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MAKING ANTIKNOCKING MOTOR FUEL AND SYNTHETIC RESINS

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This invention relates to the process of making motor fuel and by-product petroleum derivatives.

The invention relates especially to motor fuels made from heavy petroleum oils by heating in the presence of air thus obtaining certain oxidized bodies along with products of cracking, capable of reducing detonation or knocking in internal combustion engines.

The invention has for one object the production of so-called anti-knocking motor fuels which do not require any addition of special anti-knock chemicals such as lead tetraethyl or other substances recognized to have poisonous properties.

In the air-treatment of heavy oils certain by-products, principally acids and aldehydes are produced, giving the raw fuel and objectionable odor.

Refining with sulphuric acid and caustic soda in the usual way and in the customary proportions does not deodorize satisfactorily. If a large amount of sulphuric acid is employed excessive losses occur due to attack of the acid on olefins, aldehydes and the like.

The organic acid products higher than acetic acid, such as butyric, valeric, capric, caproic and the like have rather offensive odors. However since these acids have a commercial value for other purposes I propose to remove or collect them by absorbing in or washing with an alkaline solution thereby obtaining the salts of the several organic acids. Such salts may be utilized in various ways.

The problem of sweetening is not so simple with respect to removal of ordinary aldehydes. Owing to their non-acid nature it is not feasible to extract them by means of alkaline solution. A portion of the aldehydes may be destroyed by treatment with alkali owing to formation of tars or gummy substances but the conversion usually is not complete. Since the lower aldehydes have pungent and choking odors, and some of the higher aldehydes possess vile penetrating odors in some cases not without lachrymatory or tear-producing properties, I prefer to eliminate practically all traces of such evil-smelling aldehydes from the motor fuel.

Procedures which I propose for the purpose are:

(1) Hydrogenation of the raw motor fuel or the fuel after washing with alkali to remove sulphur containing bodies, or

(2) Conversion of aldehydes to polymers either capable of extraction or free from offensive odor, or

(3) Addition of phenol or other phenolic body to the raw motor fuel or any desired fractions thereof and causing reaction to take place in alkaline or acid medium to produce synthetic resins.

The oxidation of the petroleum oil or fractions thereof may be carried out either in the liquid phase or the vapor phase. In the former case the charge of oil is preferably placed in a pressure tank and heated to a temperature of 500° F. or thereabouts air being blown in and a pressure maintained preferably of approximately 20–30 atmospheres. In the vapor phase a distillate in the vapor form from a still such as a cracking still is admixed with air and passed through a reaction zone which preferably contains a catalyzer to yield the partially oxidized motor fuel and acid and aldehydic by-products.

The distillate by either procedure consists of two portions, namely an oily layer containing the naphtha and burning oil components (gasoline and kerosene fractions) in a more or less oxidized condition, some heavier oils and oxygenated by-products soluble in oil including aldehydes especially higher aldehydes and various fatty acids and the like.

Beneath the oily layer is an aqueous layer containing acetaldehyde and other aldehydes soluble to some extent in water, various lower organic acids soluble in water and so forth. The various substances, both oil and water-soluble, will be distributed between the two layers in proportion to their respective coefficients of partition.

It is proposed to treat the distillate or any appropriate part thereof at any suitable stage of the process, with phenol or cresol or other appropriate phenolic body using, for example, a proportion sufficient to combine with the aldehydes present on the basis of a mol. of phenol to a mol. of aldehyde or preferably using a moderate excess of the phenolic body.

Such treatment may be carried out in various ways. For example the phenol may be added to the hot vapors coming from the still or this substance may be fed slowly into the still itself or into the vapor dome thereof. The phenol may be applied in a liquid form or may be first vaporized. The proportions employed as indicated preferably are those which correspond roughly to the aldehyde formation preferably however employing an excess of phenol in order to obtain a fusible resinous product. With an excess of aldehyde, especially when the phenol is added to the charge in the still, the high temperature and pressure might thereupon bring about the formation of an infusible resin which could not

be readily utilized for many purposes available to the fusible product.

