March 21, 1939. H. B. COOKE 2,151,374

MANUFACTURE OF STABILIZED MOTOR FUEL

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Fig. 1.

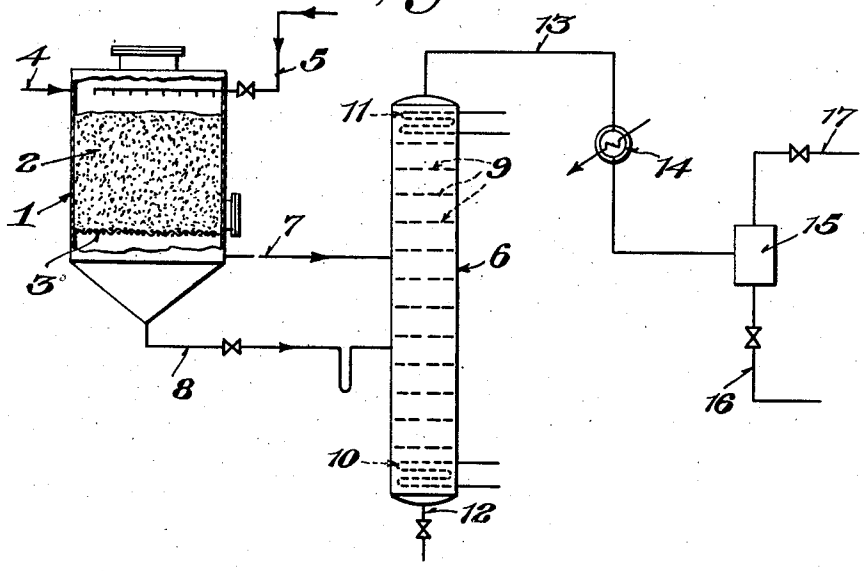
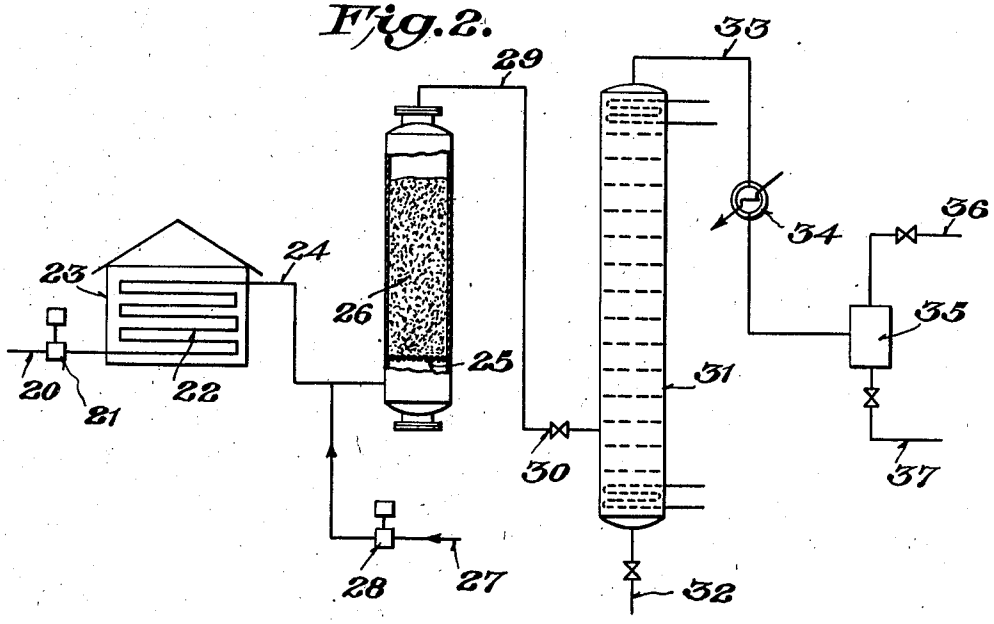


Fig. 2.



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MANUFACTURE OF STABILIZED MOTOR FUEL

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1 Claim. (Cl. 44—9)

This invention relates to the manufacture of stabilized motor fuel, that is to say, gasoline or gasoline-like hydrocarbons free or substantially free from gum-forming tendencies; all as more fully hereinafter set forth and as claimed.

