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R. B. DAY

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PROCESS OF REFINING GASOLINE CONTAINING DISTILLATES

Filed May 25, 1932

3 Sheets-Sheet 1

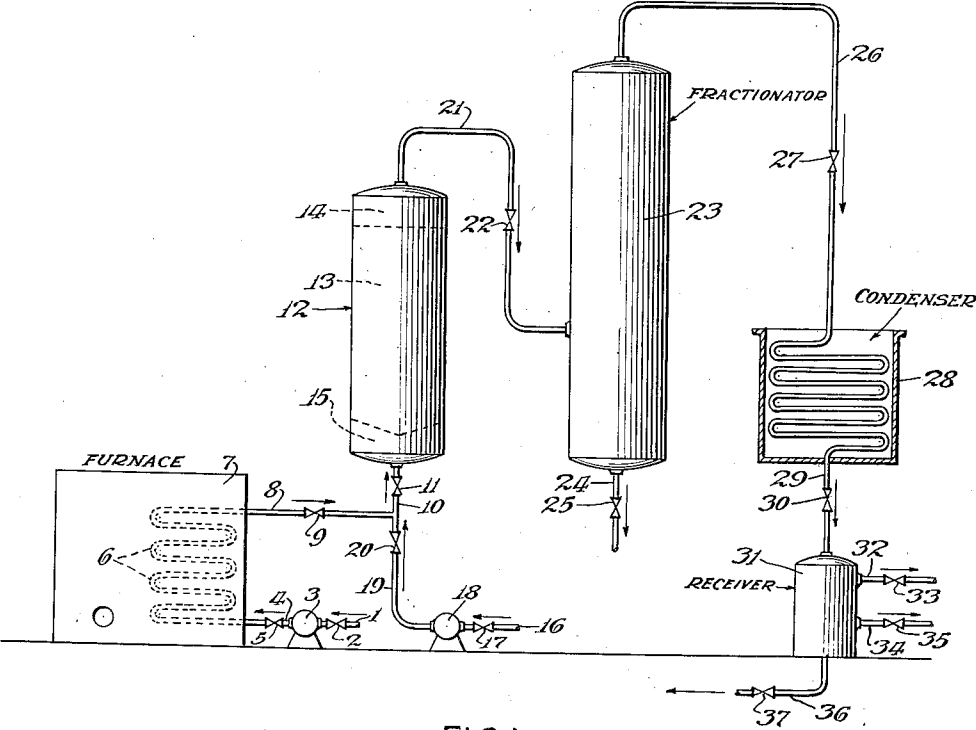


FIG. 1.

