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TREATMENT OF HYDROCARBON OILS

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This invention relates to the treatment of hydrocarbon oils, and refers more particularly to the treatment of low boiling distillates produced in the cracking of heavier higher-boiling fractions.

More specifically the invention has reference to a process for treating hydrocarbon mixtures undergoing decomposition and conversion reactions or the lower boiling vaporous products of these reactions to produce substantial amounts of compounds which add materially to the anti-knock value of the gasoline finally produced from the process.

While the cracking process as at present generally practiced in the petroleum industry tends to the production of gasolines having anti-knock characteristics superior to those possessed by corresponding gasoline fractions produced by the straight run distillation of crude petroleum, it may frequently happen that the production of a cracked gasoline of a knock rating rendering it salable as a premium motor fuel may entail the use of relatively severe cracking conditions with attendant increased losses in fixed gases and coke and a decrease in the overall yield of the desired product. In the majority of cases for any given stock charged to the cracking process there exists an optimum set of conditions for producing a maximum yield of gasoline of good anti-knock value, the use of more severe conditions, while they may produce gasoline boiling range fractions closely approximating a mixture of aromatic hydrocarbons in composition, producing not only excessive gas losses but a very material lowering in yield of gasoline so that in this respect it may be stated that the production of increased yields of anti-knock gasoline by the cracking process is limited by economic considerations.

The present invention has as one of its objects provision of a process by which any economic disadvantages of producing high anti-knock value gasoline by cracking may be offset by the production concurrently in the cracking process of compounds having a specially high anti-knock value so that the product of the operation considered as a whole is of the high quality desired and the necessary yields are maintained.

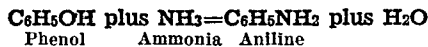
In one specific embodiment the invention comprises treating cracked hydrocarbon vapors with phenols and ammonia to produce amines for increasing the anti-knock value of the condensates, treatments being conducted in the presence of heavy metal halides which act as catalysts.

The following tabulation shows a list of a few

of the simpler phenols which may be employed:

Compound	Specific gravity	At. ° C.	Melting point ° F.	Boiling point ° F.
Phenol C ₆ H ₅ .OH	1.065	18	108	361
o-Cresol 1:2 C ₆ H ₄ .CH ₃ .OH	1.039	23	87	376
m-Cresol 1:3 C ₆ H ₄ .CH ₃ .OH	1.033	19	-----	398
p-Cresol 1:4 C ₆ H ₄ .CH ₃ .OH	1.033	23	96	395
a-Naphthol C ₁₀ H ₇ .OH	1.224	4	201	535
b-Naphthol C ₁₀ H ₇ .OH	1.217	4	252	546

The type reaction which occurs in treatments according to the process of the invention is given by the following equation:



It will be observed that the degree of completion of the reaction is contingent upon the elimination of water and that in general for high yields dehydrating conditions are advantageous.

While in some instances sufficient yields may be obtained in the absence of catalytic substances, it is generally preferable to employ certain heavy metal halides such as zinc chloride, aluminum chloride, ferric chloride, stannic chloride, et cetera. These compounds may be employed either in highly concentrated aqueous solutions, as fused salts or as sublimates depending upon their particular chemical and physical properties. The action of substantially saturated solutions of zinc chloride is typical and its use will be particularly described in reference to the operation of the process though it is to be understood that other similar compounds may be used in its place when their properties and the conditions of operation warrant.

Zinc chloride forms addition compounds with ammonia and with various amines such as aniline, diphenylamine, et cetera. Apparently these molecular complexes are indefinite in composition though there is good proof of the existence of such definite compounds as ZnCl₂.2NH₃; ZnCl₂.4NH₃ and possibly ZnCl₂.NH₃. These compounds may be formed either by adding ammonium hydroxide or ammonia to aqueous solutions of zinc chloride or by dissolving zinc oxide in ammonia solutions containing ammonium chloride. They exist usually as white crystalline solids of variable melting point, depending upon their composition and are of known value in promoting the formation of amines from phenols.

One of the advantages of the process consists in producing amines in situ at the temperatures

and pressures commonly encountered in the fractionating zones of cracking processes, these conditions being specially suitable for the reactions desired. For example, in the reaction between phenol and zinc chloride-ammonia, yields of 70-80% may be obtained at temperatures of from 500 to 600° F. at pressures of 200-300 pounds per square inch, these conditions frequently obtaining in the primary fractionator of commercial processes.