Under the high pressure and temperature in the still or in the condensing apparatus or receivers and in the presence of organic acids formed during the oxidation acting as catalysts combination takes place between the phenol and aldehydes and resinification ensues. When sulphur is present in the raw oil this usually is oxidized to sulphur dioxide and the latter acts as a catalyzer.

Or the phenol may be added to the condensate at any suitable stage during the condensation of said distillate or added to the liquid collecting in the receiver. When condensation is carried out under pressure and the liquid therein is warm the addition of phenol to the contents may readily bring about resinification therein. When the condensate is at atmospheric pressure the phenol may be brought into reaction with the aldehydes by heating under a reflux condenser in the presence of an acid or alkaline condensing agent.

Or the water layer and the oily layer may be separated and phenol added separately to either one or the other or to both of these separated products; in which case resins are obtained from the water layer which are different from those resulting from resinification in the oily layer.

When reaction is carried out separately it is desirable in some cases to wash the oily layer with water and add the washings to the aqueous layer.

Any suitable fractions of the oily layer may be treated in this manner and also concentrates or distillates obtained by boiling the water layer, to obtain a mixture of aldehydes, acids and so forth admixed with some water. By neutralizing with alkali the organic acids may be retained.

When the oily layer is first distilled before removing aldehydes by resinification it may previously be treated with caustic soda to retain any organic acids in the form of their sodium salts. When phenol is present under these conditions, especially when the solution is alkaline resin remains in the residue. The latter may be steam stilled or vacuum stilled to remove heavy oils and the like when these are present. This procedure may not be necessary when low boiling fractions only are used. If an excess of phenol has been employed it may be recovered by steam distillation.

The separation of the resin from the water layer is simpler since during resinification coagulation of the resin occurs and the latter may be collected by filtration or decantation. If however a large proportion of alkali is employed the resin may remain in solution. Made in slightly alkaline solution the coagulated resin may be washed to remove salts of organic acids and may be further modified by reaction with other substances such as formaldehyde, acetaldehyde, paraldehyde, furfural and hexamethylenetetramine and so forth; also by adding natural resins such as asphalt, copal, shellac or substances such as rubber, wax, nitrocellulose and the like.

If the resin is too soft for making varnishes or other coating compositions or for plastic molding purposes it may be steam stilled or vacuum stilled or hardened by heating.

When incorporated with the various fillers used in the plastic industry molding compositions may be made which set or cure in the mold on hot pressing. Such compositions may contain a few per cent of hexamethylenetetramine. The varnishes obtained by dissolving the resin in for example a mixture of alcohol and benzol may be used to impregnate paper, cloth or other substances which in turn may be pressed together to yield laminated pressboard, gear blanks and the like.

A considerable choice of catalysts is available carrying out the resinification process which constitutes a step in the refining operation. As noted above organic acids and sulphur dioxide are likely to be present and these are in most cases appropriate for bringing about the reaction with the phenolic body. If not however mineral acids such as sulphuric, hydrochloric or phosphoric acids may be introduced. In case acid resinification is not complete it may be followed by treatment with alkali to advantage.

In some cases the resinification may form a part of the usual refining process employing sulphuric acid and then caustic soda, the acid treatment coming first. In other cases the materials to be refined may first be rendered alkaline in order to obtain the resin in the absence of acid. Again the materials may be neutralized and the phenolic body added.

Thus it is possible to add phenol to the oil and introduce sulphuric acid in the usual refining proportions, agitate and maintain warm until resin forms and passes into the sludge. The latter is then neutralized and washed. The neutralizing may be carried out in some cases by means of barium or calcium hydroxide. The sulphate which thus forms may be utilized as a filler along with the resin. Or the sulphuric acid may first be added and the phenol introduced slowly. In accordance with either of the foregoing steps it is also possible to obtain a suphonated resin which may be used as a tanning agent in the leather industry.