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3 Sheets-Sheet 2

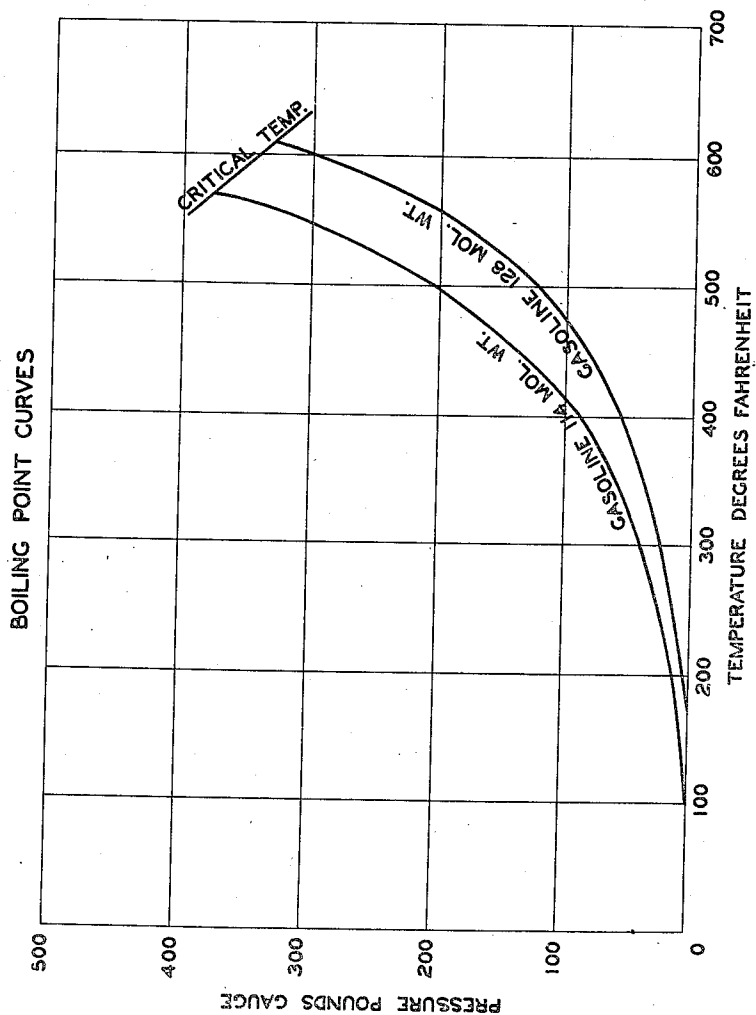


FIG. 2

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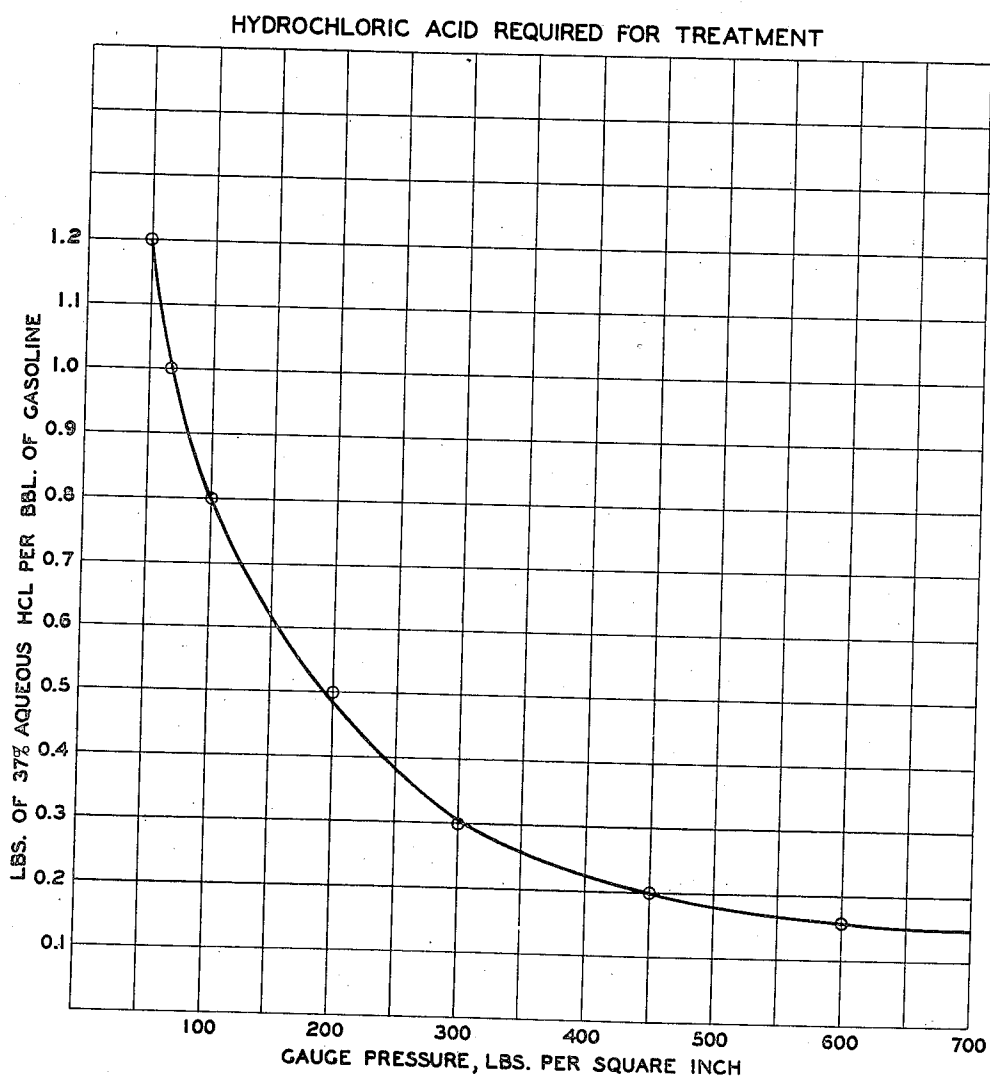


FIG. 3

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PROCESS FOR REFINING GASOLINE-CONTAINING DISTILLATES

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Application May 25, 1932. Serial No. 613,517

5 Claims. (Cl. 196—35.)

This invention relates to the treatment of hydrocarbon oils and refers more particularly to the treatment of hydrocarbon oil distillates of motor fuel boiling range produced by the cracking of heavier and less valuable portions of petroleum oils though similar motor fuel fractions produced from other sources may also be treated such as those produced in the straight run distillation of crude petroleum or in the cracking of tars produced in the primary distillation of coals, shales, etc.