In the actual operation of the process several alternatives are possible. For example, cracked vapors after the addition of regulated amounts of phenol and ammonia may be passed upwardly concurrently to down-flowing solutions of zinc chloride, the net result of the reactions being the formation of aniline which passes along with the cracked vapors and is condensed with the gasoline from the final fractionator. In such treatments it has been found that the rate of reaction under a given set of temperature and pressure conditions may be accelerated by the presence of ammonium chloride in the zinc chloride solution.

As another method of operation, the cracked vapors mixed with the same regulated amounts of phenol and ammonia may be passed over solid contact masses containing substantial amounts of zinc and/or other oxides to produce the same effect, namely, the production of the amines corresponding to the particular phenol employed with resultant increase in the anti-knock value of the finished gasoline.

The particular phenol employed in the process and the amount used will depend upon a variety of factors such as the cost of the compound, the character of the cracked products (which in turn depends upon the character of the charging stock and the conditions of operation) and the knock rating desired in the finished gasoline. Phenol is of general application, as the aniline which results from it by the reactions characteristic of the process of the invention has a high effect on the anti-knock value of a given gasoline, this being only slightly exceeded by such compounds as cumidine, xyldine, monomethylaniline, toluidine, et cetera, which result from the treatment of the corresponding phenols with ammonia.

An inspection of the tabulation showing the properties of some of the ordinary phenols shows that they are readily adaptable to use in the process since their melting and boiling points are well within the range of operations and they may be therefore injected into the cracked vapors in liquid form without particular difficulty. While the use of phenol itself as the simplest representative of the class has been particularly described it is to be understood that any derivative thereof may be used which produces desired results and that in many instances it is of advantage to use mixtures of phenols such as fractions of the tar acids extracted from coal tar by caustic soda and later liberated by acidification. Conditions of operation such as the amount and type of zinc chloride solution, the amount of ammonia, et cetera, will necessarily be varied to produce the best results from any given mixture of phenols that may be employed, the determination of the best conditions of operation being usually only a matter of a few trials and presenting no difficulties to those skilled in petroleum refining operations.

In addition to the benefits gained by the production of amines in the finished gasoline by the process disclosed other valuable treating effects may be produced such as those resulting from

the polymerizing action of the zinc chloride solutions upon the more highly unsaturated compounds in the cracked vapors such as the di and triolefins, these compounds having been shown to be the chief offenders in the matter of gum formation in cracked gasolines. The degree of this effect will depend upon the amount of zinc chloride solution used and may be controlled by proper proportioning of the compounds entering into the reactions. To control the concentration of the salt solutions the use of proper amounts of steam is contemplated, usually to prevent undue concentration of the solutions employed by increasing the partial pressure of the water vapor, whereby precipitation of solid materials and clogging of equipment is avoided. When salts are employed in the anhydrous condition as, for example, aluminum chloride sublimate when and where this is found to be of advantage, it will be obvious that the use of steam is a disadvantage.

While the process of the invention may be used as a single treatment when the desired vapor phase treating effects are obtained by its use, it may also be used in combination with other treatments both upon the vapors and upon the condensed product when such combinations are shown to be advantageous. For example, vapors prior to the use of the process may be treated by desulfurizing steps for the removal of hydrogen sulfide or other sulfur compounds and settling, filtering or adsorbent treatments may follow to insure the removal of entrained liquid or solid reaction products and further refining. In some cases the condensed gasoline may require limited washing for final purification.

As an example of a treatment which may be conducted according to the process of the invention and the results obtainable therefrom, the cracked vapors of approximate gasoline boiling point range coming from the fractionator of a cracking process operating on Mid-Continent residuum may be considered. Such vapors may be evolved from the fractionator under a pressure of approximately 200 pounds per square inch and a temperature of 500° F. Tricresol may be injected into these vapors at the rate of about ten pounds per barrel of finished gasoline and ammonia at the rate of approximately three pounds. Vapors may then be passed to a fractionating column and caused to rise counter-current to a descending concentrated solution of zinc chloride so that the reactions leading to the formation of toluidine are induced. The following tabulation shows the results obtained for the same yield of gasoline by merely fractionating the vapors compared with the results obtainable when they are subjected to the treatment just described:

	Untreated	Treated
Octane number.....	65	82
Color, Saybolt.....	12	30
Gum content by copper dish.....	300	25 mgs.
Sulphur content.....	0.20	0.05-0.10%
Color stability or loss in Saybolt degrees in the four-hour sunlight test.....	10	3-4

It will be observed from the above that the properties of finished gasoline have been markedly improved without decrease in yield particularly as regards anti-knock value. To produce the octane number shown by ordinary cracking depending upon increasing the severity of cracking conditions they entail in such an instance a reduction in yield down to from 50 to 55% so that

it will be apparent that considerable benefit has accrued from the use of the process.

