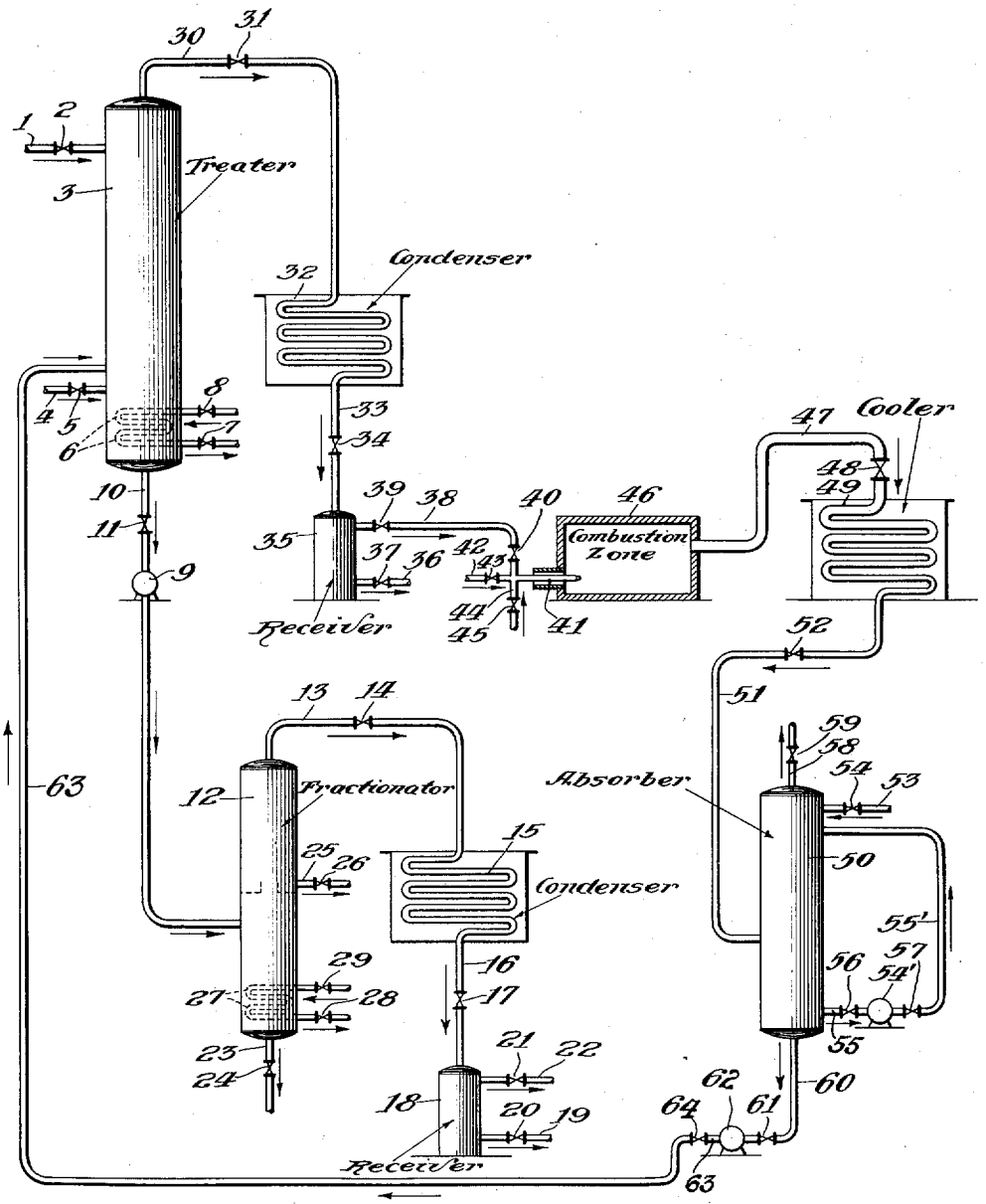
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TREATMENT OF MOTOR FUEL

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TREATMENT OF MOTOR FUEL

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This invention relates to an improved method of producing inhibitors for use in preventing the deterioration of cracked distillates of gasoline boiling range. More particularly, it refers to a process for dealkylating tars, with the resultant production of an inhibitor having improved properties over the tar originally treated.