It is well known that cracked gasoline distillates and polymer gasolines formed by the polymerization of normally gaseous hydrocarbons contain in the raw state considerable quantities of certain unsaturated constituents or impurities which tend to form gums or resinous bodies, and to discolor, upon standing. Formerly, cracked gasoline was almost entirely treated, where these impurities had to be removed, by means of sulfuric acid. But with the development of internal combustion engines and increasing requirements for high anti-knock value in gasoline fuels, the sulfuric acid washing process was found to have certain disadvantages, which eventually led to the development of new treating processes. Sulfuric acid causes high treating losses and is insufficiently selective in many instances; that is to say, it attacks or polymerizes desirable unsaturated constituents of the gasoline as well as the undesirable gum-forming constituents, and may result in a serious depreciation of the anti-knock value or octane number of the treated gasoline on this account. With the present and recent tendencies toward the production of gasolines of increasingly high octane number, the deficiencies of sulfuric acid washing have become marked; when the cracking process is made more drastic, in order to produce a gasoline of high anti-knock value, the production of both desired and undesired unsaturated constituents in the cracked gasoline is increased. Sulfuric acid is far from a satisfactory treating agent for the refining of high anti-knock cracked gasolines, and for the same reason is a poor treating agent for refining polymer gasolines which depend to a considerable extent for their high anti-knock value upon the presence of unsaturated compounds which will be attacked or polymerized by sulfuric acid.

The two most effective methods for overcoming the disadvantages of sulfuric acid treating which have been proposed and used are on the one hand, refining by means of solid adsorbent catalytic materials at elevated temperatures, and on the other hand, the use of anti-oxidants.

Of the clay treating processes there are in general two types which are known in the art as "vapor phase" and "liquid phase" processes. In the Gray vapor phase process, the cracked gasoline distillate is passed in vapor form through a bed of fuller's earth or equivalent solid adsorbent catalytic material, which exerts a selective polymerizing action upon the gum-forming and color-imparting impurities, thereby converting them to constituents boiling above the gasoline end boiling point, and hence readily separable from the treated gasoline by ordinary fractional distillation methods.

This process has come into wide spread use, but is in some instances somewhat too mild in action to result in a final gasoline product of sufficient gum- and color-stability. The so-called liquid phase clay treating process, developed by Osterstrom, is similar except that in this type of process the contact of the cracked distillate and the clay or adsorbent takes place at higher temperatures and pressures. In its preferred embodiment, temperatures above the normal vaporizing point of the gasoline distillate are used, but the pressures are such as to suppress vaporization, unless the temperature is above the critical temperature of the vapors.

There are various modifications of these processes, but those noted above are the principal and most successful types; the other modifications ordinarily involve suspending finely divided clay in a flowing stream of gasoline distillate, under elevated temperatures and usually under elevated pressures.

All of the above clay treating processes may be applied to a rerunning operation, that is to say they may be used for the treatment of previously condensed gasoline from which the cracked gases produced in the cracking process have been separated, or they may be carried out on a mixture of gasoline vapors and normally gaseous hydrocarbons, such as that issuing from the top of the main fractionator in a conventional cracking operation. In this case the hydrocarbons coming into contact with the absorbent catalyst containing, in addition to gasoline hydrocarbons, varying quantities of propane, propylene, butanes and butylenes. Such normally gaseous hydrocarbons, or at least the unsaturated normally gaseous hydrocarbons, are also capable of polymerization, not to gums but to polymers boiling within a gasoline boiling point range and of very high anti-knock value.

For this reason, it has also been proposed by Gray and others to subject normally gaseous hydrocarbons to contact with adsorbent clay or the like at elevated temperatures and pressures, in order to polymerize such gases or the unsaturates contained therein, for the production of polymer gasoline.

Such polymer gasoline or polymer gasoline otherwise produced, ordinarily requires further refining or stabilization to remove gum-forming constituents.

The use of anti-oxidants referred to hereinabove represents an attempt to attack the problem in another way; that is to say, by adding to the gasoline an inhibitor which will serve to prevent the polymerization of potential gum-forming constituents to gums or resinous bodies. However, most of the anti-oxidants which have been successfully employed as an alternative to treating cracked gasoline and the like, or an adjunct thereto, are extremely expensive and they are also, for the most part, soluble in water and dilute alkali solutions. These are severe disadvantages, even though only small quantities of such anti-oxidants may be required.

