Feb. 26, 1935. E. W. HULTMAN 1,992,310

PROCESS FOR TREATING HYDROCARBONS

Filed May 17, 1933

Fig. 1

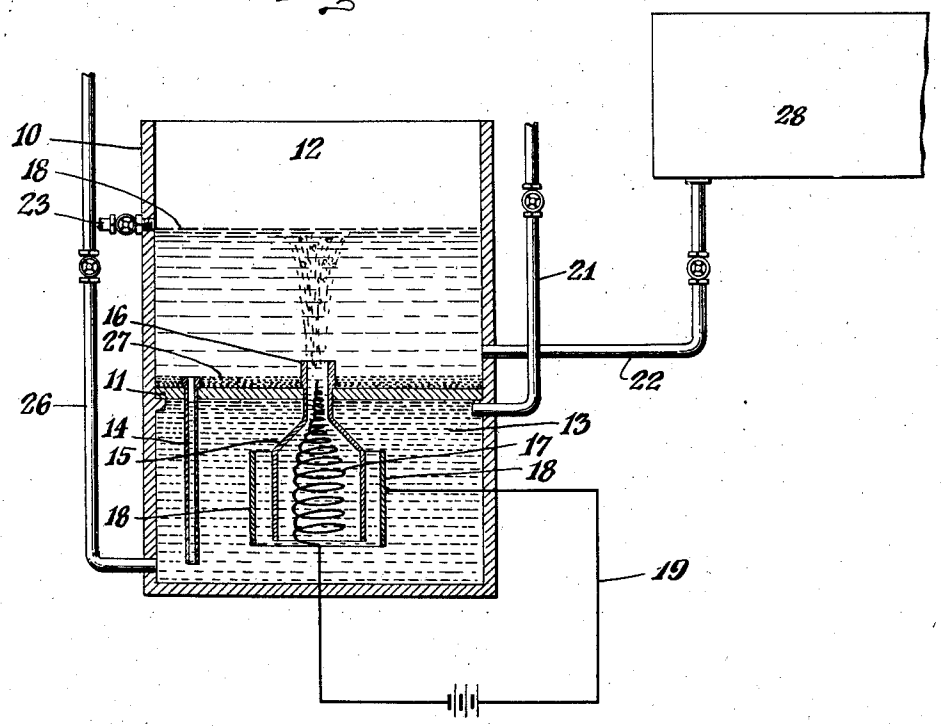
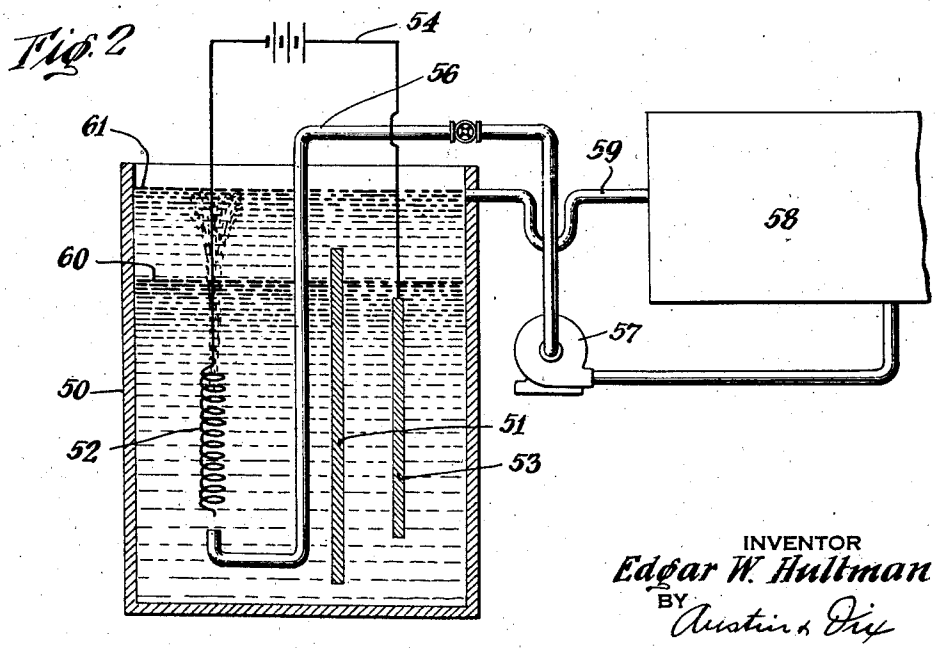


