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TREATMENT OF MOTOR FUEL

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This invention relates more particularly to the treatment of cracked distillates of gasoline boiling range or those containing a substantial proportion of gasoline, such distillates being generally characterized by a relatively high knock rating.

More specifically the invention has reference to a process for the manufacture of gasoline whereby more efficient use is made of certain types of treatment which are applied selectively to different fractions of the gasoline so that the overall efficiency of the treating process is greater than when treatments are applied to the gasoline as a whole.

In one specific embodiment the invention comprises treatment of the lower boiling fractions of cracked gasolines with inhibitors while treating the higher boiling fractions with polymerizing agents such as sulphuric acid, heavy metal salts, adsorbent earth, for example, fullers earth and the like, to separately effect their refining and stabilization and preferably redistilling the thus treated higher boiling fractions and thereafter combining the lower and higher boiling fractions after such treatment. The various polymerizing agents are not equivalent in their application or results.

The process thus appears as a treating method in which the valuable properties of the lighter fractions such as antiknock value, water white color, low gum content, etc., are conserved by the use of small amounts of inhibiting materials while the heavier fractions are subjected to sulfuric acid treatment and other refining agents for the removal of sulphur and undesirable color and gum-forming compounds.

The straight run gasolines produced either by simple distillation from crudes or by absorption from casing head and natural gases are of an essentially saturated or paraffinic character containing only negligible amounts of olefinic and cyclic hydrocarbons so that they undergo substantially no change when stored for long periods of time, particularly if reasonably protected from the influence of light and air.

Cracked gasolines, however, contain larger percentages of olefinic and cyclic compounds and the more highly unsaturated members of the former group such as the di- and tri-olefins are characterized by a tendency to polymerize and deposit gummy or resinous materials, being objectionable on account of this tendency and on account of their concurrent loss as antiknock material. The polymerization reactions are frequently accompanied by the development of a yellow or brown color or a cloudiness so that the appearance of the gasoline militates against its sale.

When cracked gasolines are produced by the pyrolysis of high sulphur oils they frequently contain too high a percentage of sulphur which may be present as hydrogen sulphide or traces of mercaptans, thioethers, thiophenes, etc., sulphur in such compounds imparting a bad odor to the gasoline and causing corrosion of engine parts either before or after combustion.

A considerable variety of treating methods have been employed to produce refined and stabilized gasolines, the oldest and most generally used being treatment of crude pressure distillates with sulphuric acid, neutralizing and redistilling with fire and steam to produce a gasoline of desired end point. It is frequently observed that olefins of good antiknock value are present in considerable quantities in the lower boiling fractions of cracked naphthas and gasoline, these being seriously affected by the sulphuric acid used which should rather act upon the heavier ends of the product and the sulphur compounds. A disadvantage of this method thus appears in the lack of selectivity of the sulphuric acid in removing only the gum-forming olefins when sufficient quantities are used to suitably reduce the sulphur content. Another inherent disadvantage of the older method is the necessity for redistilling the acid-treated distillate to separate polymers and other reaction products.

Considering the boiling range of commercial gasolines to be included within the approximate temperatures of 100 and 400° F. it has been observed that lower boiling fractions, say, those boiling below 250° F. either when arising directly from the fractionators of cracking plants or from rerun units, are of the desired water white color and of a higher antiknock value than the heavier portions so that when freshly produced they require no chemical treatment to render them suitable as a constituent of commercial gasoline. The fractions boiling above this approximate

temperature, however, may be off color and may contain increased amounts of sulphur compounds removable only by special chemical treatment. In the present process, therefore, the overhead fractions are treated with inhibitors while the heavier fractions which may appear as side cuts from a cracking plant or rerun unit fractionator are subjected to separate treatment with sulphuric acid.

The field of choice for the selection of substances to act as inhibitors in preventing the development of undesirable characteristics in cracked gasolines on storage is large and many compounds have been found to be of special value, their use, however, being sometimes limited by the scarcity of the compounds and their high cost of manufacture. It is conceivable that certain compounds or mixtures of compounds might be discovered which would inhibit separately the formation of gum, color or decrease in knock rating, although in most instances it has been found that the development of gums and color and loss in antiknock value are closely related so that whatever inhibits one type of change also inhibits the other.

Inhibitors are to be distinguished from antiknock agents in that the true antiknock agent modifies the combustion of fuel in an internal combustion engine cylinder but does not necessarily prevent the development of undesirable characteristics under storage. In fact, numerous well defined antiknock agents are themselves unstable in storage and the gasoline to which they are added needs further additions of true inhibitors to stabilize the increased antiknock value produced by the addition of the antiknock agent. Furthermore, it is usually necessary to use much higher percentages of reagents to prevent knocking than is necessary in inhibiting deterioration and depreciation of the gasoline so that it will be seen that in the great majority of cases the action of antiknock agents is distinct from that of true inhibitors, the use of which constitutes the present invention.

A large number of individual chemical compounds and mixtures as well as some more or less crude or unrefined products are available for use in inhibiting the development of undesirable properties due to the oxidation and polymerization of cracked gasolines. Certain phenolic compounds are of outstanding value such as cresols, alpha and beta naphthol, guaiacol and di- and tri-hydroxy benzene derivatives which include such compounds as pyrocatechol and pyrogallol. In fact, a phenol which possesses no inhibiting value is rather the exception than the rule. The ethers of phenols are also utilizable. Also certain amino derivatives. Among the more or less crude raw materials which may be employed may be mentioned certain fractions of coal tars, wood tars, etc. The foregoing are mentioned as possibilities for use in preventing the deterioration of the overhead fractions though the use of other compounds is comprised which are not specifically enumerated.