In a more specific sense the invention is concerned with a process which may be employed to controllably eliminate the undesirable constituents of primary or untreated motor fuel distillates, such constituents being classified generally as the gum-forming and colored compounds and the sulphur-containing derivatives, the latter imparting a bad odor to the distillates and being corrosive upon the metal parts of automobile engines either before or after combustion.

This application is a continuation-in-part of my earlier copending application Serial No. 533,852, filed April 29, 1931.

The most generally used refining method for producing a refined and stable gasoline from primary naphthas consists in regulated treatment of the same with concentrated sulphuric acid, followed by neutralization (with sweetening if necessary) and redistillation to produce refined gasoline as an overhead product. The disadvantages of this method lie generally in the cost of reagents and particularly in the high losses suffered in accomplishing the desired degree of refining. The present invention is a departure from the older method and possesses new and useful features which further differentiate it from previous attempts to overcome the difficulties encountered in producing a stable refined gasoline from the raw naphthas produced in cracking operations with minimum losses. Other features and advantages will become evident in the development of the specification.

In one specific embodiment the invention comprises the treatment of hydrocarbon oil distillates, particularly cracked hydrocarbon oil distillates of approximate motor fuel boiling range at elevated temperatures and under pressures sufficient to substantially prevent vaporization of said distillates with hydrochloric acid and metals.

A number of metals are particularly suitable for use in the process such as zinc, tin, iron, aluminum, etc. The treating effect produced by any particular metal, metal alloy or mixture of metals which may be employed in conjunction

with hydrochloric acid in the process will be distinctive in any case so that while a number of alternatives are possible they are not exact equivalents. Zinc and its alloys such as brass (an alloy of zinc and copper) and bronze (an alloy of zinc, copper and tin) have produced good results in practice.

When more than one metal is employed it is frequently of advantage to employ metals representing both those above and those below hydrogen in the electrochemical series and below is given a partial list of the electrochemical series of metals:

From + to -; or in order of diminishing tendency to enter the ionic from the elementary state

Potassium	
Sodium	
Barium	
Calcium	75
Magnesium	
Aluminum	
Manganese	
+Zinc	80
Chromium	
Iron	
Cadmium	
Cobalt	
Nickel	85
Tin	
Lead	
Hydrogen	
Antimony	
Bismuth	90
Arsenic	
-Copper	
Mercury	
Silver	
Platinum	95
Gold	

In numerous instances it has been observed that the polymerizing or gum-reducing effect of the treatment is roughly proportional to the amount of electropositive metal in mixtures or alloys of one or more metals while the desulphurizing effects are promoted in proportion to the amount of electronegative metal though this observation cannot be laid down as an invariable rule.

An important feature of the invention appears in the fact that while treatments are conducted at elevated temperatures that sufficient pressure is held upon the system to maintain the oils in

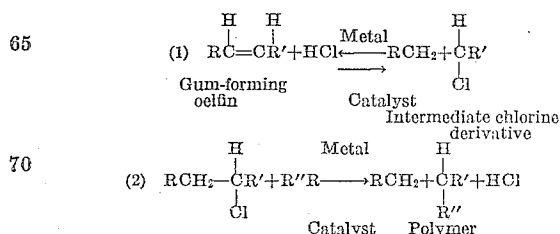
substantially liquid phase. I have determined that when treating cracked distillates that unexpectedly good treating effects in regard to selective removal of gum-forming compounds and sulphur reduction are produced when utilizing temperatures within the approximate range of 500 and 650° F., the pressure required to maintain cracked distillates containing substantial amounts of gasoline boiling range fractions in liquid phase being of the order of from 400 to 500 pounds per square inch under these temperature conditions. The exact temperature employed in the treatment will depend upon a number of factors, particularly upon the chemical composition and boiling range of the naphtha or gasoline undergoing treatment and the metal or metals which may be selected for use in conjunction with hydrochloric acid.