Again it is possible to first treat with sulphuric acid, remove the sludge and then add the phenolic body and a further quantity of an acid such as hydrochloric acid. Also it is possible to first treat with sulphuric acid, then with or without removal of the sludge, add phenol and caustic soda or other alkali or sodium phenolate and the like. Resinification also may be carried out by employing the caustic soda extract of coal tar works containing the tar acids in the form of the phenolates.

Since some phenoloid bodies ordinarily are produced by the oxidation of the petroleum oil or may be present in the original oil and may be distilled off unchanged, allowance should be made for such phenoloid substances when adding phenolic bodies from extraneous sources.

The naphthas and burning oil distillates may be appropriately separated and steam stilled if desired to obtain fractions having a narrow range of boiling point. Ordinarily the lower fractions are employed as motor fuel and these preferably should contain as much of the burning oil distillate or kerosene as is feasible. Since the oxidation procedure yields a fuel which has a less tendency to detonate in an internal combustion engine it is proposed to use a higher proportion of the burning oil distillate than is customary in ordinary gasoline (except of course when substances such as lead tetraethyl are present).

While the present invention is particularly directed to the production of a motor fuel having anti-knocking properties which so to speak are self-made rather than brought about through the addition of substances such as lead compounds, the production of motor fuels having the more customary knocking qualities is not

outside of the scope of the present invention. The motor fuel obtained as above may be blended with pressure still naphtha, ordinary gasoline, casing head naphtha and the like employing for example equal parts of the oxidized motor fuel and the naphtha from other sources; or these proportions may be varied in various ways for example from 25 per cent of one product to 75 per cent of the other. The present invention comprehends such blended products, that is oxidized motor fuel admixed with motor fuels of a normally unoxidized character such as the naphthas aforesaid as well as additions such as aniline, pyridine, benzol and the like tending to assist in reducing detonation or eliminating it entirely.

In the foregoing I have referred to aldehydes and organic acids as being important by-products of the present process. It should be understood that there are certain compounds known as aldehyde acids which contain both the aldehyde and acid group and which I preferably do not form in the process and which would be disturbing factors if combining with phenol to make certain resins. I prefer ordinarily to conduct the process to make normal aldehydes not containing any acidic grouping. However when aldehyde acids are formed these may be removed if desired along with normal organic acids by treatment with an alkali wash.

The following illustrates one method of carrying out vapor phase oxidation but it should be understood that I do not wish to be limited to the details of such description.

A catalyst was prepared by treating rough fragments of iron possibly one-eighth to one-fourth of an inch in diameter with a solution of ammonium metavanadate. The salt was dissolved in boiling water and the solution evaporated in contact with the iron fragments stirring gently. In this way a crystalline incrustation on the surface of the iron fragments was obtained. It may be added that the solution was kept alkaline during evaporation by the addition of aqueous ammonium hydroxide. This material was placed in the catalytic apparatus and ignited in a stream of air at between 200 and 250° C. In another case vanadium pentoxide was suspended in a one per cent solution of soluble cotton in acetone and a mixture allowed to dry in contact with fragments of iron. The mixture was used in such proportions that 20 grams of vanadium pentoxide were applied to 18 grams of iron. On evaporation a coating of the vanadium oxide on the iron fragments was obtained. This material could be handled to better advantage than the material mentioned above having a crystalline coating and on ignition in the catalytic apparatus yielded a catalyst which was somewhat more permanent, that is the coating of vanadium material did not appear to dislodge so easily.

Example.—Allow 300 parts of kerosene to drip into a cracking furnace maintained at a temperature of 1200–1300° F. The vapors of the cracked kerosene are passed through an air-cooled condenser where the higher boiling constituents are condensed and collected. The lighter material is passed on to the mixing chamber consisting of a Venturi tube to be mixed with air. The mixture of air and cracked kerosene vapor is passed into a catalytic chamber containing catalyzer consisting of fragments of iron coated with 10 per cent of its weight of vanadium oxide. The catalytic chamber is heated by means of the lead bath maintained at the desired temperature, namely 800–1000° F. by means of an electrically-heated coil. The temperature of the exit gases varies between 455° and 750° F. The liquid products of the oxidation of the petroleum vapor are collected by condensation and washing. React upon the aldehydic co stituents with phenol as aforesaid to form resins which are readily separable from the other products.

