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PROCESS OF TREATING CRACKED PETROLEUM DISTILLATES

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This invention relates to a process of refining petroleum oils, and more particularly to a refining treatment for material which has been subjected to a cracking process for the preparation of gasoline or higher boiling point products.

It is known that certain cracked distillates, particularly those resulting from a vapor phase cracking process, include constituents commonly referred to in the art as anti-knock compounds. These compounds are generally understood to be the aromatics and unsaturates, which are present in considerable quantities in the gasoline fractions produced from cracked distillates, the amount of said constituents in the distillates obtained by the vapor phase processes being in excess of the amount of such constituents in the distillate from the liquid phase cracking processes.

Considerable difficulty has been experienced in refining the vapor phase cracked distillates in which these constituents are present, without removing some of them and, consequently, changing the characteristics of the finished product as anti-knock motor fuel. The usual treatments to which such distillates are subjected for removing the objectionable components to provide a finished product that will satisfactorily respond to the specifications in regard to color, gum formation and the like, cannot ordinarily be employed without also affecting detrimentally the useful characteristics of the finished product by removing some of the so-called anti-knock compounds. The usual treatment of petroleum distillates with sodium hypochlorite and liquid sulphur-dioxide is not suitable because of the formation of chlorinated compounds by the hypochlorite treatment, and the removal of the aromatics by the liquid sulphur-dioxide treatment. Likewise, the usual refining with sulphuric acid, ordinarily of a strength approximating 66° Baumé, heretofore used in the treatment of cracked distillates from the liquid phase cracking processes, is unsatisfactory because of the heavy losses that ensue and also of adversely affecting the anti-knock value of the finished product. Finally, the contact treatment with absorbing earths of various types, heretofore commonly used in connection with refining of the vapor phase cracked distillates, is unsatisfactory because it is not effective for completely removing the compounds that result in an unsatisfactory final product as to odor, color, and gum formation, and because of the non-removal of compounds which reduce the anti-knock value of the final product.

The object of the present invention is to provide a new process for the treatment of material which has been subjected to a cracking process and particularly cracked distillates obtained by vapor phase cracking processes, which will substantially remove all compounds that are detrimental in the final product causing odor, color instability, gum formation, and which will not counteract the anti-knock properties due to the normal inclusion in such distillates of the desired aromatics and unsaturates.

In order that the fundamental advantages of the improved process may be understood, the theory of the treatment will first be considered by reference to the chemical basis upon which the invention is predicated.

The objectionable compounds that are present in cracked distillates, and to a larger degree in cracked distillates obtained by vapor phase cracking processes, may be generally classified in three groups, namely; first, compounds of a basic nature, particularly compounds containing nitrogen; second, compounds of acidic nature; and third, unsaturated compounds, especially those belonging to the olefine, diolefine and terpene series.

It is known that in all crude petroleum oils some nitrogen and sulphur compounds are present, the amount of which varies widely with crudes of various origin. Many of these sulphur or nitrogen compounds are of relatively high molecular weight and therefore accumulate in the residue obtained by topping the more volatile fractions from the crude. Of these compounds, the present refining process is primarily concerned with the nitrogen compounds.

When the residues, obtained from the topping operation, are cracked, either by a liquid or a vapor phase cracking process, the nitrogen compounds are cracked to yield some nitrogen containing compounds of lower molecular weight than the molecular weight of the compounds as originally present in the topped residues. Some of these compounds of lighter molecular weight have a boiling point within the boiling range of the finished products obtained by the distillation of the raw cracked distillates. Many crudes, and particularly crudes from west Texas, north Texas, California and Mexico origin, have been found to contain a relatively large amount of such nitrogen compounds. When these compounds have been converted by the cracking reaction from those of relatively heavy molecular weight to the compounds of lighter molecular weight, so that they fall within the boiling range

of the finished product and are not removed by a refining operation, the ultimate product has a bad odor, and their removal is a substantial advantage in improving the finished product from the standpoint of odor.

The effect of the refining method with sulphuric acid is not adequate for the removal of the nitrogen compounds because the sulphuric acid, used at the normal strength of approximately 66° Baumé, acts as a polymerizing agent. The polymerized gum-like compounds very probably form a protective film around the droplets of the refining agent, thus preventing the sulphuric acid from dissolving the nitrogen compounds which, because of their basic character, could normally be removed by the dissolving action of the acid. This phenomenon of the action of the sulphuric acid in regard to the removal of the nitrogen compounds is true in respect of cracked distillates from a liquid phase cracking process, but operates in a greater degree in minimizing the effectiveness of the sulphuric acid treatment in respect of cracked distillates obtained from a vapor phase cracking process, because of the larger amount of such polymerizable compounds present.

A problem, therefore, has been to remove the nitrogen compounds effectively without adversely affecting the aromatics and unsaturates that it is desired to include in the final product because of the anti-knock value thereof. It has been found that by treating the cracked distillates with a weak sulphuric acid solution of a concentration approximately within the range of from 15% to 30%, the removal of the nitrogen compounds may be effected without destroying the compounds useful in imparting the anti-knock characteristic to the final product.