The beneficial effects of pressure sufficient to insure substantially liquid phase conditions may be due to several causes. It is possible that the reactions of polymerization and desulphurization proceed with greater velocity in the liquid phase and under increased pressure conditions. At the same time the capacity of treating equipment for permitting a sufficient time factor is lowered so that the construction of suitable equipment is less costly than if any appreciable degree of vaporization is permitted.

When stabilized distillates are employed which are substantially free from dissolved gases and low boiling hydrocarbons whose critical temperatures may be below the temperatures employed in the treatment, considerably lower pressures may be employed than when unstabilized or poorly stabilized distillates are employed. The curves shown in Figure 2 indicate the limit conditions of operation which must be adhered to in treating two gasolines of 114 and 128 mean molecular weight respectively, if substantially liquid phase treating conditions are to be maintained.

The nature of the reactions which have been found to produce the unusually good refining effects upon cracked gasolines when treated according to the process of the invention is difficult of exact determination on account of the complex character of the hydrocarbon distillates, particularly in regard to the chemical nature of the gum-forming compounds and the form of combination of the sulphur which is present. It may be assumed that the gum-forming compounds consist of di- and tri-olefins of a conjugated character, to a large extent, since these compounds are known to readily undergo polymerization. The sulphur compounds may be mercaptans, sulphides, disulphides, thioethers, thiophenes, etc., besides hydrogen sulphide.

The following equations suggest a possible explanation of the course of the reactions of treatment:



It is assumed that hydrochloric acid is the most active material in producing reactions of

polymerization among compounds such as the di- and tri-olefins which are present in cracked distillates, the metal present functioning catalytically. However, there may be some formation of chloride and possibly some formation of intermediate organic compounds between metals or metal chlorides. The determination of the exact course of the reactions of the treatment is beset with great difficulties both from the experimental and analytical standpoint. Apparently a very small amount of moisture must be present to insure effective treatment, the necessary quantities being introduced along with the hydrochloric acid. The addition of any excess of water above a certain minimum requirement has been found to be quite uniformly detrimental to the efficacy of the treatment.

To account for the extraordinary efficiency of the process in removing sulphur from cracked distillates which are refractory from the standpoint of ordinary sulphuric acid treatments, two types of reactions may be considered, the first involving polymerization of sulphur compounds along with the highly unsaturated hydrocarbons so that the sulphur appears in the heavy polymers and, second, those involving a preliminary combination of organic sulphur with a metal to form metal sulphide which is later decomposed by hydrochloric acid to evolve hydrogen sulphide as a gas. These reactions are merely assumed and their proof would involve a series of difficult analyses which if not impossible would add little value to the present specification. Some evidence is at hand to show that combined sulphur in high sulphur oils appears after the treatment in mercaptans as a result of secondary reactions of hydrocarbons with hydrogen sulphide originally formed. However, with suitable precautions which will be developed in connection with a description of an operation, this tendency toward mercaptan formation can be minimized. The unusual effects along the line of desulphurization will be referred to in the examples which appear later.

Improved results along the line of desulphurization are sometimes observed when the metallic contact mass comprises metals both above and below hydrogen in the electrochemical series either alloyed or in mechanical admixture, improved desulphurizing effects being possibly due to the initial formation of sulphides of the electronegative metals which are later decomposed by the hydrochloric acid to liberate hydrogen sulphide.

Very small amounts of hydrochloric acid are required in the treatments. From the equations given above the hydrochloric acid would be completely regenerated at the end of the polymerizing cycle so that the initial addition of a definite amount of acid would suffice. However, certain small losses are unavoidable and these are preferably counter-balanced by the addition of the necessary small amounts of acid.

There is apparently some definite relationship between the amount of hydrochloric acid necessary for efficient treatment and the pressure employed upon the system which is shown by the curve in Figure 3. An inspection of this curve indicates that at the preferred pressures, to-wit: 400 to 600 pounds per square inch, that the consumption of hydrochloric acid is reduced to a practical minimum whereas it increases sharply at lower pressures. Aside from the effect of greater concentration of the hydrochloric acid

due to the use of higher pressures than have heretofore been employed in similar treating processes, it is possible that the hydrochloric acid functions in a concentrated solution considerably

5 above its maximum solubility in water at ordinary pressures. The treating effects observed may thus be due to the joint action of hydrochloric acid and metal chloride in the presence of extremely small amounts of moisture.