In the prior co-pending applications of Troy L. Cantrell, there are disclosed various methods of making gum-inhibitors for addition to cracked gasolines and the like by reacting phenols with olefins in the presence of sulfuric acid. Under the catalytic influence of the sulfuric acid the olefins are absorbed in the phenols, through an alkylation mechanism of some sort, thereby resulting in the formation of compounds of high utility as anti-oxidants. However, the alkylated phenols produced in accordance with these processes are insoluble in water and dilute alkali solution and the alkylations which take place are probably of secondary and tertiary types.

My invention contemplates the manufacture of anti-oxidants suitable for addition to cracked and polymer gasolines and the like, by reacting phenolic and olefinic bodies in the presence of solid adsorbent catalysts, such as fuller's earth, clays, acid-treated clays, activated carbon, silica gel and the like, primarily those solid adsorbent catalysts which are also polymerization catalysts.

My process is carried out by contacting phenolic and olefinic bodies in the presence of a solid adsorbent catalyst, preferably in a continuous manner and preferably at somewhat elevated temperatures of from 100° to 800° F. Pressures up to several hundred pounds per square inch may also be employed.

Where it is desired simply to manufacture an anti-oxidant the olefinic materal is preferably used in concentrated form, or at any rate in such form that the liquid product will consist substantially entirely of the formed anti-oxidant. Propylene, the various butylenes and amylene, in substantially pure form, may thus be employed, or mixtures of paraffinic and olefinic gases may be employed, as for example cracked refinery gases, inasmuch as the paraffinic constituents thereof do not polymerize during the operation. If polymerization occurs to some extent, the gasoline-like polymers thereby obtained may be removed by distillation if desired, and the liquid product may in any event be fractionally distilled to recover relatively narrow boiling fractions, primarily those falling within the gasoline boiling point range, or in some instances between about 300° and 550° F.

My invention further contemplates however, as an especially advantageous feature thereof, the formation of anti-oxidant material, in the general manner stated hereinabove, in the course of a clay treating operation or in the course of a gas polymerization operation, so that the final treated or polymerized gasoline contains a sufficient amount of the anti-oxidant to make up for any deficiency in treating which would result from the use of the treating or polymerizing process alone.

Thus, in the treatment of cracked or polymer gasoline with adsorbent clay or the like, either in the liquid phase or in the vapor phase, I introduce a small quantity of a phenolic material into the zone of contact between the vapors and the solid catalyst, whereby, under the catalytic influence of the adsorbent, a reaction is caused to occur between the phenolic and olefinic constituents of the hydrocarbons undergoing treatment, thereby resulting in the formation of an anti-oxidant product. When gasoline vapors are treated alone, as in a "rerun" operation, there are ordinarily sufficient low boiling olefinic constituents present in the gasoline to form anti-oxidant by reaction with the phenol introduced. But wherever the gasoline is deficient in such constituents or wherever the anti-oxidant thus produced tends to be too high boiling in character to fall within the gasoline boiling point range, normally gaseous olefins are introduced, along with the gasoline, to contact with the adsorbent, in the presence of phenol.

In polymerizing normally gaseous olefins to gasoline-like bodies, a small quantity of phenol is introduced for reaction with a portion of the olefins, in the presence of sold adsorbent catalyst. Where the polymerization process relies primarily upon the use of such adsorbent catalyst as a catalytic polymerizing agent, the phenol is simply introduced into the stream of gases traversing the catalyst. In applying my invention however to a thermal polymerization process, it is necessary to introduce some solid catalyst along with the phenol or to provide an adsorbent bed or zone at some point in the system, so that the gases undergoing polymerization may be contacted with phenol in the presence of the catalyst.

Where, as aforesaid, the formation of the anti-oxidant is accomplished as an incident to the treating of cracked or polymer gasoline or as an incident to the formation of polymer gasoline by polymerization of normally gaseous hydrocarbons, the amount of phenol employed will be extremely small, merely sufficient phenol being added to produce, by reaction with olefin, enough anti-oxidant within the gasoline boiling point range to provide the desired degree of stabilization of the final product against such gum-forming tendencies as it would otherwise have. It will be obvious that the specific amounts added will vary, but at the outside they will not ordinarily exceed 1 or 2 per cent of phenol by weight, based upon the weight of the final gasoline product, and in most instances the amount of phenol required will be considerably less.

