

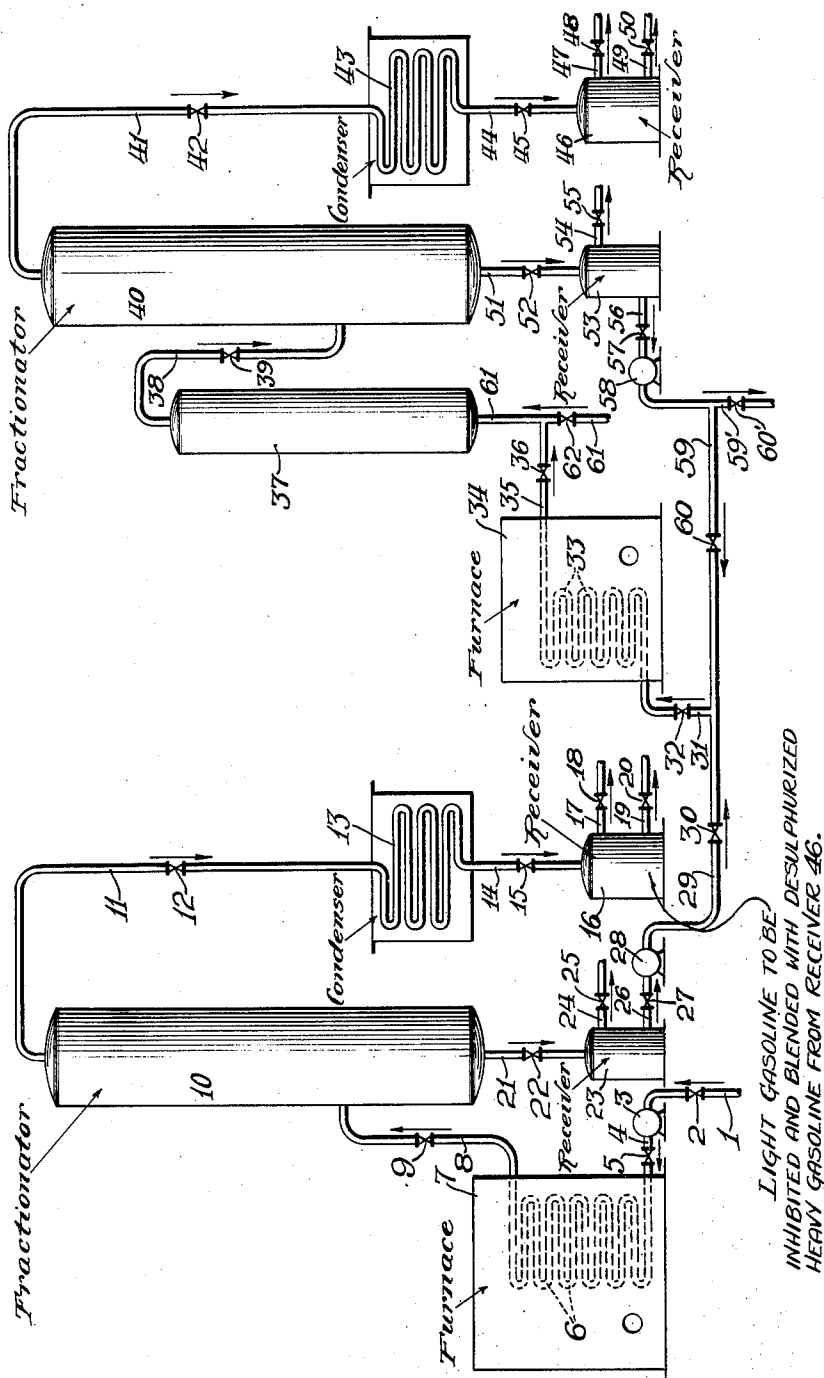
Feb. 9, 1937.

