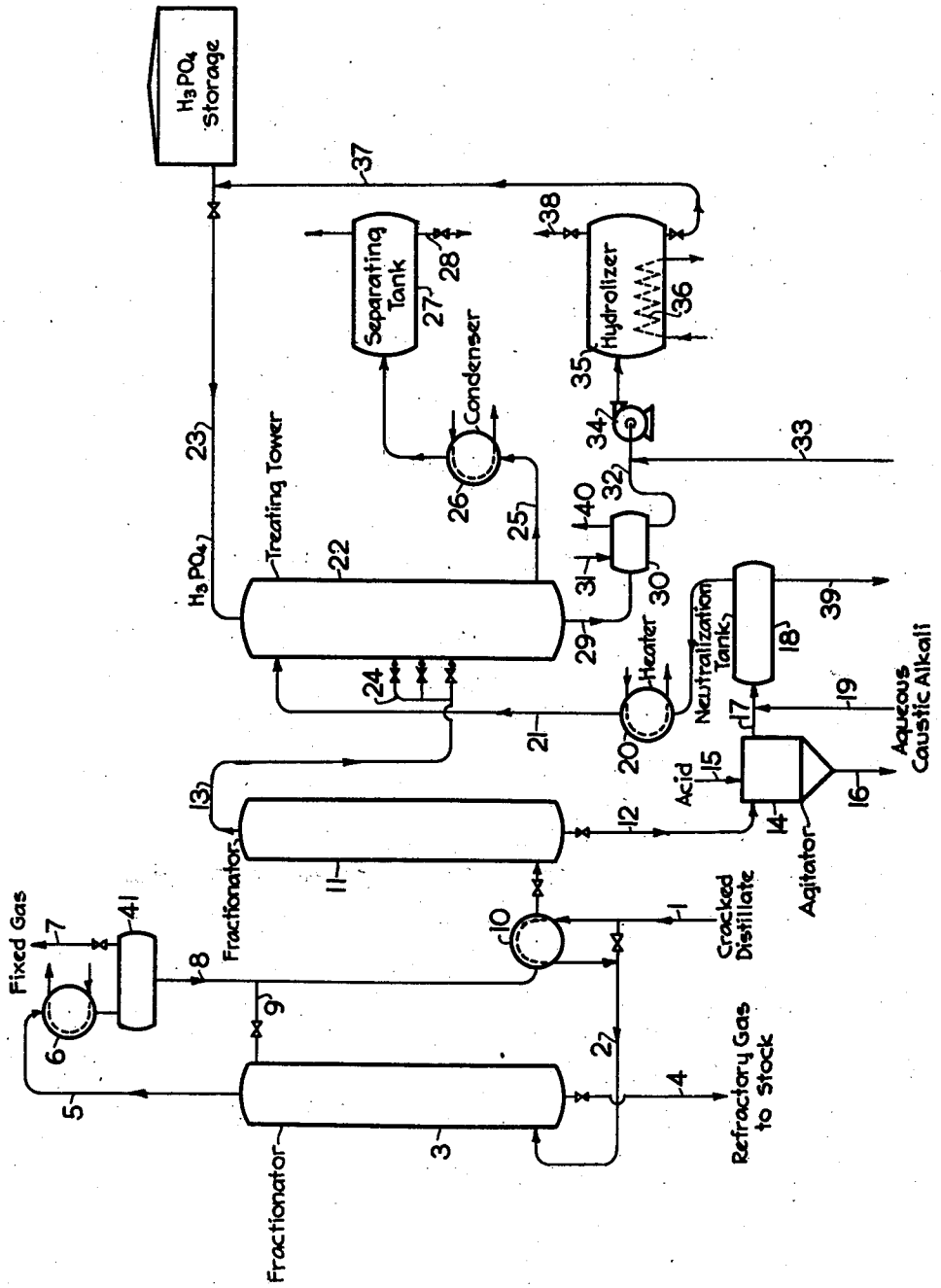
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PROCESS FOR REFINING HYDROCARBONS

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PROCESS FOR REFINING HYDROCARBONS

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16 Claims. (Cl. 196—36)

This invention relates to a process for refining hydrocarbon oils in a heated condition, and preferably in the vapor phase, by contacting the same with a chemically acting acid refining agent, and more particularly is concerned with the vapor phase refining of fuel distillates such as gasoline distillates at elevated temperatures with mild polymerizing agents capable of selectively polymerizing olefins.