Fig. 2



INVENTOR
Edgar W. Hultman
BY
Austin & Dix
ATTORNEYS

Patented Feb. 26, 1935

1,992,310

UNITED STATES PATENT OFFICE

1,992,310

PROCESS FOR TREATING HYDROCARBONS

Edgar W. Hultman, Los Angeles, Calif., assignor to Hultman & Powell Corporation, Dover, Del., a corporation of Delaware

Application May 17, 1933, Serial No. 671,522

8 Claims. (Cl. 204—9)

This invention relates broadly to a method for purifying and improving the characteristics and quality, for certain purposes, of hydrocarbons such as gasolines, motor fuels, kerosene, distillates, mineral oils and other similar hydrocarbons both liquid and gaseous and of the hydrocarbon products from the destructive distillation of organic materials such as tars and derivatives thereof.

This method may be practised as a part of usual and customary refining operations or it may be carried out as an addition to or auxiliary to a refining operation. It may also be practised as an entirely independent and separate process depending upon the nature of the substance to be treated or the particular characteristics or qualities it is proposed to modify or improve.

The invention relates particularly to contacting the substance to be treated with electrolytes which, if desired, may be rendered more active by electrolysis. It has been found that sulphuric acid when so activated is most effective in accomplishing the results to be obtained by practising the invention.

In addition to its application for improving the characteristics of the substance treated, the process lends itself to the accomplishment of other desirable results; more particularly to the production of certain oxidation products such as alcohols, aldehydes, glycols, fatty acids and the like from a variety of materials. The method of producing oxidation products may be practised as an independent process or as an auxiliary process or it may be carried out simultaneously with the treatment of hydrocarbon products.

When sulphuric acid is used in practising the invention it may be subjected to electrolysis in a cell provided with a platinum anode and a lead cathode separated by a diaphragm to keep the gases formed at the cathode separated from those formed at the anode. The decomposition of sulphuric acid thereby caused results in the production of substantial amounts of persulphuric acid, Caro's acid, hydrogen peroxide, oxygen and ozone. The so treated acid, in varying degrees of strength but preferably of less than approximately 70% concentration, has been found to be admirably suited for the purpose of refining the hydrocarbon products, hereinbefore mentioned.

In the treatment of kerosene with the acid so activated, undesirable sulphur may be removed and the kerosene improved in color, odor and burning qualities. If it is desired to treat gasoline or motor fuels, sulphur may be removed and at the same time the anti-knock characteristics or octane rating may be improved by proper manipulation of the concentration of the acid used in the process.

If desired, oxidation products such as alcohols, aldehydes, glycols and fatty acids may be produced by intimately contacting hydrocarbons with sulphuric acid activated by electrolysis in a cell similar to that hereinbefore described. The products formed in the anode compartment of the cell may be passed into the hydrocarbons to be treated, agitated therewith, and then returned to the cell in a continuous cycle. The reaction thereby effected results in the formation of oxidation products which are soluble in the acid solution and which may be separated therefrom either by fractional distillation or other methods.

The process may be carried out in apparatus such as is illustrated diagrammatically in the annexed drawing forming a part of this application, in which

Fig. 1 is a diagrammatic illustration partly in section of one form of apparatus; and

Fig. 2 is a diagrammatic illustration partly in section of another form of apparatus.

Referring now to the drawing, 10 represents a chamber which may be made of non-conductive and acid-resisting material. Said chamber is divided by a partition 11 of like material forming a compartment 12 for the stock under treatment and sulphuric acid compartment 13. The spout 16 of funnel-shaped cup 15 extends through a suitable orifice in the partition 11. An acid return conduit 14 extends through the partition 11 through another orifice in the partition.

Positioned within the inverted cup-shaped funnel 15, which forms a diaphragm, is a platinum anode 17. The anode is connected by an electrical circuit 19 to a lead cathode 18 positioned about the exterior of the diaphragm formed by funnel 15.

A hydrogen vent 21 leads from the sulphuric acid compartment 13 and a suitable conduit 26 is provided for charging acid into the compartment 13. Stock to be treated may be introduced into compartment 12 through conduit 22 connected to a suitable source 28. Outlet 23 is provided in compartment 12, if desired, for drawing off the stock introduced through conduit 22.

In operation of this form of apparatus, acid of suitable concentration is charged into compartment 13 up to about the level indicated at 27. Stock to be treated is introduced into compartment 12 through conduit 22 to about the level indicated at 18. A suitable current is passed through the electrical circuit and the electro-

lytic action thereby set up causes gases formed at the anode to pass upwardly through the spout 16 also providing circulation of the acid on the principle of the "air lift." The acid and gaseous products from the anode are thus intimately mixed with the stock under treatment in compartment 12. The acid then settles out from the stock under treatment by gravity and is returned through acid return conduit 14 to the acid compartment 13. Hydrogen formed at the cathode may be vented through conduit 21.

