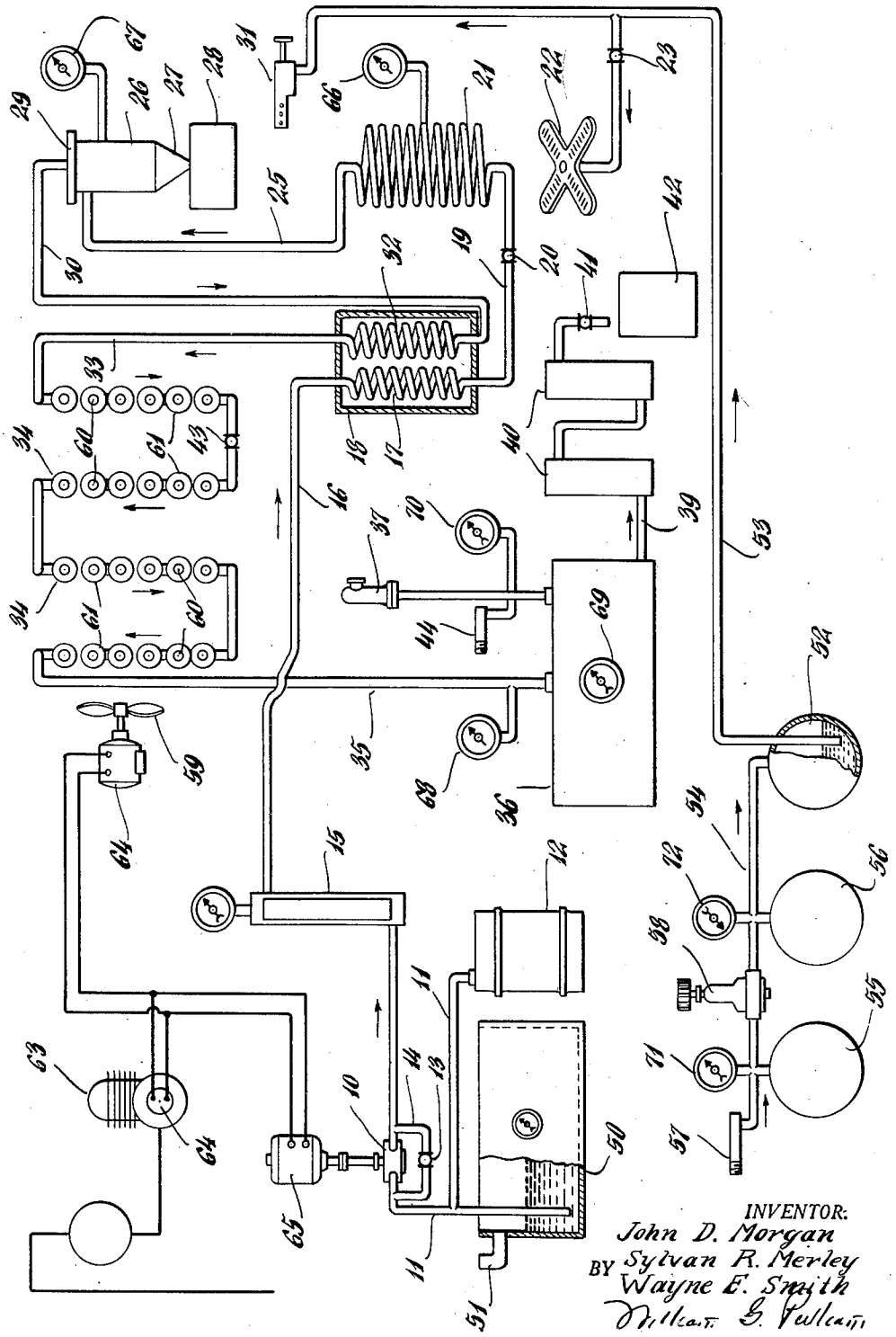
May 17, 1949. J. D. MORGAN ET AL 2,470,634

APPARATUS FOR DELEADING GASOLINE

Original Filed May 8, 1945



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Patented May 17, 1949

2,470,634

UNITED STATES PATENT OFFICE

2,470,634

APPARATUS FOR DELEADING GASOLINE

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Original application May 8, 1945, Serial No. 592,578. Divided and this application February 7, 1946, Serial No. 646,032

2 Claims. (Cl. 196—2)

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This invention relates to an apparatus for removing the ethyl anti-knock agents from motor gasoline in accordance with the process described in our copending application, Serial No. 592,578, filed May 8, 1945, now abandoned, of which this application is a division.