Many processes in which cracked hydrocarbon distillates are refined to remove gum-forming constituents by contacting them with various polymerizing agents are well known. Among them are a few which permit a more or less selective polymerization of diolefins, whereby a reasonably gum stable product can be obtained with a minimum of polymerization loss. Processes which permit such selective polymerization of the diolefins are particularly those employing polymerizing agents in very low ratios of the reagent to the gasoline, such as those described in Retailliau Patents Nos. 2,200,703 and 2,200,704 and in my U. S. Patent 2,224,636. In these processes very small amounts of dilute aqueous solutions of strong polybasic oxy acids, such as sulfuric acid, various sulfonic acids, phosphoric acids, etc., are injected into a stream of gasoline vapors at temperatures sufficiently high so that water vaporizes, but insufficient to cause substantial oxidation of the hydrocarbons.

It is known that these mild selective treating processes of the type described above frequently do not satisfactorily stabilize highly cracked gasolines, such as are normally obtained in the so-called vapor phase cracking processes which operate at temperatures above about 1000° F. and at low pressures. The exact reason for this was not known, but it had generally been assumed that the amount of gum-forming constituents was simply too high to be handled by these treating processes.

Now I have discovered a method of selectively polymerizing diolefins in highly cracked gasolines without causing excessive polymerization losses and yet stabilizing these gasolines satisfactorily. My process employs as treating agents the strong oxy acids of the before-mentioned patents, and in carrying out the process I proceed as follows:

A cracked hydrocarbon distillate such as gasoline distillate, containing gum-forming components and possibly other impurities, is fractionally distilled to produce at least two fractions of different boiling ranges. These fractions are introduced in the vapor phase into a treating tower, into the upper part of which small amounts of an aqueous solution of the treating agent are admitted to flow downward through the tower. Vapors of the highest boiling fractions are introduced at a point nearest the entrance of the treating agent, and the remaining fractions are introduced in the order of decreasing boiling ranges at points successively further removed from the point of introduction of the treating agent. The treating agent and vapors pass through the tower in concurrent flow, and as a result of the manner of introducing the several fractions as described, the heaviest fraction has not only the longest time of contact with the treating reagent, but also comes in contact with the freshest reagent. This fraction, therefore, is most severely treated, and lighter fractions receive successively lighter treatments, i. e., treatments of shorter duration and with relatively smaller amounts of reagent, which reagent, furthermore, is already partly spent. Alternately countercurrent flow of treating agent and vapors may be employed, in which case vapors of the heaviest fraction are introduced into the tower at a point farthest away from the point of introduction of the treating agent solution, and the lighter fractions are introduced at intermediate points.

During the contact, water is vaporized and sludge is formed. This sludge is separated from the remaining vapors, and the latter are separately condensed.

The several fractions produced from the distillate may for convenience be of about equal volume, although this is not necessary. When treating gasoline distillates, it is usually preferred to produce two fractions only, the lower one of which has a 95% A. S. T. M. distillation point of between about 230° F. and 300° F. and preferably 240° F. to 260° F., and the higher boiling fraction boiling above that temperature. To fractionate in this manner is desirable, because it permits of certain advantages, for example, in connection with the removal of nitrogen bases, as will be described later.