Cracked gasolines which are now produced in huge quantities almost invariably contain highly unsaturated olefinic hydrocarbons which are characterized by a tendency to deposit gummy resinous material upon standing, particularly under the influence of light and air. Several well-known treating methods have been used for the elimination of these gum forming constituents. Cracked distillates have been treated with sulphuric acid for the removal of the unsaturated hydrocarbons. Clay treating means have also been utilized for the elimination of the olefinic constituents, such as di and tri-olefins. These methods, while useful, have certain inherent disadvantages:

(1) They are quite expensive, and

(2) In addition to removing the undesirable, highly unsaturated constituents, they remove relatively stable olefinic hydrocarbons which are useful and highly desirable in the gasoline.

By removing these more stable olefinic hydrocarbons the antiknock value of the cracked gasoline is depreciated and also good gasoline constituents are converted to heavy polymers having no value as motor fuel. The present invention is directed to improving the value of certain primary tars for inhibiting the formation of these undesirable gums and the reduction in knock rating of the motor fuel. Although it is to be particularly pointed out that gum and color formation and reduction in antiknock value are not necessarily related, the accomplishment of the two objects may be brought about simultaneously.

Compounds having inhibiting effectiveness have been found in distillates or tars, resulting from the destructive distillation of coal, lignite and wood. The present invention contemplates improving the inhibiting effectiveness of these tar fractions. We have found that by treating tar distillates with hydrogen halides, comprising hydrogen chloride, hydrogen bromide and hydrogen iodide, the resultant product is an inhibitor with increased potency. The following reaction probably typifies those which take place when treating the tar distillates with a hydrogen halide

$$(R'OR+HX \rightleftarrows R'OH+RX)$$

R'OR represents the member of a group of ether-like compounds in a tar wherein R' is an aryl radical, while R designates an aliphatic alkyl group of low molecular weight, usually a methyl or ethyl radical. Products of reactions of the above character are more highly phenolic and are more effective as inhibitors than their corresponding ethers. Alkyl halides RX are also produced.

One of the features of our invention is the regeneration of halogen acid from the alkyl halide. We have found that burning the alkyl halide in the presence of air produces hydrogen halide, carbon dioxide and water. The hydrogen halide thus liberated may be utilized again in treating the tar distillates for the production of improved inhibitors.

The following reaction typifies those which take place in the oxidation of the alkyl halides:

$$\underset{\text{Methyl bromide}}{[CH_3Br+3O \rightarrow HBr+CO_2+H_2O]}$$

In one specific embodiment, the present invention comprises the treatment of tar fractions with hydrogen halides, removing and fractionating the tar reaction products, liberating alkyl halide from the reacted mixture, oxidizing the alkyl halide produced therefrom and returning the hydrogen halide produced by the oxidation for further treatment of the tar fractions.

The process of this invention may be carried out in a number of ways and with various arrangements of apparatus. To illustrate the process of the invention, one form of the apparatus will be described, but it is understood that this in no way is to be taken as a limitation on the scope of the invention. The attached drawing is a diagrammatic view of an apparatus adapted for carrying out the process.

A preheated tar fraction is pumped through line 1 and valve 2 into the top of a treating tower 3. A halogen acid or a hydrogen halide is introduced into the bottom of treating tower 3 through line 4 and valve 5, for example, a concentrated solution of hydrobromic acid, which has been found to give good results in practice. For every gallon of tar fraction to be treated the amount of hydrogen halide may vary from one to five pounds, depending on the characteristics of the tar to be treated and the extent of treatment desired.

Pressure on the treating tower may vary from substantially atmospheric to several hundred pounds superatmospheric pressure. A treating temperature above the boiling point of water with a range of from 200 to 500° F. is preferred. The

acid flows upwardly countercurrent to the tar fraction coming from the top of the treating tower. For the purpose of insuring intimate contact between the tar fractions and the acid, treating tower may contain any suitable filling material, such as, for example, coarse silica fragments.

In order to control the temperature in the tower a closed steam coil 6 having valves 7 and 8 for regulating quantity of steam in the steam coil 6 is placed in the bottom of tower 3.

Treated tar fractions collect in the bottom of treating tower 3 and from thence are taken by pump 9 through line 10 and valve 11 and discharged into fractionating column 12. A small quantity of low boiling material is removed from the top of fractionating column 12 through line 13 and valve 14, subjected to condensation in condenser 15 and thence passed and collected through line 16 and valve 17 in receiver 18. This liquid condensate may be withdrawn from the bottom of receiver 18 by means of line 19 and valve 20. Pressure on the fractionating system is controlled by withdrawing fixed gases through valve 21 in line 22. Subatmospheric pressure is preferably maintained in fractionating column 12, condenser 15 and receiver 18 for the purpose of minimizing further decomposition and polymerization. From the bottom of fractionating column 12 a heavy pitch is removed from the system by means of line 23 and valve 24. The improved inhibitor will constitute an intermediate boiling point fraction and may be removed as a side-cut from fractionator 12 through line 25 and valve 26. In order to assist in the fractionation of the treated tar steam coil 27 is shown in the bottom of fractionator 12. A quantity of steam passing through coil 27 is regulated by valves 28 and 29.

