said treating agent at a temperature not substantially below 100° F. to reduce its moisture content to 0.5 to 1.0 per cent, treating sour hydrocarbon oil with said treating agent, and regulating the amount of moisture present in the system so that the maximum water content of said treating agent at any time is never more than twice the minimum water content thereof at any time.

11. A process as set forth in claim 10, wherein the initial drying step is effected prior to introduction of the treating agent into the treating system.

12. A process as set forth in claim 10, wherein said initial drying step is effected during sweetening and after introduction of the treating agent into the treating system.

LESLIE U. FRANKLIN.  
WALTER H. WEEKS.  
JACK W. HARRIS.