The foregoing general description of the process of the invention and the example of the results obtainable by one operation thereof is sufficient to enable one skilled in the art to recognize its value but since the exact type of operation may be considerably varied and the amounts of reagents also varied in the treatment of different stocks, the process as disclosed is not to be construed in any way as a limitation upon the broad scope of the invention.

I claim as my invention:

1. In a process for the improvement of the anti-knock properties of the distillate resulting from the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons, the improvement which comprises introducing into the cracked vapors a phenol and ammonia and reacting the same in the presence of the vapors at a temperature sufficient to cause the formation of an amine of such characteristics that it is recovered in the overhead distillate product of the process.

2. In a process for the improvement of the anti-knock properties of the distillate resulting from the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons substantially within the boiling range of gasoline, the improvement which comprises introducing into the reaction zones wherein the said conversion is taking place, a phenol and ammonia and reacting the same in the presence of a dehydrating catalyst to cause the formation of an amine of such characteristics that it is recovered in the overhead distillate product of the process.

3. In a process for improving the anti-knock properties of the distillate product of a cracking process wherein hydrocarbon oils of relatively higher boiling characteristics are converted into lower boiling hydrocarbons, the improvement which comprises introducing into the vapors of the said cracking process a phenol and ammonia and reacting the same in the presence of a dehydrating catalyst to produce an amine of such characteristics that it will be recovered in the overhead distillate product of the process.

4. In a process for improving the anti-knock properties of the distillate product of a cracking process wherein hydrocarbon oils of relatively higher boiling characteristics are converted into lower boiling hydrocarbons, the improvement which comprises introducing into the vapor zones of the said cracking process in the presence of a zinc chloride a phenol and ammonia to produce an amine of such characteristics that it will be recovered in the overhead distillate product of the process.

5. In a process for improving the anti-knock properties of the distillate product of a cracking process wherein hydrocarbon oils of relatively higher boiling characteristics are converted into lower boiling hydrocarbons, the improvement which comprises introducing into the vapor zones of the said cracking process in the presence of a

zinc chloride and ammonium chloride a phenol and ammonia to produce an amine of such characteristics that it will be recovered in the overhead distillate product of the process.

6. A process for increasing the anti-knock value of motor fuel distillate which comprises introducing a phenol and ammonia to the distillate, contacting the resultant mixture with a dehydrating catalyst at a temperature adequate to react the ammonia and phenol to form an amine, and recovering as the product of the process the distillate containing the amine thus formed.

7. A process for increasing the anti-knock value of motor fuel distillate which comprises introducing a phenol and ammonia to the distillate, contacting the resultant mixture with zinc chloride at a temperature adequate to react the ammonia and phenol to form an amine, and recovering as the product of the process the distillate containing the amine thus formed.

8. A process for producing anti-knock motor fuel which comprises introducing a phenol and ammonia to gasoline vapors, at a temperature adequate to effect an amine-forming reaction between the phenol and ammonia, reacting the phenol and ammonia in the vapors to form an amine, condensing the vapors containing the amine thus formed, and collecting the resultant condensate.

9. A process for producing anti-knock motor fuel which comprises introducing a phenol and ammonia to gasoline vapors, at a temperature adequate to effect an amine-forming reaction between the phenol and ammonia, reacting the phenol and ammonia in the vapors and in the presence of a dehydrating catalyst to form an amine, condensing the vapors containing the amine thus formed, and collecting the resultant condensate.

10. A process for producing anti-knock motor fuel which comprises introducing a phenol and ammonia to gasoline vapors, at a temperature adequate to effect an amine-forming reaction between the phenol and ammonia, reacting the phenol and ammonia in the vapors in the presence of zinc chloride to form an amine, condensing the vapors containing the amine thus formed, and collecting the resultant condensate.

11. A process for producing anti-knock motor fuel which comprises introducing a phenol and ammonia to gasoline vapors at a temperature in the neighborhood of from 500° F. to 600° F., reacting the phenol and ammonia in the vapors to form an amine, condensing the vapors containing the amine thus formed, and collecting the resultant condensate.

12. A process for producing anti-knock motor fuel which comprises introducing a phenol and ammonia to gasoline vapors at a temperature in the neighborhood of from 500° F. to 600° F., reacting the phenol and ammonia in the vapors to form an amine in the presence of a dehydrating catalyst comprising a heavy metal halide, condensing the vapors containing the amine thus formed, and collecting the resultant condensate.

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