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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.

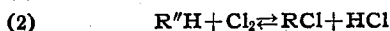
While the cracking process as at present generally practiced in the petroleum industry tends to the production of gasolines having anti-knock characteristics superior to those possessed by corresponding gasoline fractions produced by the straight run distillation of crude petroleum, it may frequently happen that the production of a cracked gasoline of a knock rating rendering it saleable 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 the 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.

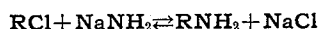
In one specific embodiment, the invention comprises treating cracked hydrocarbon vapors with halogens to produce halogen derivatives and subjecting the halogenated vapors to further treatment with sodamide for the production of amines to increase the anti-knock value of the gasoline.

The halogenation of cracked hydrocarbon vapors of approximate gasoline boiling point range will follow a course depending upon the chemical composition of the vapors, the temperature

and pressure of treatment and the presence of catalytic material, as well as the amount of halogen and the particular halogen used. Since such vapor mixtures include representatives of the principal hydrocarbon groups, that is, paraffins, olefins, naphthenes and aromatics in varying proportions, the ease of halogenation will depend to some extent upon the percentage of the unsaturated compounds present. For example, in cracked vapor mixtures containing relatively high percentages of olefins, the addition of halogen may proceed with great rapidity independent of catalytic influences and light and electrical effects. When the vapors contain larger percentages of saturated compounds of the straight chain and cyclic series, sufficient halogenation may involve the use of catalysts such as iron, aluminum, zinc, etc., or their halides. The degree of halogenation which it is best to employ in any particular case will depend upon the type of amines which are produced from the halogenated derivatives in the succeeding treatment with sodamide so that the selection of exact quantities of reagents and conditions of operation will be usually best determined by trial runs. While the individual reactions occurring between the hydrocarbons and the treating reagents are necessarily complicated owing to the great variety of hydrocarbon compounds present in the original mixture, it is possible to represent the net result by equations such as the following:



in which R' represents an unsaturated hydrocarbon having one double bond between carbon atoms and R''H represents a saturated hydrocarbon. It will be seen in the first equation that a molecule of chlorine has added directly with saturation of the double bond while in the second equation that the chlorine molecule has been split with one atom of chlorine adding to the hydrocarbon radical and the other joining with an atom of hydrogen. The succeeding reactions resulting when the halogen derivatives are contacted with sodamide may be shown as follows:



Sodamide is a compound well known in the arts, and is used extensively in the manufacture of dyes and in other chemical processes. It is usually manufactured by conducting dry ammonia gas into molten sodium or by dissolving sodium in liquid ammonia. Other methods less commonly used consist in treating sodium oxide with ammonia or by treating sodium hydride with ammonia. Amides strictly analogous to that of sodium have been prepared from each of the other metals of the alkali group, that is,

potassium, lithium, rubidium and caesium by the same general methods but none are of great commercial importance on account of the higher cost of the base materials and in that they offer no decided advantages over the sodium compound in most instances. The sodium compound melts at approximately 310° F. and boils at 750° F. It will be evident from its constitution that it provides a powerful reagent for use in many chemical processes, particularly those in which a reducing action is required or when it is necessary to introduce sodium into the sphere of reaction.

Several alternative methods of operation are possible, and are comprised within the scope of the invention. As a general rule, the reactions of halogenation and subsequent amine production by treatment with sodamide are brought about readily under the temperature and pressure conditions under which cracked vapors are evolved from the reaction zone of a cracking process, these conditions commonly involving temperatures of approximately 250° to 600° F. and pressures in the approximate range of 100 to 400 pounds per square inch. According to one method of operation the vapors entering a primary fractionator or separator may receive increments respectively of chlorine or other halogen and at approximately the same point the proper amount of sodamide, the separator serving to remove the sodium salts produced incidentally to the main reaction as a fused or soluble mass in the bottom of the separator and produce amines which are later recovered with the overhead fractions of approximate gasoline boiling point range from the final fractionator.

Another possible method of operation which may, however, require more precautions as to exact control of operation, may consist in either passing the cracked vapors after the addition of the halogen through a stationary body of molten sodamide or upwardly countercurrent to a down-flowing stream in suitably designed apparatus.

The relative effect on the anti-knock value of gasoline of amines of the alkyl and aryl groups respectively is indicated by the following table which shows part of the figures given in the International Critical Tables, vol. 2, page 163.

Relative effects of some compounds of nitrogen for suppressing detonation in engines

Aniline in concentrations up to 3% of the fuel by volume taken as standard of effect. All measurements made with bouncing pin apparatus, using kerosene as fuel (4). The values given below are, respectively, (a) amount of grams required to give an "anti-knock" effect equivalent to 1 g. of aniline, and (b) reciprocal of the number of mols required to give an "anti-knock" effect equivalent to 1 mol. of aniline. Negative values are marked (-).