The demand for gasoline as a fuel for internal combustion engines is so great as to overshadow substantially all other uses. The petroleum industry accordingly devotes its major effort to the improvement of its product for this one special use, blending together those fractions which will give best performance, and adding various agents which serve to reduce the knocking qualities of the fuel. The best of the anti-knock agents so far developed is a mixture of lead tetra-ethyl, and ethyl bromide, and under ordinary conditions substantially all gasoline contains a greater or lesser percentage of ethyl fluid. There is always a need, however, for some straight gasoline, as a fuel for stoves, for dry cleaning purposes, as a grease solvent, and for hundreds of other purposes where the use of a leaded gasoline may be dangerous because of its essentially poisonous nature, or where it may be unsatisfactory from other points of view. Interestingly enough, the use of high octane leaded gas as a fuel for small air-cooled engines of from ¼ to 5 rated horsepower has proven highly unsatisfactory, the lead deposits, gummy matter and other decomposition products having a tendency to cause the valves to stick and to clog the engine parts, and in some cases, to result in the burning of the valves within a very short operating period. Straight gasoline has been proven to be a more effective and less destructive fuel for this specialized purpose, and where it is employed, these little engines will stand up under field conditions for many thousands of hours of active service.

The quantity of straight gas which is required for the foregoing and other miscellaneous uses is, of course, very small in proportion to the vast amounts of leaded fuel that must be furnished for automobile, tractor, aircraft, and other uses. In an industry where bulk transportation forms the backbone of the distribution system, the supplying of what may be thought of as minute quantities of straight gasoline raises extremely troublesome problems, all of which become peculiarly acute in maintaining a flow of various grades of gasoline to the armed forces in the field. Even the slightest consideration of the great difficulties which must be involved in furnishing a few gallons of straight gasoline to each

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of the field kitchens of the army, and to each of the many thousands of small motor generator sets of the kind employed by the Signal Corps should suffice to illustrate the gravity of the overall problem.

The principal object of the invention is to provide an apparatus for removing lead-bromine anti-knock compounds from commercial motor gasoline or the like to produce a fuel which is as suitable for cooking stoves, small gasoline engines, etc. as is conventional straight motor gasoline, and more especially to provide a small and highly mobile gasoline treating unit of this kind which lends itself to ready transportation from place to place, which is sufficiently self contained to require only a supply of leaded gasoline for continuous operation, and which is of such simple design and construction as not to require technically trained help for its safe and efficient operation.

The full nature of the invention and the manner in which the foregoing and other objects may be attained, will be more fully understood from a consideration of the following description, in the light of the accompanying drawing, in which the single figure is a diagrammatic showing of a preferred form of gasoline treating apparatus.

The gasoline treating process which forms the subject of our above identified parent application may be briefly described as comprising the steps of passing leaded gasoline in a confined stream through a heating zone, of heating the gasoline in that zone to a temperature at which its contained ethyl anti-knock compounds will decompose into gasoline insoluble products, of simultaneously vaporizing the gasoline so that it may sweep the ethyl decomposition products from the zone, of mechanically separating the gasoline vapors and the ethyl decomposition matter, and of finally condensing the clean vapor to form a product having substantially the properties and characteristics of the original gasoline prior to the addition of the ethyl anti-knock fluid. We have obtained excellent results in the deleading of 80-octane all-purpose motor fuel at temperatures between 700 and 850° F., with a reaction time of from 2 to 5 seconds. It will be appreciated, however, that both the temperature and time factors which are employed will depend to some extent upon the type of gasoline under treatment, these factors being varied appropriately to avoid excessive thermal cracking, reforming, or other chemical change in the fuel during the deleading treatment.