The modification illustrated in Fig. 2 comprises a chamber 50 of non-conducting, acid-resisting material, separated into an anode and cathode compartment by a diaphragm 51 of like material. A platinum anode 52 and lead cathode 53 are connected to an electrical circuit 54. An inlet conduit 56 is led to the bottom of chamber 50 and has its discharge positioned in proximity to the platinum anode 52. A pump 57 is provided which may take suction from tank 58 containing stock to be treated and for forcing said stock through conduit 56 and discharge same beneath the surface of the sulphuric acid contained in the chamber 50. An overflow conduit 59 is provided for returning treated stock to the tank 58 or to any desired place.

In operation, sulphuric acid of suitable concentration is charged into the chamber 50 up to about the level indicated at 60. Current is passed through the electrical circuit to set up electrolysis in the acid and the pump 57 is set in motion to force stock to be treated through conduit 56. The stock as it is discharged from the conduit 56, rises to the surface of the acid in proximity of the platinum anode and when the level indicated at 61 is reached it overflows into conduit 59 and may be returned to tank 58. The circulation is continued until the desired action is complete.

While various adaptions of the invention will become apparent, the following are set forth as specific examples of the applicability of the process with different substances under certain typical conditions:

(A) Sulphuric acid of about 50% concentration was activated by electrolysis in a cell comprising a lead cathode and a platinum anode separated by a diaphragm in such manner as to form separate compartments for the gases formed at the anode and cathode. The gas formed at the cathode was drawn off and kept separate. The acid and products formed at the anode comprising substantial quantities of persulphuric acid, Caro's acid, hydrogen peroxide, oxygen and ozone were drawn off, contacted immediately with a cracked distillate and returned to the cell in a continuous cycle. The sulphur contained in the distillate was reduced from 0.6% to 0.1% in thirty minutes. After prolonged treatment the distillate contained 18% of unsaturated compounds as against 16% before treatment. The odor of the distillate after neutralization with a caustic wash was sweet and the color was satisfactory.

(B) One thousand pounds of 50% sulphuric acid were circulated through a battery of six electrolytic cells, arranged in parallel at the rate of 100 pounds per minute, then into the top of an agitator containing 1,000 barrels of cracked gasoline from a California crude oil. The acid which separated out by gravity was continuously drawn off from the bottom of the agitator and returned to the cells for reactivation by electrolysis, then returned to the top of the agitator, thus completing the cycle. In about thirty minutes of continuous re-cycling the circulation was discontinued and the acid drawn off from the agitator. The gasoline was then given a suitable neutralization with caustic and water washing. The sulphur content had been reduced from 0.6% to 0.1% in the finished gasoline. The odor was sweet, the color water white, it was negative to the copper strip test, sweet to the sodium plumbite (doctor) test and showed no appreciable deposit when evaporated in a copper dish.

(C) Straight-run gasoline was charged into the agitator and the same procedure as hereinbefore described was followed, except that acid of 30% concentration was used and re-cycled for forty-five minutes. The finished gasoline was water white, sweet to the doctor test, negative to the copper-strip test and showed no appreciable deposit when evaporated in a copper dish. The anti-knock characteristics of the finished gasoline were substantially improved, the octane number of the finished gasoline being 80 as against 65 for the untreated stock.

(D) A straight-run petroleum ether boiling between 40° C. and 70° C. was treated by agitating electrolyzed acid of about 50% concentration activated in a continuous cycle through the electrolytic cell. After about five minutes the electrolyte solution contained substantial quantities of alcohols, including butyl, amyl, hexyl and heptyl. After about fifteen minutes the corresponding aldehydes were found to be present, and after a half an hour the corresponding fatty acids were present. In another instance in which a cracked distillate boiling between 40° C. of 70° C. was treated in accordance with the invention, oxidation products with substantial quantities of glycols were produced.

While certain specific examples have been set forth it is not intended to confine the invention to the illustrations given, as heavier fractions of petroleum, such as kerosene and the light and heavy lubricating oils and also other hydrocarbons, whether liquid or gaseous or whether mineral oils or hydrocarbon products from destructive distillation, coal, wood or other organic materials, may be treated in accordance with the invention. Also it is readily apparent that owing to the immiscibility of oil or fractions thereof with the acid and the difference in specific gravity the invention lends itself to the accomplishment of the desired results by circulating the hydrocarbon through the cell instead of circulating the acid. In this case the acid is maintained in the cell and the hydrocarbon may be delivered to the bottom whereby it may pass upwards in proximity to the anode to the surface of the acid solution as hereinbefore described.