The acidic compounds referred to are present to an appreciable extent in cracked distillates produced either from the liquid or vapor phase cracking processes. These compounds affect odor and color stability of the finished product adversely. Their presence in the final product also adversely affects the anti-knock value of the finished gasoline obtained from the raw cracked distillates. It has been discovered that these specific compounds are not easily removed by caustic soda of low or moderate concentration, but that they are removed by caustic soda of relatively high concentration, that is to say, in excess of 30° Baumé. A concentration within the range of from 30° to 45° Baumé has been found to give the most satisfactory results.

The cracked distillates produced from the cracking processes contain a very considerable amount of the unsaturated compounds, the amount of such compounds resulting from a vapor phase cracking process being greater than from a liquid phase cracking process. These unsaturated compounds may generally be classified as olefines, diolefines and terpenes, as above pointed out. It is recognized that the olefines are compounds that are useful in the final product in giving to the product the anti-knock characteristic. Therefore, as small an amount of the olefine compounds as possible is removed in the treatment under the present process.

It is known that the compounds comprising the polysubstituted olefines, diolefines and terpenes are acted upon by a weak sulphuric acid solution, while normal chain olefines resist the action of sulphuric acid of low concentration, but will react with sulphuric acid of approximately 80% concentration. Therefore, by the use of sulphuric acid solution of a weak concentration, that is to say approximately 30%, the olefines will remain unaffected. The polysubstituted olefines and terpenes are acted upon by the dilute sulphuric acid to form the corresponding alcohols with a small evolution of heat. It has been found that with the weak sulphuric acid solution, a degree of polymerization takes place in addition to the removal of the substituted olefines and terpenes as alcohols, and the removal of the basic compounds.

After the substituted olefines and terpenes have been removed, together with the basic compounds, the cracked distillates may be further treated with sulphuric acid of a higher degree of concentration at a higher temperature without causing any sudden considerable rise of temperature. It is an advantage, therefore, so to conduct the treatment as to prevent a sudden rise in temperature to an uncontrolled degree, and thus prevent to a considerable extent the combination of the sulphuric acid with the unsaturates, thereby destroying their value as anti-knock components in the final product.

Based upon the chemical considerations above referred to, and to remove effectively the compounds from the distillates produced by either a liquid phase or a vapor phase cracking process, I have discovered that the following sequence of treatment produces results that are more efficient than the known processes.

The process preferably includes the following sequence of steps, or procedure.

The untreated cracked distillate is first subjected to the usual treatment for the removal of the hydrogen sulphide content by passing it through a stabilizer or a weak caustic soda solution. This step is one that is obvious in the art and is not considered as a novel separate step of the present invention.

The cracked distillate, free from the hydrogen sulphide content, is then contacted with caustic soda of relatively high concentration, such, for example, as from 30° to 45° Baumé, for a sufficient length of time to remove all acidic compounds and to cause some compounds to polymerize. The treatment with caustic soda of relatively high concentration also tends to break up possible esters formed during the cracking reaction by the action of the organic acids and bases. After the material has been subjected to the caustic soda treatment, and allowed to settle, it is subjected to a water wash until all traces of the alkali are removed.

The material is then treated with a weak acid solution, from 15% to 30% sulphuric acid concentration. The approximate percentage of the solution in respect of the material treated need not exceed 1%, by volume. The duration of the treatment by the sulphuric acid of the relatively low concentration continues for a time sufficient to remove all of the basic compounds. This treatment, as above pointed out, incidentally removes the polysubstituted olefines and terpenes and causes a degree of polymerization of some of the unsaturated compounds, but does not affect the normal olefines.

After the treatment with the weak acid solution, the cracked distillate is separated from water by settling, and thereafter treated with a relatively stronger sulphuric acid solution of approximately 75% to 85% H_2SO_4, the quantity of such solution constituting approximately one-half to five per cent, preferably one per cent, by volume, of the material treated.

I have found that it is an advantage to heat the material while undergoing the treatment with the relatively stronger sulphuric acid solution to a controlled temperature of 150° to 250° F. The treatment with the relatively stronger sulphuric acid within this temperature range removes from the distillate the compounds causing gum formation and color instability. The treatment at the specified temperatures also permits the use of a relatively lower concentration of sulphuric acid to greatly reduce the time of treatment, as compared with the usual treatment with a concentrated 66° Baumé acid at atmospheric temperature, and more efficiently removes the gum forming constituents and color unstable compounds.

After the second sulphuric acid treatment, the acid sludge is completely settled and the material further treated with a second strong caustic soda solution to decompose, as far as possible, the esters formed during the sulphuric acid treatment and thereby reduce the sulphurous acid formed during the subsequent distillation.

It should be noted that it is intended that the material shall not be subjected to a water wash following the second acid treatment. A water wash of the material after this second acid treatment causes hydrolysis of unstable compounds and thereby yields compounds that impart to the finished product poor color and cause high gum formation.