The following illustrates the procedure of oxidation in the liquid phase but it should likewise be understood that the invention is not limited to the particular temperatures, pressures and other details set forth for illustrative purposes.

Example.—Heat a body of gas oil to about 500° F. in a still adapted to withstand a pressure of well over 20 atmospheres. By means of a pressure pump force air at 15–20 atmospheres into the body of oil in the lower part so that the air passes up through a deep column of the oil in the form of small bubbles thus coming in intimate contact with the oily material. The air is preheated to between 200 and 300° F. Allow the products from the still to pass into a condenser which should likewise be capable of withstanding high pressures. The walls of the condenser may be made of copper to avoid attack by acids which would result if steel were employed. Allow the temperature to rise spontaneously by the action of the air on the oil. Regulation may be effected by adjusting the temperature of the incoming air or the rate at which it passes through the oil. Oil may be fed continuously into the receptacle in the upper part and the residues may be continuously withdrawn from the lower part. The condensate obtained consists of two layers, an upper one containing the hydrocarbons and oxidized products insoluble in water and the lower layer containing acids, aldehydes and other substances. Wash the hydrocarbon layer with water and add the washings to the aqueous layer. Distill the water-insoluble layer to make fractions appropriate as a motor fuel for example fractions boiling within the range of ordinary gasoline or slightly higher. Make the aqueous layer slightly acid with 2 or 3 per cent of sulphuric acid and add phenol somewhat in excess of the amount required to resinify the aldehydic substances present. This may be determined approximately by preliminary test on the small scale. Filter off the resin and remove any undesired excess of phenol by steam distillation. The resin may then be dissolved in a mixture of equal parts of benzol and denatured alcohol in the proportion of one pound of resin to one or two pounds of the solvent mixture. Hexamethylenetetramine may be added and the solution employed to impregnate wood flour or other filler to make molding composition or to impregnate sheets of paper which are subsequently hot pressed to obtain laminated pressboard. Or the resin may be ground in a ball mill with asbestos, wood flour or other filler and 5 to 10 per cent of hexamethylenetetramine. This mixture is then passed through hot milling rolls and is finally ground to yield a molding composition.

In the last described procedure there is no need of a fire under the still hence the risk of overheating a still bottom is obviated. Thus it is possible to employ pressures in excess of 30 atmospheres. Thus it becomes possible to oxidize the less heavy oils such as kerosene or easily sublimable substances such as naphthalene at pressures of 50 to 150 atmospheres. Still higher pressures for example 200 to 300 atmospheres also are contemplated. To apply such super-ab-

normal pressures to an ordinary direct fired still the bottom of which when coked may reach the temperature at which steel softens, would be out of question. The present invention however makes such super-abnormal pressures utilizable with accompanying compactness of still and condensation apparatus and with the possibility of securing peculiar and specific oxidation effects at pressures above 35 atmospheres.

When treating a comparatively volatile substance at super-abnormal pressures (e. g. above 35 atmospheres) the still may be started with a heavy oil and the more volatile substance gradually fed in, the super-abnormal pressure applied being that giving the most desirable oxygen relationship (ratio of oxygen to charge in the still at any given time) for the purpose in hand. Super-abnormal pressures make possible a great variation in this oxygen relationship with consequent specific oxidizing effects. The invention thus embraces a process of oxidation which comprises bringing an oxygen containing gas, preferably air, into intimate contact with an oxidizable organic body in a heated state at super-abnormal pressures, preferably in excess of 35 atmospheres; said organic body being, for instance, a readily-volatile hydrocarbon preferably at least in part in a liquid condition while in the oxidizing chamber.

Example.—Carry out the method described under the second example treating kerosene at a pressure of 100 atmospheres and a temperature between 750° F. and 950° F.