10 The small amount of hydrochloric acid necessary for the treatment may be added as a substantially dry gas or in concentrated solution. The metal contact masses apparently react with the hydrochloric acid to an extent depending

15 upon their particular composition and may yield limited amounts of chlorides on the surfaces of the metal particles, which chlorides may also function catalytically to assist in the degumming and desulphurizing reactions. It is frequently

20 observed that when the metal contact masses are "preconditioned" by treatment with hydrochloric acid prior to their use in the process that the efficiency of the contact materials remains at a high value over an extended period of time

25 without further addition of hydrochloric acid. In such cases it is possible that the chlorides undergo hydrolysis in the presence of small amounts of moisture so that sufficient hydrochloric acid is for a time available for the treating reactions.

30 The process may be conducted in any suitable type of apparatus and Figure 1 shows diagrammatically by the use of conventional figures in side elevation the essential features of a plant layout which can be used.

35 Distillates to be treated may be introduced to the plant through a line 1 containing a control valve 2 and pumped by a pump 3 through a line 4 containing control valve 5 into and through a heating element 6 disposed to receive heat from a furnace 7. After being brought to a suitable temperature for treatment the heated products may be discharged through a line 8 containing a control valve 9 and leading to a line 10. Acid

45 necessary for the treatments may be supplied to a pump 18 through a line 16 containing a control valve 17 and discharged through a line 19 containing a control valve 20 into line 10 where it mixes with the heated oils. As previously stated the acid may be introduced in a solution of proper concentration to insure the presence of the small amounts of water which are apparently necessary in the treating reactions or may be introduced as a substantially dry gas, the type of

50 pumping equipment represented by number 18 being suitably modified.

The acid and oil pass under selected temperature and pressure conditions within the ranges previously mentioned, through valve 11 and enter pressure treater 12 which contains a metallic contact mass 13 dividing the interior of the treater into upper and lower liquid spaces 14 and 15 respectively. During the passage of the oil and acid through the contact mass, degumming and desulphurizing reactions are effected and the products of the treatment pass through line 21 containing control valve 22 to fractionator 23, valve 22 being so manipulated in conjunction with valves subsequent to the fractionator that the pressure obtaining on the pressure treater is substantially reduced in the fractionator

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75 the finished gasoline appear in the fractionator

as heavy polymer refluxes and comprise high boiling and substantially unaffected hydrocarbon fractions which may have been present in the raw naphtha if such was treated, and also polymers of olefins. Some sulphur may appear

80 in the polymers in the case of high sulphur stocks and some of the original sulphur may be present in the fractionator in the form of hydrogen sulphide. It is frequently advantageous in the case of high sulphur oils to utilize pressure

85 treaters in series, the hydrogen sulphide formed in the treating reactions in the first of such a series being vented before further contact is brought about, thus reducing the tendency for metal sulphide formation with corresponding

90 depreciation in the value of the metallic contact materials. By venting the fixed gases and thus removing the majority of hydrogen sulphide present, the formation of mercaptans may be reduced to a practical minimum so that desulphurization is more effective. Any hydrochloric acid which may be lost when the hydrogen sulphide and other low boiling hydrocarbons or fixed

95 gases are released may be counter-balanced by further additions of acid prior to the succeeding pressure treater. The vented gases may be passed through auxiliary beds of granulated metals and the chlorides and sulphides recovered, if desired.

100 The refluxes from fractionator 23 may be removed through a line 24 containing a control valve 25 and disposed of in any suitable manner. In case these refluxes are of fairly low sulphur content and otherwise suitable, they may be used as recycle stock in the cracking plant which may

105 have produced the naphtha or gasoline treated.

The vapors and fixed gases from the fractionator may be conducted through a vapor line 26 containing control valve 27 and be cooled during passage through a condenser 28, the

115 cooled gases and condensed gasoline passing through a rundown line 29 containing control valve 30 to a receiver and separator 31 which has a line 32 containing control valve 33 for the controlled release of fixed gases, a draw line 34 containing control valve 35 for the removal of the finished gasoline and a bottom draw line 36 containing control valve 37 for removal of water or aqueous solution which may accumulate in the receiver.

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The field of application of the process is extensive and the examples of the results obtainable upon different stocks could be multiplied to a considerable extent. A few, however, will suffice to show the advantages of the process over the more commonly used systems of treatment.