Oils susceptible to my treatment are in particular cracked gasoline distillates, although my process is applicable as well to most cracked hydrocarbon fuel distillates having boiling ranges up to about 575° F. My process is particularly suited to the treatment of highly cracked gasolines, such as are normally obtained in the so-called vapor phase cracking processes which operate at temperatures above about 1000° F. and at low pressures. Such highly cracked distillates

usually have maleic acid anhydride numbers in excess of about 15. Maleic acid anhydride number, defined as the mg. of maleic acid anhydride which will react with 1 gm. of distillate under a given set of conditions, is a fairly accurate measure for the content of diolefins having conjugated double bonds in the distillate.

To provide an effective contact between the solution of the reagent and the vapors, the former is effectively dispersed within the latter as by spraying, spreading over a large contact surface such as that of a packing, or other suitable means. The volume ratio of the reagent solution to hydrocarbon vapors being very small in my process in spite of the high degree of dilution of the former, treatment by passing the vapors through a liquid pool of the solution is impractical, if not impossible.

The treating zone may conveniently consist of a vertical tower or column containing an inert relatively coarse packing such as broken brick, tile, pumice, coke, steel wool, rings made from silicious materials, iron, copper, etc. In general it is unnecessary that the packing be corrosion resistant against any of the oxy acids used as treating agents, because within a short time it is completely covered by a protective coating of sludge. It is, however, necessary that the packing materal be inert towards the sludge, and it should preferably have a compressive strength sufficient to support a bed at least 20 to 40 feet deep, even after prolonged exposure to the sludge.

The most suitable treating reagents for use in my process are dilute aqueous solutions of strong oxy acids, such as sulfuric acid, soluble hydrosulfates, organic sulfonic acids, phosphoric acids, etc. Water-soluble hydrosulfates embrace the alkali metal bisulfates, aluminum hydrosulfate, chromium hydrosulfate, ferrous hydrosulfate, etc. Sulfonic acids to be suitable should be capable of forming aqueous solutions at temperatures below 212° F. of at least ½% concentration. Especially suitable for my purpose are the mono- and poly-sulfonic acids of benzene, toluene, xylene, naphthalene and other aromatic hydrocarbons. Also, aliphatic mono- and poly-sulfonic acids of methane, ethane, propane, etc., are useful. The organic radicals of these acids may contain substitution radicals, negative substituents such as halogens being in general preferable to positive substituents such as amino groups. Thus I may use chlor benzene sulfonic acids, sulfonic acids of phenols and cresylic acids, etc. Also mixtures of different sulfonic acids are often very useful, and the sulfonic acids may contain varying amounts of sulfuric acid. On the other hand, metal salts of sulfonic acids are substantially ineffective in my process, the refining effect of salts of monobasic acids such as zinc and other metal sulfonates being too weak under the conditions of my process and having the disadvantage of tending to plug the treating zone.

Certain reagents such as phenols which may facilitate the refining with oxy acids or spacing agents other than steam or water, such as organic bases, may be introduced together with or as part of the aqueous solution. However, the treating solution should always contain some free oxy acid, the free acid being the active treating agent.

The most essential factors are amounts and concentration of reagent, temperature and time of the reaction. As is more fully explained below, all of these factors will vary depending on the particular distillate being treated and the treating agent employed.

When sulfuric acid, sulfonic acids, or hydrosulfates are employed, the concentration of the aqueous reagent solution may affect the process in at least two ways: it influences the effectiveness of distribution of the reagent throughout the vapors, and if too high may cause the charring, burning and/or oxidation of the vapors. The greater the dilution, the greater the volume of treating solution to be used and the more efficiently can it be injected into and distributed throughout the vapors. From this point of view it is in general desirable to use concentrations not in excess of about 10% by weight, although when operating at relatively low temperatures, concentrations up to about 20% by weight may be employed without substantial danger of charring and burning. On the other hand, at relatively high temperatures I have successfully used solutions having concentrations as low as .5% and even lower concentrations may be employed, if desired.