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2,070,295

TREATMENT OF HYDROCARBON OILS

Filed Sept. 15, 1933



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UNITED STATES PATENT OFFICE

2,070,295

TREATMENT OF HYDROCARBON OILS

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Application September 15, 1933, Serial No. 689,529

1 Claim. (Cl. 196—24)

This invention refers more particularly to the treatment of gasolines and is especially directed to the treatment of cracked gasolines produced from various charging stocks though it is also applicable to straight run gasolines.

In a more specific sense the invention is concerned with a process for refining gasolines, particularly high sulfur gasolines, to effect their desulfurization in an efficient manner and at the same time produce other refining effects such as, for example, decrease in color and gum content and increase in anti-knock value.

The distribution of sulfur in gasolines varies with the boiling point of the material and while no absolute rule can be laid down, it is frequently observed that the total sulfur content of the higher boiling fractions is higher than that of lower boiling fractions, and also that the nature of the sulfur compounds in the higher boiling fractions is such that they are less readily decomposed and desulfurized. It may happen in the case of cracked gasolines produced from high sulfur charging oils that considerable hydrogen sulfide is present in solution in the gasoline. However, this dissolved hydrogen sulfide is readily removed either in the stabilizing step or by simple treatment with caustic soda and constitutes no essential constituent of the gasoline. Thus, in redistilling the primary cracked naphtha hydrogen sulfide is lost as a gas and the succeeding low boiling fractions are relatively low in sulfur until a certain point in the distillation is reached which varies with the particular gasoline in question. After this point the sulfur content frequently increases rapidly so that the higher boiling fractions account for the major portion of the total sulfur content of the gasoline.

The present process is directed to a method of treatment for selectively desulfurizing these heavier high sulfur fractions while removing and preserving the lower fractions which require substantially no treatment.

In one specific embodiment the invention comprises fractionating gasoline to produce overhead fractions of low sulfur content and good color and anti-knock value which are cooled, condensed, collected and treated with inhibitors and refluxes of high sulfur content which are subjected to a limited hydrogenation under pressure, the hydrogenated products being fractionated to produce low sulfur overhead fractions of gasoline boiling range and insufficiently treated refluxes which are resubjected to the hydrogenating and desulfurizing step.

The general nature of the process may be conveniently described in connection with a characteristic plant operation and the attached drawing which shows a characteristic arrangement of parts in side elevation will be used in the description.

Referring to the drawing, the plant shown therein will be seen to consist essentially of two inter-connected units, the first serving to fractionate gasoline into a low boiling, low sulfur fraction having good color and anti-knock value and a relatively high-sulfur high-boiling fraction, while the second unit contains the elements necessary for hydrogenating and desulfurizing the heavy fraction. Gasoline such as cracked gasoline may be admitted to the system from a source not shown through line 1, containing control valve 2 and pumped by pump 3 through line 4, containing control valve 5, through tubular heating element 6 disposed in furnace 7. There is no need for excessive pressure in the primary distilling step other than to increase the capacity of the distilling unit and the temperature employed at the outlet of the heating coil will be determined by the percentage of the gasoline which it is found practicable to remove as a low-boiling fraction which needs only the addition of an inhibitor to preserve its properties. The mean boiling point of present day commercial gasoline is generally within the range of 250 to 300° F. and in the case of cracked gasolines treated by the present process it is usually possible to remove from about 30 to 60% of the gasoline as an overhead fraction. Thus, the temperatures at the exit of coil 6 may vary from 200 to 300° F. at atmospheric pressure depending upon the efficiency of the fractionating column and the type of gasoline undergoing treatment.

The heated gasoline then passes through line 8, containing control valve 9, and enters fractionator 10, from which fixed gases and low-boiling hydrocarbon vapors leave through line 11, containing control valve 12, to pass through condenser 13 from which the liquefied low boiling gasoline fractions and the fixed gases pass through line 14, containing control valve 15, to receiver 16, which has a gas release line 17, containing control valve 18, and a liquid draw line 19, containing control valve 20, from which the low boiling overhead fractions may be removed to storage for inhibitor treatment prior to their blending with the desulfurized heavy fractions produced in the second stage in a manner to be presently described. Gases withdrawn through line 17 usually comprise a major portion of the hydrogen sulfide which may have been in solution in the original gasoline.