It is also apparent that the process may be carried out either as a continuous process through treating towers in series, or by the batch system, or by a combination of the two, as is well known in the art.

Moreover, the invention is not confined to sulphuric acid as the solution to be electrolyzed and used in the refining process. Various other electrolytes, such as sodium chloride, which may be converted into sodium hypochlorite solution containing free dissolved chlorine may be used. Other examples of solutions are mercury salts, copper salts and phosphoric acid. In some cases the reaction can be accelerated by the use of suitable catalytic agents such as, for example, cerium sulphate. Other metals such as tantalum in the presence of a suitable catalyst are satisfactory for the anode of the cell in place of platinum.

From the foregoing description it may be readily seen that the invention is adapted to a variety of purposes. In the treatment of gasoline, kerosene and other hydrocarbon products, refining losses will be materially lessened by reason of the use of much weaker acid than otherwise would ordinarily be used and in addition the qualities of the treated products may be substantially improved. Furthermore, oxidation products of great value may be made from very cheap raw materials, thus opening a wide field for commercial utilization.

While certain novel features of the invention have been disclosed and are pointed out in the annexed claims, it will be understood that various omissions, substitutions, and changes may be made by those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. The process of treating gasoline to increase its octane rating which comprises passing a solution of sulphuric acid through an electrolytic cell having an anode and cathode compartment, passing the products of electrolysis formed in the anode compartment both liquid and gaseous into intimate contact with the gasoline to be treated, separating the acid and the reaction products dissolved therein from said gasoline, and returning said separated acid and said dissolved products and passing same through the cell for further electrolysis.

2. The process of treating motor fuel which comprises passing a solution of sulphuric acid through an electrolytic cell having an anode and cathode compartment, passing the products of electrolysis both liquid and gaseous formed in the anode compartment into intimate contact with the motor fuel to be treated, separating the acid and the reaction products dissolved therein from said motor fuel, said treatment being continued until the octane number of the motor fuel is raised, and its anti-knock characteristics are increased, returning said separated acid and said dissolved products to the cell for further electrolysis in a continous cycle.

3. The steps in treating gasoline to increase its octane rating which comprises passing a solution of sulphuric acid of less than approximately 70% concentration through an electrolytic cell having an anode and cathode compartment, passing the liquid and gaseous products of electrolysis formed in the anode compartment into intimate contact with the gasoline to be treated, and continuing the treatment until the octane rating of the gasoline is raised, separating the acid and the reaction products dissolved therein from said gasoline, returning said acid and said dissolved products to the cell for further electrolysis and recycling the electrolyzed solution.

4. The method of treating a hydrocarbon with sulphuric acid which comprises maintaining said acid in solution in an electrolytic cell, subjecting the solution to electrolysis, passing the hydrocarbon into the bottom of said solution and allowing the hydrocarbon to pass upwards in proximity to the anode of said cell.

5. The method of treating gasoline to increase its anti-knock qualities which comprises maintaining a solution of sulphuric acid in an electrolytic cell, subjecting the solution to electrolysis, passing the gasoline into the said solution in intimate contact with the products formed at the anode of said cell and maintaining said gasoline in intimate contact with said products sufficient time to increase the anti-knock qualities of said gasoline.

6. In the art of treating motor fuels, the method of increasing its octane rating which comprises electrolyzing a dilute solution of sulphuric acid in an electrolytic cell having an anode and cathode compartment, immediately and intimately intermixing the products formed in said anode compartment with the motor fuel until the octane rating of said motor fuel is substantially raised, separating the solution from the motor fuel and then washing the motor fuel with an alkali.

7. In the art of treating motor fuel to improve its anti-knock qualities, the improvement which comprises intimately intermixing said motor fuel with an aqueous solution of sulphuric acid of less than 70% concentration activated by electrolysis in an electrolytic cell having an anode and cathode compartment, the activated solution in said anode compartment being immediately contacted with said motor fuel and intermixed therewith until the anti-knock qualities of the motor fuel are improved.

8. The improved steps in treating motor fuels to increase the anti-knock rating comprising passing a solution of sulphuric acid continuously through an electrolytic cell, continuously subjecting the solution to electrolysis, intimately contacting and intermixing the liquid and gaseous products formed at the anode pole of said electrolytic cell with the motor fuel, continuing the intermixing until the anti-knock rating of said motor fuel is increased, separating the motor fuel from said solution and washing the separated motor fuel with a neutralizer for acids.

EDGAR W. HULTMAN.