In the case of treatment with phosphoric acid, the concentration of the aqueous phosphoric acid solution is of influence only in so far as it affects the ease with which the solution can be distributed through the vapors. Aqueous phosphoric acid solutions of high concentration are very viscous, and because of this, and the small amounts of the solutions required, there is danger of uneven distribution and consequent uneven treatment of the hydrocarbons if the solution is too concentrated. Therefore, it is in general desirable to use concentrations of about 30% or less, although I have successfully injected solutions having concentrations as high as 85% and 90%. On the other hand, at relatively high treating temperatures I have used with equal success solutions having concentrations as low as .5% and even lower concentrations may be employed if desired.

I use an amount of treating reagent which is completely used up in a single pass, that is, one which results in a substantially uniform sludge. This sludge, though containing some free acid or easily hydrolyzed esters, fails to separate a layer of free acid after prolonged standing. This has the advantage, in addition to forming a non-corrosive sludge, of obviating recirculation of unconsumed reagent, a feature which greatly simplifies the treating equipment and reduces the cost of installation.

In the split feed treatment of hydrocarbons wherein it is desired to subject one fraction to a more vigorous treatment than the other, the use of small quantities of reagent presents certain advantages over the use of larger quantities. Thus when using large quantities of reagent, the single advantage to be realized consists in providing for different times of contact for the several fractions. In such case, however, the intensity of the treatments received by each of the fractions will differ to a lesser extent, due to the fact that only a portion of the large amount of reagent introduced is consumed by its contact with a heavier fraction, the remaining unconsumed reagent then being available to treat the lighter fraction. On the other hand, when a small amount of reagent is used, all or practically all of it is consumed by its prior contact with the heavier fraction, and therefore the lighter and easier to stabilize fraction is then subjected to a treatment with sludge acid resulting from the heavier fraction or sludge con-

taining a minor amount only of unused reagent. This latter treatment is thus disproportionately lighter than that of the heavier fraction.

In the light of the above, amounts of reagents suitable for my treatment are between about .001 and 1 pound and preferably less than about ¼ pound of reagent per barrel of distillate. In the treatment of full range Dubbs cracked gasolines with phosphoric acid on plant scale ⅛ to ½ pound per barrel has proven very satisfactory. In all cases, to minimize consumption of reagent, the minimum amount which gives a satisfactory treating result and which is completely consumed in a single pass, is obviously the most desirable. This minimum varies considerably with the type of distillate under treatment.

In all cases temperatures should be substantially below that at which cracking occurs in the presence of the treating reagent. Thus, in the case of sulfuric acid, sulfonic acid, and hydrosulfates, suitable contact temperatures are in general of the order of about 200° F. to 400° F., temperatures between about 230° F. and 300° F. being preferred. In the case of phosphoric acid the suitable contact temperatures are of the order of about 250° F. to 750° F., temperatures between about 350° F. and 500° F. normally being optimum.

The times of contact within the treating tower will be different for each of the fractions, it being more important, however, to specify the limiting times of contact for the heavier fraction, since the contact time required for the lighter is relatively short and may be easily varied at any time by changing the level at which it enters the treating tower. The time of contact for the heavier fraction may be varied between the limits of about 3 to 300 seconds and may if desired be extended beyond these limits, times from 9 to 90 seconds being preferred. In general, at relatively low temperatures longer times of contact are permissible and required than at higher temperatures under otherwise equal conditions. Reaction times of less than about 3 seconds are normally insufficient. With increasing time of contact above about 3 seconds, the stability of the hydrocarbon oil increases while treating losses may rise but little. On the other hand, if the contact is extended beyond a certain time, which depends largely upon the temperature as well as on the properties of the treating distillate, stability is not further improved materially, and certain disadvantages make themselves felt, such as increased losses and the extremely large size of the reaction vessel which is required for a given throughput.