Compound	Formula	(a) Wt. for given effect	(b) Rel. mol. effectiveness
Aniline	C ₆ H ₅ NH ₂	1	1
Cumidine	(CH ₃) ₂ CHC ₆ H ₄ NH ₂	0.96	1.51
Monomethylaniline	C ₆ H ₅ NHCH ₃	0.83	1.4
Toluidine	CH ₃ C ₆ H ₄ NH ₂	1.04	1.22
Ethylaminobenzene	C ₂ H ₅ C ₆ H ₄ NH ₂	1.14	1.14
Methyl-o-toluidine (7)	CH ₃ C ₆ H ₃ (NH ₂)CH ₃	1.15	1.13
Diethylamine	(C ₂ H ₅) ₂ NH	1.59	0.495
Diethylaniline	C ₆ H ₅ N(C ₂ H ₅) ₂	6.7	0.24
Dimethylaniline	C ₆ H ₅ N(CH ₃) ₂	6.2	0.21
Ethylamine	C ₂ H ₅ NH ₂	2.4	0.20
Triethylamine	(C ₂ H ₅) ₃ N	7.05	0.14

¹ Average of o-, m-, and p-values.

It will be seen that the aryl amines have in general a more pronounced effect than the alkyl amines. The proportions of these two general types which may be produced by reactions characteristic of the invention will depend as already stated upon the composition of the vapors under-

going treatment and other operating conditions but in general it may be stated that to produce a given known rating in a finished gasoline that heavier treatments will be required upon vapors of a saturated or straight chain character than upon vapors containing relatively higher percentages of cyclic hydrocarbons.

In addition to the production of amines which add to the anti-knock value of the gasoline, other treating effects may be produced by the use of sodamide if this is used in excess over that required for interaction with the products formed by the action of the halogens in the first step. It has at times a very pronounced desulphurizing action on account of the great affinity of the sodium for sulphur in such compounds as mercaptans, sulphur ethers, etc., and may effect a substantial sulphur reduction in the finished product depending upon the types of sulphur compounds present in the cracked vapors and other conditions of operation as well as the excess of sodamide used.

The process of the invention may be used as a single treatment on cracked vapors or in combination with preceding or succeeding treatments for producing as an overall result a finished product of desired characteristics. For example, the vapors may be treated by special desulphurizing and/or polymerizing steps prior to the introduction of the reactants for the production of amines and still further vapor phase treatments, suitable settling periods or filtering by inert or adsorbent materials may follow. In the majority of instances a final rectification to produce an end point gasoline is preferable. Furthermore, the condensed product may require a light final washing to remove traces of reaction products.

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. Chlorine may be injected into these vapors at the rate of about 10 pounds per barrel of final distillate along with approximately 5 pounds of sodamide, the vapors then passing to settling and filtering equipment to remove sludge mixtures and salts produced by the reactions. The gasoline produced by fractionating and contacting these vapors with solid adsorbent materials without the use of chlorine and sodamide upon the vapors according to the process of the invention may have the properties shown in the "untreated" column following, while gasoline produced by applying the process of the invention may have the properties shown in the "treated" column.

	Untreated	Treated
Octane number	85	80
Color, Saybolt	10	30
Gum content by copper dish	310	20
Sulphur content	0.26	0.09
Color stability or loss in Saybolt degrees in the four-hour sunlight test	10	4

The yield of gasoline in both cases may be approximately 60% of the residuum processed, with the maximum cracking temperature employed 930° F. with a pressure of 250 pounds per square inch. To produce the 80 octane number by

straight cracking and fractionation without the addition of a special treating reagent according to the process of the invention it may entail a reduction in yield to approximately 52%, which is a serious consideration in commercial work and which might render the process uneconomical. Thus the application of the present invention is shown to have a definite commercial value.

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.

We claim as our invention:

1. In a process for improving the anti-knock characteristics of the overhead distillate product resulting from the conversion of higher boiling into lower boiling hydrocarbons by the cracking process, the improvement which comprises introducing a halogen in the presence of a catalyst in the vapor zones of the said cracking process and subjecting the mixture containing hydrocarbons and the resulting halogen derivatives of hydrocarbons to treatment with sodamide, and condensing the thus treated vapors.

2. In a process for improving the anti-knock characteristics of the overhead distillate product resulting from the conversion of higher boiling into lower boiling hydrocarbons of gasoline characteristics by the cracking process, the improvement which comprises introducing chlorine in the presence of a catalyst in the vapor zones of the said cracking process and subjecting the mixture containing hydrocarbons and the resulting chlorine derivatives of hydrocarbons to treatment

with sodamide, and condensing the thus treated vapors.

3. The method of improving the overhead product of a distillatory gasoline-producing system, which comprises introducing a halogen to a vapor zone of said system where a halogenating temperature prevails, reacting the halogen with a part of the vapors to form a halogenated hydrocarbon, treating the vapors containing the halogenated hydrocarbon with sodamide, and condensing the thus treated vapors.

4. The method of improving the overhead product of a distillatory gasoline-producing system, which comprises introducing chlorine to a vapor zone of said system where a chlorinating temperature prevails, reacting the chlorine with a part of the vapors to form a chlorinated hydrocarbon, treating the vapors containing the chlorinated hydrocarbon with sodamide, and condensing the thus treated vapors.

5. In the cracking of hydrocarbon oils for the production of gasoline, the method which comprises introducing a halogen to a vapor zone of the cracking process where a halogenating temperature prevails, reacting the halogen with a part of the vapors to form a halogenated hydrocarbon, treating the vapors containing the halogenated hydrocarbon with sodamide, and condensing the thus treated vapors.

6. In the cracking of hydrocarbon oils for the production of gasoline, the method which comprises introducing a halogen to a vapor zone of the cracking process where a chlorinating temperature prevails, reacting the chlorine with a part of the vapors to form a chlorinated hydrocarbon, treating the vapors containing the chlorinated hydrocarbon with sodamide, and condensing the thus treated vapors.

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