The amount of any particular inhibiting material chosen which is necessary to preserve the properties of the gasoline will depend upon the efficiency of the compound itself and upon the susceptibility to change of the gasoline which in turn is determined by the chemical character of its constituents. Therefore the choice of any particular inhibitor and the amount which it is necessary to use will be determined by a large number of factors such as the cost and availability of the materials, the exact character of the gasoline fractions and the average period of time for which it is to be stored.

According to the present invention the heavier or higher boiling fractions of cracked gasoline are subjected to a carefully regulated treatment with sulfuric acid. The fractions to be treated may be withdrawn as a side cut from the final fractionator of a cracking plant or from a rerun unit, cooled and may be submitted to the action of the acid in a manner well known, e. g. either in the ordinary type of batch agitator or in the continuous type of plant commonly employed in petroleum refineries and consisting of alternate mixing devices and settlers, the acid, neutralizing and washing liquids being injected into the line of flow preceding the mixers. The amount of sulfuric acid necessary to effect the desired degree of refining will be lowered for two reasons, first, because only a portion of the gasoline is undergoing treatment, and second, because the treatment to remove refractory sulfur compounds which many times tend to accumulate in the higher boiling fractions of cracked gasolines is more selective due to the absence of large quantities of easily polymerizable and oxidizable olefins. Thus the amount of acid necessary is reduced further than merely in proportion to the amount of distillate treated. Obviously such ordinary expedients as varying the strength of the acid and choosing the optimum temperature for best effects will be employed in any given case. The acid-treated heavy ends are neutralized and washed as usual and may be subjected to redistillation if necessary.

Heavy metal salts such as zinc chloride, zinc sulphate, aluminum chloride, and the like, may be employed to refine the heavy side cut and may be used as such or in solution as desired or required. Likewise, treatments such as with hydrochloric acid and a metal, e. g. zinc preferably at elevated temperatures may be employed.

The use of inhibitors in the lighter fractions in the present instance does not preclude the use if desired of such minor treatments as caustic washes to remove dissolved hydrogen sulfide and the use of sodium plumbite to sweeten although when using the latter considerable care must generally be exercised to avoid any excess of sulfur which may tend to accelerate gum and color formation and in this sense acts against any inhibitor which may be present.

It will be recognized that, when the lighter fraction plus inhibitor is blended with the heavier treated fractions, the inhibitor may be used in sufficient quantity to assist in stabilizing the latter so that the necessary acid treatment or other treatment on the heavy ends is further reduced.

While numerous examples might be given to show the results obtainable by the use of the invention the following is given as characteristic and shows the commercial advantages of the process.

The invention may be applied to the treatment of a cracked gasoline from a Mid-Continent residuum. By the use of a secondary fractionater the cracked gasoline may be split up to a 45% overhead cut and a 55% bottoms cut, the overhead fraction being treated with 0.03% of a hardwood tar fraction boiling within the approximate range of 260 to 280° C., while the 55% heavier fraction (withdrawn as a side cut from the fractionator) is treated with 90% sulphuric acid at the rate of 5 pounds per barrel after which it is rerun to produce a cut having a 400° F., end point. The

properties of the gasoline produced by this method of operation in conformity with the present invention are given in column 1 of the appended tabulation while in column 2 the corresponding properties of a gasoline made by treating the raw naphtha with 7 pounds per barrel of 90% sulphuric acid and distilling are shown:

Properties of gasolines

	1	2
Gravity °A. P. I.	59.0	58.5
Color, Saybolt	+30	25
Color stability*	26	16
Mg. of gum by copper dish	20	60
Total sulphur, per cent	0.04	0.05
Octane number	70	69

*After 4 hrs. exposure to sunlight.

The data shows that the split selective treatment of the present invention is to be preferred over the older method since all the desirable properties are improved and the acid treatment is cut down to a low value. The color and color stability are better, the gums are lower and the sulphur content and octane number are slightly better. The yield was also in favor of the present method of treatment being 65% of the raw oil charging stock as finished gasoline while the gasoline made by the other method of treatment constituted only 63.5% of the total oil charged to the cracking plant.

The foregoing specification and example have sufficiently described and exemplified the process of the invention and since both are given for illustrative purposes only, neither is to be construed as imposing limitations upon the broad scope of the invention.

I claim as my invention:

1. A process for treating cracked gasoline which comprises separating the gasoline into a light cut requiring no substantial refining and a heavier cut containing an objectionable amount of impurities, adding to the light cut an oxidation and polymerization inhibitor in sufficient amount to substantially prevent deterioration of the total gasoline, subjecting said heavier cut, in the absence of the light cut, to a refining operation to remove impurities therefrom, and, upon completion of the refining operation, blending the refined heavier cut with the light cut containing the inhibitor to produce a satisfactorily refined and inhibited motor fuel product.

2. A process for treating cracked gasoline which comprises separating the gasoline into a light cut requiring no substantial refining and a heavier cut containing an objectionable amount of impurities, adding to the light cut an oxidation and polymerization inhibitor in sufficient amount to substantially prevent deterioration of the total gasoline, refining said heavier cut, in the absence of the light cut, by treatment thereof with a polymerizing agent to remove impurities therefrom while the light cut is exposed to the action of the inhibitor, and, upon completion of the refining operation, blending the refined heavier cut with the light cut containing the inhibitor to produce a satisfactorily refined and inhibited motor fuel product.

3. The process as defined in claim 2 further characterized in that said polymerizing agent comprises adsorbent earth.

4. The process as defined in claim 2 further characterized in that said polymerizing agent comprises sulphuric acid.

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