Instead of using a single oxy acid as the sole refining reagent, I may also employ mixtures, e. g., mixtures of different sulfonic acids, sulfonic acids with varying amounts of sulfuric acid, or soluble hydrosulfates, and phosphoric acid with other acids capable of effecting the refining of the hydrocarbons, in particular sulfuric acid. Mixtures of phosphoric acid and substantial amounts of sulfuric acid require in general somewhat lower refining temperatures than phosphoric acids alone, normally below 500° F., the optimum temperature depending largely upon the relative proportions of the two acids. If sulfuric acid predominates in the mixture over phosphoric acid, treating temperatures below 300° F. and as low as 200° F. may be effective. Since the sulfuric acid is much less expensive than phosphoric acid, some saving may be realized by using mixtures rather than the phosphoric acid alone without materially sacrificing advantages which are characteristic of the treatment with phosphoric acid. However, as pointed out previously, the concentration of the sulfuric acid in the aqueous solution should be below about 10% to avoid burning and charring of the hydrocarbons.

When sulfuric acid, sulfonic acid or hydrosulfates are employed, nitrogen bases contained in the distillates may be and usually are completely removed in the course of my treatment; however, prior to phosphoric acid treatment, nitrogen bases if present should be removed from the distillates. This removal is usually carried out by extraction with dilute sulfuric acid, waste acid or some other acid that may be available. The extraction of the nitrogen bases, however, is never complete because the resulting amine salts are partially hydrolyzed, causing at least an equilibrium amount of the free base to remain in the oil. The nitrogen bases contained in highly cracked gasolines are mainly of the alkyl pyridine and quinoline types, pyridine and picolines, the lowest boiling members, having boiling temperatures between 239° F. and 289° F. By fractionally distilling the gasoline, as explained above, I concentrate the nitrogen bases in the higher boiling fraction and by carrying out the division at 240° F. to 260° F., as preferred, substantially all of the nitrogen bases are concentrated in the higher boiling fraction, the degree of the concentration under these circumstances being at or near the maximum obtainable by simple fractional distillation. The lower boiling fraction thus is substantially free from nitrogen bases, and as a result, it is necessary to subject to the extraction with an acid only a relatively small volume of gasoline; and the removal of nitrogen bases is more complete because of the smaller volume of gasoline distillate to be extracted, which smaller volume is capable of retaining a smaller equilibrium amount of nitrogen bases only.

Alkyl phenols naturally occurring in cracked distillates will accumulate in fractions boiling above about 360° F. If it were desired to recover alkyl phenols, it would be necessary to wash only the heavier fractions with strong aqueous caustic alkali.

It is understood from the above that the several gasoline fractions produced in accordance with my invention may be, and usually are, treated individually to remove various impurities other than gum-forming components, e. g., nitrogen bases, alkyl phenols, mercaptans, etc., by methods complementary to my stabilizing treatment, the latter serving to eliminate primarily the gum-forming components. These complementary or supplementary treatments may precede or follow the stabilizing treatment as conditions may require.

When using phosphoric acid, if the treating distillate is substantially free from nitrogen bases, at least a portion, i. e. usually about 90% of the phosphoric acid consumed in the treatment, may be recovered from the sludge in the most simple manner, by first separating it from entrained hydrocarbon oil, washing it with a light hydrocarbon oil such as naphtha and then hydrolyzing it at an elevated temperature preferably not below about 200° F., as by steaming or heating it with liquid water if desired, under superatmospheric pressure sufficient materially to raise the treating temperature to above the normal boiling point of water. At substantially

atmospheric pressure, a time of about 1 to 8 hours and more often 2 to 4 hours for hydrolysis and liberation of readily hydrolyzable phosphoric acid is usually sufficient.

The attached drawing represents a simplified flow diagram illustrative of my process.

Cracked vapors such as those obtained from a conventional high temperature vapor phase cracking process, e. g., Gyro, TVP (true vapor phase), etc., cracking process, not shown, enter the system through line 1 passing through heat exchanger 10 in countercurrent to distillate from fractionator 3, and are then conveyed through line 2 directly to fractionator 3. A refractory gas oil stock is separated from the bottom of the fractionator through line 4, which oil contains the components boiling above gasoline boiling range. This oil is disposed of in a manner not shown.