The art of using inhibitors to preserve the desirable properties of gasolines is well known at the present time and is not claimed as a special feature of the invention, which may utilize any of the well known inhibitors or anti-oxidants to preserve the properties of the low boiling overhead fractions produced, while treating the high boiling gasoline fractions by the more drastic method of hydrogenation. Commercial inhibitors com-

prise many individual chemical compounds of a more or less pure character and numerous semi-refined compounds and mixtures which have sufficient inhibiting action and are cheaper. Among the chemical compounds which are employed the phenols and naphthols are outstanding and include such compounds as catechol, hydroquinone, ortho and para cresol, etc. and also alpha naphthol and alkylated derivatives thereof. Examples of crude or semi-refined mixtures are tri-cresol (a commercial mixture of o-, m- and p-cresol) and various selected fractions from the tars produced in distilling such carbonaceous materials as coal, wood, lignite, water gas tar, etcetera. The selection of a particular inhibitor and the amount used will be determined by the cost of the same and its inhibiting value in the particular overhead cut in which it is used.

The condensates from fractionator 10 may be passed to receiver 23 through line 21, containing control valve 22, and any fixed gases may be removed from the receiver through line 24, containing control valve 25. The liquids themselves are withdrawn through line 26, containing control valve 27 to high pressure pump 28 which discharges the liquids into the heating element of the hydrogenating unit by way of line 29, containing control valve 30, and line 31, containing control valve 32.

Conditions employed in the hydrogenating step upon the heavy fractions of the gasoline are generally moderate, the temperatures used being below the usual cracking range, say in the neighborhood of 600 to 850° F. while the pressures may be varied over a wide range depending upon the stability of the sulfur compounds. Pressures of from moderately superatmospheric in the neighborhood of 100 pounds per square inch up to pressures as high as 3,000 pounds per square inch may be employed if desired. The selection of conditions is usually best determined as a matter of trial, since they can hardly ever be predicted from analytical data on the composition of the gasoline fractions.

The heating element 33 of the hydrogenating unit is shown disposed to receive heat from the furnace 34, the heated products passing through line 35, containing control valve 36, and entering a pressure hydrogenator 37 after the introduction of hydrogen from an outside source (not shown) through line 61, containing control valve 62. The quantity of hydrogen necessary will depend upon the relative stability of the sulfur compounds and their percentage in the distillate fractions, but as a rule the amount required is not large and may constitute approximately 1 to 3% by weight of the oils undergoing treatment.

A number of catalysts are suitable for accelerating the reactions of hydrogenation and desulfurization in the hydrogenating chamber, although materials which may be employed alternatively are not to be construed as strict equivalents as each will exert its own special catalytic function depending upon its own inherent properties, its physical condition and the temperature and pressure under which it is used. Metals of the iron group, iron, nickel and cobalt and their oxides and sulfides may be employed and also chromium, molybdenum and tungsten and their corresponding compounds. The sulfides of molybdenum and tungsten, while possessing somewhat lower activity than metals such as nickel, are on the other hand less susceptible to sulfur poisoning and maintain their efficiency over much longer periods of time. The invention is not lim-

ited to the use of any particular catalyst but may employ any single catalyst or composite mixture which may have previously been found to have value in hydrogenation of petroleum or other substances or which may function with special efficiency in the cases in point.

The products of the hydrogenating step are now fractionated passing through line 38, containing control valve 39, to fractionator 40 for the production of low sulfur oils which can then be blended with the overhead cuts from the first fractionating stage to produce a refined and desulfurized gasoline. The vaporous products from the fractionator comprising the desired low sulfur liquid fractions and fixed gases pass through line 41, containing control valve 42, condenser 43, run down line 44 and valve 45 to enter final receiver 46 having gas release line 47 containing control valve 48 and liquid draw line 49, containing control valve 50. From the latter point the desired fractions from the hydrogenating step are removed for final light treatment if necessary followed by blending with the overhead distillates from receiver 16.