The cracked distillate thus treated for the removal of the detrimental compounds may be subjected to a final distillation for the separation of the various fractions desired.

As an alternative of the procedure outlined above, I have found that, instead of the second acid treatment at elevated temperatures, this treatment may be conducted at atmospheric temperatures using a somewhat increased percentage of the acid solution and then, after neutralization and prior to or during the final distillation, subjecting the material to a high heat zone at a temperature of 400° to 500° F., for a period of time sufficient to further polymerize the undesirable unsaturated components of the material.

The process, as above disclosed, has been demonstrated to give results of an improved character over all known processes for the treatment of cracked distillates. The finished product is within a satisfactory color range, gum content and color stability, with a low sulphur content, and good odor and has the characteristics of an anti-knock motor fuel. The refined product resulting from the process is, therefore, well within standard specifications.

I am aware that the invention may be modified in various particulars without departing from the spirit and scope thereof. I do not limit myself to the exact procedure disclosed, but what I claim and desire to secure by Letters Patent is:—

1. The process of treating cracked petroleum distillates which consists in subjecting such distillate to a treatment with caustic soda of a concentration of from approximately 30° to 45° Baumé, then washing the distillate free of the alkali, then treating the distillate with a sulphuric acid solution of from approximately 15% to 30% acid concentration, then settling out the distillate from the water content, then treating the distillate with a sulphuric acid solution of from approximately 75% to 85% acid concentration, and then neutralizing the distillate.

2. The process of treating cracked petroleum distillates which consists in subjecting the distillate to a treatment with caustic soda of a concentration of from approximately 30° to 45° Baumé, then washing the distillate free of the alkali, then treating the distillate with a sulphuric acid solution of from approximately 15% to 30% acid concentration, then settling out the distillate from the water content, then treating the distillate with a sulphuric acid solution of from approximately 75% to 85% acid concentration at a temperature of approximately 150° to 250° F., and then subjecting the distillate to an alkali treatment to neutralize the same.

3. The process of treating cracked distillates of petroleum which consists in subjecting such distillate to a treatment with caustic soda of a concentration of from approximately 30° to 45° Baumé, then washing the distillate free of the alkali, then treating the distillate with a sulphuric acid solution of from approximately 15% to 30% sulphuric acid concentration, then settling out the distillate from the water content, then treating the distillate with a sulphuric acid solution of from approximately 75% to 85% acid concentration, then neutralizing the distillate, and then subjecting the distillate to a relatively high temperature.

4. The process of treating cracked petroleum distillates which consists in subjecting such distillate to a treatment with caustic soda of a concentration of from approximately 30° to 45° Baumé, then treating the distillate with a sulphuric acid solution of from approximately 15% to 30% sulphuric acid concentration, then settling out the distillate from the water content, then treating the distillate with a sulphuric acid solution of from approximately 75% to 85% acid concentration, and then treating the distillate to neutralize the same.

5. The process of treating a petroleum oil which comprises a distillate from a vapor phase cracking process, which consists in first removing the hydrogen sulphide therefrom by a treatment with a weak caustic soda solution, then subjecting the oil to a treatment with caustic soda of a concentration from 30° to 40° Baumé to remove substantially all acidic compounds and to cause substantial polymerization of other compounds, then washing the oil free from the alkali, then treating the oil with a weak solution of sulphuric acid from 15% to 30% acid concentration, the volume of acid being approximately 1% of the oil treated to remove the basic compounds and the polysubstituted olefines and terpenes and to cause a substantial polymerization of unsaturated compounds without affecting the normal olefines, then subjecting the oil to a treatment with sulphuric acid of a concentration from approximately 75% to 85% and of a quantity between .5% and 5% by volume of the oil treated, and then subjecting the oil to a second caustic soda treatment.

6. The process of preparing a vapor phase cracked distillate of petroleum oil for a final fractional distillation which consists, esssentially, in subjecting the oil to a weak alkali treatment to remove the hydrogen sulphide, then treating the oil with a strong caustic soda within the range of from 30° to 45° Baumé, then washing the oil free from the alkali and subjecting the oil to a treatment with weak sulphuric acid not exceeding 30% sulphuric acid concentration and of approximately 1% by volume, then treating the oil with a sulphuric acid solution between .5% and 5% by volume and of a concentration from 75% to 85% acid concentration, and then subjecting the oil to a further caustic soda wash.

7. The process of preparing a vapor phase cracked distillate of petroleum oil for a final fractional distillation which consists, essentially, in subjecting the oil to a weak alkali treatment to remove the hydrogen sulphide, then treating the oil with a strong caustic soda within the range of from 30° to 45° Baumé, then washing the oil free from the alkali and subjecting the oil to a treatment with weak sulphuric acid not exceeding 30% sulphuric acid concentration and of approximately 1% by volume, then treating the oil with a sulphuric acid solution between .5% and 5% by volume and of concentration from 75% to 85% acid concentration at a controlled temperature of from 150° to 230° F., and then subjecting the oil to a further caustic soda wash.

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