Where the operation is conducted for the purpose of manufacturing concentrated anti-oxidant material, a considerably larger proportion of phenol, with respect to the olefinic starting material, should be employed. Thus, for example, for this purpose, the phenol may be used in such amount as to react with all or substantially all of the olefins present, and so as to secure an anti-oxidant product representing a gain in volume of from 50 to 150 per cent on the phenol employed. It is preferred always to carry out the reaction to such extent that none of the original phenol is left entirely unreacted upon.

Various phenols may be employed, such as phenol (C_6H_5OH) itself, or the higher homologues thereof, such as the various cresols. It is not necessary to employ these constituents in

pure form. For example, commercial 90 per cent phenol and crude cresylic acids may be employed. The phenols may be of the mono-hydric or poly-hydric type, although the mono-hydric phenols are preferred by reason of their cheapness and availability.

Wherever, as a result of the contact between the reacting constituents and the catalyst, compounds boiling above the desired gasoline end boiling point are produced, these may be readily removed by fractional condensation or fractional distillation. Such compounds may include both heavy polymers and anti-oxidants, and these may in turn be separated in many instances, resulting in the recovery of further anti-oxidant which, if not too high boiling and if sufficiently free from gummy material, may also be added to cracked or polymer gasoline as gum-inhibitors.

In order that my invention may be fully set forth and understood I now describe various specific embodiments thereof, with reference to the drawing accompanying and forming a part of this specification. In this drawing, Fig. 1 is a more or less diagrammatic elevational view of apparatus for refining gasoline in which provision is made for the performance of the process of my invention, the operation being conducted in the vapor phase; and Fig. 2 is a similar view of apparatus for refining gasoline in the liquid phase, in which provision is also made for the performance of the process of my invention.

Referring now to the drawing, and more particularly Fig. 1, there is illustrated a tower 1 adapted to contain a bed 2 of solid adsorbent catalytic material such as fuller's earth or the like, the bed 2 being conveniently supported upon a foraminous partition 3. Raw gasoline vapors, which may consist entirely of gasoline constituents but which in the preferred instance also include normally gaseous olefins such as propylene and butylenes, are introduced into the upper part of the tower 1 through a line 4. The line 4 may lead from a rerun still or from the fractionator of an oil cracking unit. A small quantity of a phenol, either alone or in admixture with hydrocarbon oil, is introduced into the upper portion of the tower 1 through a line 5. Wherever the amount of phenol introduced is extremely small it is desirable, for good distribution and contact purposes, to employ the phenol in admixture with a hydrocarbon oil as a carrier therefor. In many instances it is desirable to introduce a solvent to the clay bed for the purpose of assisting in the removal of polymers therefrom, and where this is true the phenolic material may be admixed with the solvent so introduced. In any event, however, provision is ordinarily made for the presence of some liquid material in the bed 2, as a solvent, and this solvent serves to carry and distribute the phenol. In some instances the solvent may be supplied by permitting a portion of the heavier constituents of the gasoline vapors to condense in the clay bed.

During the passage of the gasoline through the clay bed 2, a portion of the gum-forming constituents present in the gasoline are polymerized to higher boiling compounds, and a reaction takes place between olefinic constituents present and the phenols introduced through the line 5 or otherwise, resulting in the formation of anti-oxidant material, at least a considerable portion of which boils within the gasoline boiling point range.

The treated vapors may then be simply condensed, but ordinarily it is preferable to conduct the treated vapors, and also the liquid polymers separating in the tower 1, to a fractionating tower 6, through lines 7 and 8 respectively. The fractionating tower 6 is shown as of conventional design having plates or trays 9 located therein and having a heating coil 10 or other heating means at the bottom of the tower and a cooling coil 11 or other cooling or refluxing means at the top of the tower. In the tower 6 fractional distillation and condensation, or rectification, is effected, separating the constituents introduced into a liquid fraction consisting largely of polymers and high boiling constituents and a vapor fraction consisting of treated gasoline, as well as any unreacted gases present. The polymer fraction is removed from the tower 6 through a line 12 and may be redistilled if desired for the separation of any high boiling anti-oxidant constituents contained therein, while the treated gasoline vapors pass through a line 13 to a condenser 14 and a separator 15. The gasoline condensate is removed from the separator 15 through a valved line 16 while any gases which remain uncondensed are removed from the separator 15 through a valved line 17. The treated gasoline may then be washed with dilute caustic solution and water if desired, it being one of the advantages of the process of my invention that the anti-oxidant formed in the tower 1 is insoluble in dilute caustic solution and water, so that it will not be removed from the gasoline when the gasoline is so washed.