As the result of the interaction between the tar fraction and the halogen acid, a mixture of alkyl halides is generated. Under the conditions existing in treating tower 3, water and alkyl halide will be in vaporous form and will pass out through the top of treating tower 3 through line 30 and valve 31 into condenser 32 wherein the steam is condensed and thence through line 33 and valve 34 into receiver 35. Separation of the water and alkyl halides (ethyl and methyl bromides for example) will take place in receiver 35 since the boiling point of water is 212° F., and the boiling point of methyl bromide is 40.3° F. and ethyl bromide is 100.4° F. The alkyl halides are at most only slightly soluble in water and, therefore, only a very small quantity will be removed in solution when the water is withdrawn from the bottom of the receiver through line 36 and valve 37.

For the purpose of regenerating hydrogen halide for use in treating further amounts of tar the alkyl halide is now burned. The alkyl halides, which are as a rule principally methyl bromide, have a low heat of combustion and need to be first heated to high temperatures or else oxidized with air at high temperatures by means of a heated surrounding medium if they are to be continuously burned. In order, therefore, to aid combustion of the alkyl halide a combustion-supporting gaseous medium is added. The alkyl halide may pass from receiver 35 through line 38 and valves 39 and 40 into burner 41. Air and extraneous fuel gas are supplied to burner 41 by means of line 42 and valve 43 and line 44 and valve 45 respectively. Any hydrocarbon or other fuel gas will be satisfactory in aiding the combustion of the alkyl halides. Air or pure oxygen may be utilized as the oxidizing medium, the former having the advantage of cheapness and the latter the advantage in that no nitrogen is introduced. Combustion of the alkyl halide along with the fuel gases forms the following products: Hydrogen halide, carbon dioxide, water, nitrogen, if air is used.

The products of combustion leave furnace 46 through line 47 and valve 48 and are subjected to cooling in cooler 49 prior to introduction to scrubbing tower 50 by means of line 51 and valve 52. Hydrogen halides are very soluble in water, therefore scrubbing tower 50 is utilized for contacting water with the cooled combustion gases resulting from furnace 46 for the purpose of recovering halogen acids for further use. The water is introduced into the top of the scrubbing tower 50 by means of line 53 and valve 54. Preferably the aqueous acid withdrawn from the bottom of receiver 35 is recirculated to the top of the tower. A local cyclic circulation to induce greater absorption of the acid in water may be set up by returning a portion of the liquid acid from the bottom of scrubbing tower 50 and pumping the same to the top of the tower by way of line 55 containing valve 56, pump 54', line 55' and valve 57. Residual gases after contacting the water in scrubbing tower 50 are released at the top of the tower through line 58 and valve 59, and the concentrated acid solution is removed from the bottom of scrubbing tower 50 through line 60 and valves 61 and forced by pump 62 through line 63 containing valve 64 into the bottom of the treating tower 3 for further treatment of tar. Fresh acid may be injected directly in line 60 or may be introduced into the treating tower by means of line 4 and valve 5.

As an alternative method of operation, although not shown in the drawing, the products of combustion may be sent directly to the treating tower. In that event provision would have to be made to eliminate the non-reactive constituents, leaving the top of receiver 35 together with the alkyl halides. This may be accomplished by dissolving the alkyl halides in ethyl alcohol or any other suitable solvent (nitrogen and carbon dioxide are insoluble in these solvents) recovering the alkyl halides by distillation and subsequently burning the alkyl halides to produce hydrogen halide together with carbon dioxide, water, and nitrogen, all of which are sent directly to the treating tower. Thus this invention may be practiced with the use of substantially gaseous hydrogen halide or with varying concentrations of hydrogen halide acid.

Diluents such as the lower aliphatic acids, consisting of acetic, propionic and butyric acids, may be added to the tar for the purpose of lowering the viscosity of such tar and assuring more intimate contact between the acid and the tar.

The following is given as an example of the results of operating the process of this invention:

The source of raw material was a tar precipitated from the vapors leaving the wood distillation retorts by means of a Cottrell electrical precipitator and known as Cottrell tar, and contained about 18% water. This tar was distilled and a fraction obtained boiling between approximately 140 and 500° F., which was used as a source of material for the production of the improved inhibitor.