Remaining gasoline and lighter vapors pass through condenser 6 in line 5, the heavier portions being condensed and accumulated in tank 41 while the lighter fixed gases are removed through line 7. Accumulated condensate leaves tank 41 through line 8, a portion being returned as reflux through line 9 to fractionator 3 and the remainder passing through heat exchanger 10 to fractionator 11 to separate a heavier gasoline fraction boiling above 240° F. to 260° F., and a lighter vapor. The heavy portion emerges from the bottom of the fractionator through line 12 and passes to agitator 14 where it is washed with dilute sulfuric acid or other suitable acid to remove nitrogen bases. The acid is admitted to the agitator through line 15 from a source not shown and sludge is withdrawn through line 16. The acid-washed distillate leaving agitator 14 through line 17 is neutralized in tank 18 with caustic alkali, which is introduced into line 17 through line 19. If alkyl phenols are to be recovered, an excess of strong caustic may be used for the neutralization in tank 18. Caustic extract is withdrawn through line 39.

Neutralized distillate freed from nitrogen bases (and if desired from alkyl phenols) then proceeds through heater 20 in line 21 to be vaporized, and resulting vapors pass to the upper portion of treater 22. A small amount of dilute phosphoric acid is admitted continuously through line 23 and is sprayed into the top of treater 22 to contact the heavy distillate vapors in the upper part of the tower.

Returning to fractionator 11; remaining vapors escape through line 13 and pass directly to treater 22, entering the treater at a point lower than the heavier fraction, to contact the mixture of heavy gasoline vapors and phosphoric acid. The exact point of entry is controlled as shown by manifold 24. The light and heavy vapors, after passing through the treater concurrent with aqueous phosphoric acid, being thereby thoroughly mixed within the tower, are released as treated vapors through line 25. The treated vapors then pass through condenser 26 in line 25 and the resulting condensate is accumulated in tank 27. Water separates out and may be withdrawn through line 28.

The sludge formed in treater 22 is withdrawn through line 29 and passes to tank 30 where it is washed to remove emulsifying material with a liquid hydrocarbon such as gasoline which enters tank 30 through line 31. The liquid hydrocarbon and emulsifying material are withdrawn through line 40. The washed sludge is removed through line 32, mixed with water from line 33, and the mixture is conveyed by pump 34 in line 32 to pressure hydrolyzer 35 which is equipped with heating means such as steam coil 36. Sludge is hydrolyzed. Dilute phosphoric acid solution settles out and the solution is returned to the top of the treater through lines 37 and 23. Organic residue from the hydrolysis, i. e., hydrocarbon polymer, is withdrawn from the hydrolyzer 35 through line 38.

While in the foregoing I have disclosed water only as a suitable solvent for oxy acids, I may use other solvents which are substantially chemically inert and substantially completely vaporizable under the conditions of the treatment. For instance, when carrying out my treatment with oil-soluble petroleum sulfonic acids such as are obtained in the treatment of viscous petroleum oils with fuming sulfuric acid to produce medicinal oils, I may dissolve these acids in pentane, hexane, straight run gasoline, etc.

I claim as my invention:

1. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce at least two fractions, a low boiling one having a 95% A. S. T. M. distillation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, contacting said higher boiling fraction in the vapor state with a small amount of a dilute aqueous solution of a strong free oxy acid at an elevated temperature substantially below that at which cracking occurs in the presence of said acid, contacting said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

2. The process of claim 1 wherein said distillate and aqueous solution are conducted through the reaction zone in concurrent flow.