The bottom refluxes from fractionator 40 will comprise oils of higher boiling point than desired in finished gasoline which may have been in an original naphtha treated or have been produced by secondary polymerization reactions in the course of the treatment. These fractions are withdrawn through line 51, containing control valve 52, to receiver 53 which has gas release line 54 containing control valve 55, and liquid draw line 56 having control valve 57, and leading to recycle pump 58 which in turn discharges through line 59, containing control valve 60, to line 31 and ultimately to heating element 33. It may happen that the conditions of treatment in heating element 33 in the succeeding hydrogenator are not of sufficient intensity to decompose fractions recycled from fractionator 40 in which case the refluxes may be withdrawn from the system through branch line 59', containing control valve 60', for use as fuel or as a component of charging stock to an oil cracking plant.

Alternative modes of procedure other than those shown in the drawing may at times be indicated, for instance, hydrogen may be added to line 31 prior to the admission of the heavy gasoline fractions to the heating element of the hydrogenating unit and downflows may be employed through hydrogenator 37 instead of the upflow shown in the drawing.

A particular set of results obtainable by the invention will serve to indicate its value. The case in point concerns the treatment of the cracked naphtha produced from a North Texas straight run residuum, this naphtha having the properties shown in the following table along with the properties of the gasoline produced therefrom by straight distillation without treatment of any kind.

Properties of naphtha and gasoline

	Naphtha	Gasoline
Gravity, °A. P. I.	48.0	53.0
Initial boiling point	90° F.	100° F.
50% point	310° F.	285° F.
End point	475° F.	410° F.
Total sulfur content	0.36%	0.30%
Mg. gum by copper dish		200
Octane number		68

This naphtha may be charged to a plant similar

to that shown in the drawing, the initial fractionation taking over about 60% of the gasoline content of the naphtha which is treated with 0.01% of a fraction of hardwood tar boiling with-
 5 in the range of 240 to 280° C. which is sufficient to preserve its properties and also the properties of the treated heavy end after blending. The remaining naphtha fractions are introduced to the
 10 hydrogenating plant and treated with 2% of hydrogen by weight at a temperature of 750° F. and a pressure of 500 pounds per square inch using a molybdenum sulfide catalyst. After fractionating to produce 400° F. end point and blending
 15 back the products from the receiver of the hydrogenating unit with the receiver of the distilling unit the properties of the gasoline blend after a light caustic wash to remove hydrogen sulfide may then be as follows:

Properties of finished gasoline

20	Gravity °A. P. I.....	53.5
	Initial boiling point.....	95° F.
	50% point.....	283° F.
	End point.....	405° F.
25	Total sulfur content.....	0.05%
	Mg. of gum by copper dish.....	20
	Octane number.....	70

A treatment such as the foregoing, while some-
 30 times sufficing to produce a completely refined

product, may also be combined with other necessary treatments, even to the extent of using small quantities of sulfuric acid on either of the fractions if necessary. It may sometimes happen
 5 that the products from such hydrogenating steps are not up to color in which case the use of small quantities of clay or fuller's earth may be resorted to to avoid further treatment and fractionation.

The character of the invention should be clear
 10 from the foregoing specification and the commercial value is shown by the data presented, but neither is to be used in imposing undue restrictions upon the scope of the invention.

I claim as my invention:

A process for treating cracked gasoline which
 15 comprises separating the gasoline into a light cut requiring no substantial refining and a heavier cut containing an objectionable amount of sulphur, adding to the light cut an oxidation and
 20 polymerization inhibitor in sufficient amount to substantially prevent deterioration of the total gasoline, desulphurizing said heavier cut, in the
 25 absence of the light cut, by treatment thereof with hydrogen in the presence of a hydrogenating catalyst, and, upon completion of the desulphurizing operation, blending the desulphurized
 heavier cut with the light cut containing the inhibitor to produce a satisfactorily desulphurized and inhibited motor fuel product.

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