Apparatus and procedure similar to that described in connection with Fig. 1 may also be employed when polymerizing normally gaseous olefins to gasoline-like polymers. However, in this instance the temperatures and pressures will in general be higher than when a gasoline treating operation is being conducted; for example, gas polymerizing temperatures and pressures will ordinarily run from 500° to 800° F. and from 200 to 2000 pounds per square inch, respectively, whereas in treating gasolines the temperatures are in this instance simply the temperatures of vaporization and the pressures will not ordinarily exceed 300 pounds per square inch.

In the instance illustrated in Fig. 2, however, the treating pressures and temperatures are somewhat higher. In this instance, the gasoline to be treated is introduced through a line 20 by means of a pump 21 to a heating coil 22 located in a suitable furnace setting 23. In passing through the coil 22 the gasoline is heated to a temperature above its normal vaporizing temperature, under high pressure. Pressures of from 500 to 1000 pounds per square inch are in the most cases suitable and the temperatures may run from 500° to 700° F., the preferred temperatures being somewhat below the critical temperatures of the hydrocarbons, so that the hydrocarbons can be maintained in the liquid phase.

The liquid or vapor stream leaving the heating coil 22 then passes through a line 24 to a chamber 25 wherein is located a bed 26 of solid adsorbent catalytic material such as fuller's earth or the like. A small amount of phenol is introduced at the same time, for example by means of a line 27 having a pump 28. As in the instance previously described, and particularly where the amount of phenol required is extremely small, the phenol may be introduced in admixture with a suitable hydrocarbon oil, preferably one boiling within the gasoline boiling point range, although a somewhat higher boiling solvent may be employed for this purpose. The treated material

then passes through a line 29 wherein is located a pressure reducing valve 30 and is flashed into a fractionating tower 31, the design and purpose of which are in general similar to those of the fractionator 6 illustrated in Fig. 1. High boiling constituents, which may include polymers, solvent and high boiling anti-oxidant, are removed from the tower 31 through a valved line 32, while the treated gasoline, containing some anti-oxidant material, passes through a vapor line 33 to a condenser 34 and a separator 35. Gases and gasoline are removed from the separator 35 through valved lines 36 and 37 respectively. As in the previous instance, the gasoline may be washed with dilute caustic solution and water.

In each of the instances described hereinabove, the gasoline as ultimately condensed and collected, contains a small quantity of anti-oxidant material, produced by reaction between olefinic and phenolic bodies in the presence of the solid adsorbent catalyst. The amount thereof will depend upon the amount of phenolic material introduced and, as has been stated hereinabove, is in the instances referred to in connection with the foregoing figures merely such as to provide the necessary stabilization of the final gasoline product.

Where the manufacture of more concentrated anti-oxidant is desired, procedures similar to those described specifically hereinabove may be employed, except that in such instance the material introduced for reaction with the phenol will ordinarily be more concentrated with respect to olefins, and the amount of phenolic material will be considerably greater. However, in making concentrated anti-oxidants from olefinic gases, according to the process of my invention, it is not necessary that the gases should be predominantly olefinic in character; gaseous paraffinic constituents are not affected by the process and pass through unchanged.

While I have described and illustrated my invention hereinabove with reference to various specific embodiments and exemplifications, it will be obvious to those skilled in the art that my invention in its broadest aspects is not limited to the details thereof but may variously be practiced and embodied within the scope of the claim hereinafter made.

I claim:—

The process of obtaining a gasoline of high anti-knock value, stabilized against formation of gums, which comprises subjecting normally gaseous olefines to contact with a solid adsorbent catalytic material, at such elevated temperature and pressure as will be effective to promote polymerization of normally gaseous olefines to normally liquid gasoline like polymers, in the presence of a phenol, whereby said phenol is caused to react with a portion of the olefinic constituents present, forming an anti-oxidant reaction product, and recovering from the resultant products gasoline containing at least a portion of the anti-oxidant material thereby formed.

HORACE B. COOKE.