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An untreated cracked gasoline made from a relatively high sulphur California charging oil may be treated in equipment generally similar to that shown in Figure 1 at a temperature of 550° F. and a pressure of 450 pounds per square inch. The contact mass employed in the pressure treater may consist of zinc or brass turnings, and hydrochloric acid may be admitted to the treating zone at a rate corresponding to from 0.1 to 0.2 pounds per barrel of finished gasoline, the small amount passing out of the treating zone being absorbed during passage of the treated oils and fixed gases through auxiliary beds of granulated zinc. The following table shows the relative properties of the raw or untreated gasoline and the properties of the finished gasoline, the properties of the latter being determined after the passage of approximate-

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ly 6,000 barrels of gasoline through 1 ton of contact materials.

Comparison of raw and treated gasolines

	Raw	Treated
Color.....	Red.....	+30
Color stability*.....		28
Mg. of gum/100 cc. by copper dish.....	251	13
Total sulphur %.....	0.35	0.15
Doctor test.....	Positive.....	Negative.....
End point °F.....	400	400
Odor.....	Bad.....	Good.....

*After 4 hours' exposure to sunlight.

A further example may be cited involving the treatment of cracked gasoline from a Mid-Continent semi-asphaltic residuum. The conditions of operation were substantially the same as those given in the first example and the properties of the treated gasoline are those after the passage of 5000 barrels, of gasoline per ton of contact material.

Comparison of raw and treated gasolines

	Raw	Treated
Color.....	Yellow.....	+30
Color stability*.....		26
Mg. of gum/100 cc. by copper dish.....	750	17
Sulphur.....	0.06	0.04
Doctor test.....	Positive.....	Negative.....
End point °F.....	406	404
Odor.....	Bad.....	Good.....
Octane number.....	69	69
Induction period in oxygen bomb—minutes.....	180	810

*After 4 hours' exposure to sunlight.

The results obtained by the process as evidenced by the two preceding examples are striking from several standpoints. It will be observed that in both cases the color and color stability were better than those obtainable even by the use of commercially prohibitive amounts of sulphuric acid as shown in other experiments. The gum content was reduced to a figure below that required in premium gasolines and the odor was perfectly sweet. In the first example the sulphur reduction is especially noteworthy since California pressure distillates are notoriously refractory in regard to desulphurization by sulphuric acid or other methods of treatment.

The treating losses suffered were considerably less than 1% in both cases and this fact coupled with the extremely high quality of the treated product is of itself sufficient to recommend the process for the treatment of cracked gasoline of any character. The selectivity of the treatment in regard to the removal of gum-forming olefins without affecting mono-olefins is evident from the second example in the maintenance of the octane number after treatment while the oxygen bomb test which generally indicates the

stability of the gasoline on storage is raised to a point considerably in excess of the minimum of 240 minutes which is at present accepted as indicating a gasoline sufficiently stable under average storage conditions.

The foregoing disclosure of the nature of the invention and the numerical data presented in support of its commercial value are sufficient for their respective purposes but none of the particular details given are to be construed as imposing limitations on the process which is generally broad in scope.

I claim as my invention:

1. A process for refining gasoline-containing distillates which comprises treating the distillate with added aqueous hydrogen chloride in the presence of zinc at a temperature substantially above the normal initial boiling point of gasoline while under sufficient superatmospheric pressure to preclude substantial normal vaporization and to maintain a substantial portion of the gasoline in liquid phase.

2. A process for refining gasoline-containing distillates which comprises treating the distillate with added aqueous hydrogen chloride in the presence of metallic zinc at a temperature substantially above the normal boiling point of gasoline while under sufficient superatmospheric pressure to preclude substantial normal vaporization and to maintain a substantial portion of the gasoline in liquid phase.

3. A process for refining gasoline-containing distillates which comprises treating the distillate with added aqueous hydrogen chloride in the presence of zinc and copper at a temperature substantially above the normal initial boiling point of gasoline while under sufficient superatmospheric pressure to preclude substantial normal vaporization and to maintain a substantial portion of the gasoline in liquid phase.

4. A process for refining gasoline-containing distillates which comprises treating the distillate with added aqueous hydrogen chloride in the presence of brass at a temperature substantially above the normal initial boiling point of gasoline while under sufficient superatmospheric pressure to preclude substantial normal vaporization and to maintain a substantial portion of the gasoline in liquid phase.

5. A process for refining gasoline-containing distillates which comprises treating the distillate with added aqueous hydrogen chloride in the presence of copper at a temperature substantially above the normal initial boiling point of gasoline while under sufficient superatmospheric pressure to preclude substantial normal vaporization and to maintain a substantial portion of the gasoline in liquid phase.

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