3. The process of claim 1 wherein said amount is from .001 to 1 pound per barrel of said distillate.

4. The process of claim 1 wherein said distillate is a cracked gasoline distillate.

5. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce two fractions, a low boiling one having a 95% A. S. T. M. distillation point between 240° F. and 260° F. and a higher boiling fraction boiling above this temperature, contacting said higher boiling fraction in the vapor state with a small amount of a dilute aqueous solution of a strong free oxy acid at an elevated temperature substantially below that at which cracking occurs in the presence of said acid, contacting said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

6. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce at least two fractions, a low boiling one having a 95% A. S. T. M. distil-

lation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, subjecting said higher boiling fraction to a treatment to remove nitrogen bases, contacting the resulting treated fraction in the vapor state with a small amount of a dilute aqueous solution of a strong free oxy acid at an elevated temperature substantially below that at which cracking occurs in the presence of said acid, contacting said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

7. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce at least two fractions, a low boiling one having a 95% A. S. T. M. distillation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, contacting said higher boiling fraction in the vapor state with a small amount of a dilute aqueous solution of a strong free oxy acid at an elevated temperature substantially below that at which cracking occurs in the presence of said acid for a period of from 3 to 300 seconds, contacting during said period said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

8. The process of claim 7 wherein said period is from 9 to 90 seconds.

9. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce at least two fractions, a low boiling one having a 95% A. S. T. M. distillation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, contacting said higher boiling fraction in the vapor state with a small amount of a dilute solution of phosphoric acid at an elevated temperature of between 250° F. and 750° F., contacting said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

10. The process of claim 9 wherein said elevated temperature is between 350° F. and 500° F.

11. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce at least two fractions, a low boiling one having a 95% A. S. T. M. distillation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, contacting said higher boiling fraction in the vapor state with a small amount of a dilute aqueous solution of sulfuric acid in a concentration of from .5% to 20% at an elevated temperature of from 200° F. to 400° F., contacting said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

12. The process of claim 11 wherein said elevated temperature is from 230° F. to 300° F.

13. In the process of refining an unstable cracked hydrocarbon distillate containing diolefins to produce a stable distillate, the improvement comprising fractionally distilling said distillate to produce at least two fractions, a low boiling one having a 95% A. S. T. M. distillation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, contacting said higher boiling fraction in the vapor state with a small amount of a dilute aqueous solution of sulfonic acid in a concentration of from .5% to 20% at an elevated temperature of from 200° F. to 400° F., contacting said lighter fraction in the vapor state with the resulting mixture, said amount being such that said acid is completely consumed during said contacts and forms a uniform sludge, and separating said sludge from the resulting combined vapors.

14. The process of claim 13 wherein said elevated temperature is from 230° F. to 300° F.

15. Improved process for the vapor phase refining of unstable cracked hydrocarbon distillates containing diolefins to produce a stable distillate, comprising fractionally distilling said unstable distillate under conditions to segregate same into several fractions of different boiling ranges, introducing a small amount of a dilute aqueous solution of a strong free oxy acid into the top of an elongated vertical treating zone, flowing said solution downward through said zone, simultaneously introducing the several fractions in the vapor state at spaced points in the direction of flow of said treating solution in the order of successively decreasing boiling ranges, flowing said vapors concurrently with said solution through at least a portion of said zone, said amount being such that said acid is completely consumed while flowing through said zone and a uniform sludge is produced, and separating said sludge from the resulting combined vapors.

16. Improved process for the vapor phase refining of unstable cracked hydrocarbon distillates containing diolefins to produce a stable distillate, comprising fractionally distilling said unstable distillate to segregate same into a low boiling fraction having an A. S. T. M. distillation point between 230° F. and 300° F. and a higher boiling fraction boiling above this temperature, introducing a small amount of a dilute aqueous solution of phosphoric acid into the top of an elongated vertical treating zone, flowing said solution downward through said zone, simultaneously introducing in the vapor state said higher boiling fraction into the upper portion of said treating zone and the low boiling fraction at a point below the point of introduction of said higher boiling fraction, flowing said vapors concurrently with said solution through at least a portion of said zone, said amount being such that said acid is completely consumed while flowing through said zone and a uniform sludge is produced, and separating said sludge from the resulting combined vapors.

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