The tar fraction was introduced into the top of the treating tower while a concentrated solution of hydrobromic acid was injected into the bottom. An acid solution of hydrogen bromide

containing 2.26 pounds of bromine equivalent was used per gallon of tar fraction. A reaction temperature of 280° F. and a pressure of 25 pounds per square inch was maintained on the treating tower. As the result of the interaction between the tar fraction and the hydrobromic acid methyl bromide was liberated together with water vapor. The quantity of methyl bromide recovered per gallon of tar fraction was 1.98 pounds, of which 1.66 pounds was bromine. The water vapor and methyl bromide removed from the top of the treating tower were subjected to condensation and collected in a receiver at a temperature of 110° F. Separation of practically all of the methyl bromide from the water takes place under those conditions because methyl bromide is only slightly soluble in water and even more insoluble in hot water.

The methyl bromide was subjected to combustion in a small furnace with the simultaneous addition of city gas and air. The products of combustion were cooled and scrubbed with a portion of the water condensed from the treating tower. A concentrated solution containing approximately 45% by weight of hydrobromic acid was recovered from the acid-absorbing tower. The bromine recovered in the hydrobromic acid scrubbing solution was 1.45 pounds per gallon of Cottrell tar, thus making 64% of the original hydrobromic acid again available for use. Concentrated acid solution recovered by scrubbing of the combustion gases was then mixed with additional fresh hydrobromic acid from an external source, such that the quantity of bromine in the hydrobromic acid in the latter mixture was once again 2.26 pounds per gallon of Cottrell tar fraction. The restored acid mixture was then returned for further treatment.

The treated tar was withdrawn from the bottom of the treating column and subjected to fractional distillation under subatmospheric pressure. Approximately 5% of light low boiling material is taken off from the top of the vacuum distillation column. 25% of the treated Cottrell tar is removed from the bottom of the tower as a heavy pitch.

An intermediate cut constituting 70% of the original material used is removed as a side-cut. To a crude cracked gasoline was added 0.05% of the original tar fraction. The induction period as tested by an oxygen bomb maintained at 212° F. was found to be 410 minutes whereas when 0.025% of the treated side-cut was added to a sample of the same gasoline, the induction period was 480 minutes. This side-cut is an improved inhibitor and is more than twice as effective as the original Cottrell tar fraction.

It is to be understood, of course, that the above example is given merely for purposes of illustration and is not intended to serve as a limitation on the invention.

We claim as our invention:

1. A process for improving the inhibiting value of tars from the distillation of solid carbonaceous materials, which comprises reacting said tar with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

2. A process for improving the inhibiting value of tars from the distillation of wood, which comprises reacting said tars with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

3. A process for improving the inhibiting value of tars from the distillation of lignite, which comprises reacting said tars with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

4. A process for improving the inhibiting value of tars from the distillation of coal, which comprises reacting said tars with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

5. A process for improving the inhibiting value of selected fractions of tars from the distillation of wood, which comprises reacting said fractions with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydogen halides for further use.

6. A process for improving the inhibiting value of selected fractions of tars boiling within the approximate range of 200–300° C. from the distillation of wood which comprises reacting said fractions with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydogen halides, and returning the regenerated hydrogen halides for further use.

7. A process for improving the inhibiting value of selected fractions of tars from the distillation of lignite, which comprises reacting said fractions with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydogen halides, and returning the regenerated hydrogen halides for further use.

8. A process for improving the inhibiting value of selected fractions of tars from the distillation of lignite boiling within the approximate range of 200–300° C. which comprises reacting said fractions with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

9. A process for improving the inhibiting value of selected fractions of tars from the distillation of coal, which comprises reacting said fractions with hydrogen halides, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

10. A process for improving the inhibiting value of selected fractions of tars from the distillation of coal boiling within the approximate range of 200–300° C. which comprises reacting said fractions with hydrogen halides, fraction-

ating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

11. A process for improving the inhibiting value of selected fractions of tars from the distillation of wood which comprises reacting said fractions with halogen acids, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

12. A process for improving the inhibiting value of selected fractions of tars from the distillation of wood boiling within the approximate range of 200–300° C. which comprises reacting said fractions with halogen acids, fractionating the products into volatile alkyl halides and tar fractions of improved inhibiting value, recovering the latter, burning the alkyl halides to regenerate hydrogen halides, and returning the regenerated hydrogen halides for further use.

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