The employment of super-abnormal or super-cracking pressures ranging from 35 atmospheres to 200 atmospheres or higher is not restricted to the treatment of lighter oils such as kerosene or xylol but may be applied to the super-cracking oxidation of coal tar and its distillates, shale oil, pitches, asphalts, bituminous coals, petroleum residues and tars, vegetable oils and other glycerides and their fatty acids. Organic substances which are liquid or are liquefied by heating are best adapted for the heat-and-pressure oxidation treatment.

The process especially when conducted at super-cracking pressures may be carried out by causing the oil to flow along the lower half of a long pipe, slightly inclined from the horizontal, and allowing the air to move in counter-current manner in the upper portion of the pipe. This permits air of highest oxygen content to first contact with the residues of oxidation. The pipe may be cooled at any zones of too intense reaction.

In lieu of applying external cooling, when overheating is observed in carrying out any of the above procedures, the air may be diluted with the nitrogen and other waste gases of the operation, or steam may be introduced along with the air. On the other hand the enrichment of air by adding oxygen, or gases richer in oxygen than is air, is not precluded.

What I claim is:—

1. The process which comprises treating hydrocarbon oils containing sulphur to produce motor fuel constituents containing aldehydes and sulphur dioxide, and removing the aldehydes by resinification with phenols in the presence of the sulphur dioxide.

2. The process which comprises subjecting heavy oils to a cracking temperature in the presence of air, whereby light hydrocarbon motor fuel constituents and normal aldehydes are formed, and reacting on the aldehyde-containing motor fuel constituents with a phenol in the presence of a catalyst, whereby resins result, and separating the resins from the motor fuel constituents.

3. The process which comprises subjecting heavy oils to a cracking temperature in the presence of air, whereby light hydrocarbon motor fuel constituents and normal aldehydes are formed, and reacting on some portion at least of the aldehyde-containing product with a phenol in the presence of a catalyst, whereby resins result.

4. The process which comprises treating hydrocarbon oils to produce therefrom light hydrocarbon motor fuel constituents containing aldehydes and organic acids, and removing the aldehydes by resinification with phenols in the presence of said acids.

5. The process which comprises treating hydrocarbon oils to produce therefrom light hydrocarbon motor fuel constituents containing aldehydes and acidic oxidation products, and removing the aldehydes by resinification with phenols in the presence of said acidic oxidation products.

6. The process of producing motor fuel components which comprises subjecting a heavy hydrocarbon oil to a cracking temperature in the presence of air whereby light hydrocarbon motor fuel constituents and aldehydes are formed, removing the aldehydes by resinification, and recovering the substantially non-aldehydic light hydrocarbon motor fuel constituents.

7. The process of partially oxidizing heavy oils which comprises bringing air into intimate contact with a heavy hydrocarbon oil in a heated state under pressures exceeding 35 atmospheres under conditions to produce light hydrocarbon motor fuel constituents and volatile oxygen-containing compounds, and recovering the light hydrocarbon motor fuel constituents.

8. The process of partially oxidizing heavy oils which comprises bringing air into intimate contact with a liquid oxidizable organic body in a heated state under pressures exceeding 35 atmospheres under conditions to produce volatile oxygen-containing compounds and other organic derivatives, and recovering the volatile oxygen-containing organic compounds.

9. The process which comprises subjecting heavy oils to a cracking temperature in the presence of air under pressures exceeding 35 atmospheres, whereby light hydrocarbon motor fuel constituents and normal aldehydes are formed, and reacting on the aldehyde-containing motor fuel constituents with a phenol in the presence of a catalyst whereby resins result, and separating the resins from the motor fuel constituents.

10. A motor fuel component comprising a motor fuel distillate of the partial oxidation products of heavy hydrocarbon oil cracked in the presence of air at cracking temperatures under pressures exceeding 35 atmospheres, said products including light hydrocarbon motor fuel constituents and volatile oxygen-containing compounds, but being substantially free from aldehydic partial oxidation products in any objectionable amount.

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