In carrying out this process in the apparatus illustrated in the drawing, pump 10 serves to withdraw leaded gasoline through inlet line 11 from a source such as drum 12 and to discharge it at a rate determined by the setting of valve 13 in bypass line 14, through a flowmeter 15 and line 16, to the cold side 17 of a heat exchanger which is indicated diagrammatically by numeral 18. It will be assumed for the purpose of description that the leaded gasoline enters the exchanger at ordinary atmospheric temperature, say around 70° F., and that when the unit is operating under equilibrium conditions, leaves the exchanger at a temperature of from 300° to 320° F. This stream of warm gasoline is discharged at a substantially constant rate through line 19, and check valve 20, to the inlet of a confined heating zone represented by pipe coil 21, wherein it is further heated by the products of combustion flowing from burner 22.

We have demonstrated in repeated tests that the heating of an average grade of leaded gasoline in coil 21 to a temperature of between 750° and 850° F. under the control of burner valve 23 results in a complete and rapid decomposition of its lead tetra ethyl and ethyl bromide components into gasoline-insoluble products. An analysis of the decomposition products which were thrown down in the treating of leaded gasoline having a fairly high sulfur content, showed about 71.2 per cent of lead sulphide, 4.03 per cent of lead bromide, 1.08 per cent of bromine and about 23.7 per cent of free lead, while the deleading of gasolines of lower sulfur content resulted in decomposition products containing very much lower percentages of free lead and free bromine, correspondingly higher percentages of lead bromide, and only insignificant quantities of lead sulphide.

The reduction of the ethyl anti-knock agents to heavy insoluble substances by the foregoing thermal treatment makes their subsequent separation from the gasoline vapors a relatively simple matter, and one which may be carried out in any of a number of ways. We prefer, however, to allow the high velocity gasoline vapors to sweep the decomposition products from coil 21, and to bear them through line 25 to a separator 26. This device, which is shown diagrammatically in the drawing, is in the nature of a centrifugal separator having a cylindrical section into the upper portion of which the stream of vapors and solids is introduced tangentially in conventional fashion. The resulting rapid rotation of the mixture forces the heavier solids to the sides of the chamber, and swirls them through cone section 27 into the relatively quiet collecting bin 28 from which they may be withdrawn from time to time, all in a well understood manner. Cleaned vapors in the nature of substantially straight gasoline may therefore be withdrawn from the center portion of top 29 of the separator through line 30 for subsequent condensation.

In starting up the apparatus it is necessary to preheat separator 26 so as to minimize condensation of gasoline therein, and for this purpose we provide a preheating burner which is shown diagrammatically at 31. Once the deleading apparatus has been raised to a condition of temperature equilibrium, however, the separate heating of this element may be dispensed with, its insulation being adequate to provide undue heat loss and excessive vapor condensation. Under these circumstances, vapors leave separator 26

at a temperature which closely approximates that maintained in coil 21, that is to say, at some value between 750° and 850° F. Both for reasons of operating economy, and in order to minimize the overall size of the condenser section to which reference will be made later, high temperature vapors are led through line 30 to the hot side 32 of exchanger 18, where they give up a portion of their heat to the incoming leaded gasoline in the cold side 17. Under normal equilibrium operating conditions it can be expected that the temperature of the outgoing vapor will be reduced in the exchanger to somewhere in the neighborhood of from 300° to 400° F.

The partially cooled gasoline is led from exchanger hot side 18 through line 33 to a condenser 34, wherein it is liquefied, and the resulting condensate is discharged through line 35 into receiver 36 at a temperature of about that of the surrounding atmosphere. Line 35 preferably terminates in a distributor extending along the bottom of reservoir 36 with its outlet holes near the bottom so that wet vapors which are entrained with the rundown product may be uniformly distributed to promote their absorption by the stored product. It will be further evident that these wet vapors, together with any fixed gases in the run-down product, produces a more or less constant agitation of the stored gasoline and thus serve to prevent the settling out in reservoir 36 of any of the fine insoluble matter which may not have been removed by centrifugal action in separator 26.

In any internal heating process of this kind there is some tendency towards the formation of fixed gases and to their collection in the run-down tank. Tank 36 is therefore preferably maintained vapor tight, and is provided with a safety valve 37 which is set to release fixed gases in the event that the pressure in the tank rises above a value of about 2½ pounds per square inch. The vapor pressure in tank 36 is accordingly sufficient under normal conditions to establish a flow of straight gasoline through discharge line 39, and filters 40 which serve to collect any fine insoluble matter which has not been removed by centrifugal action in separator 26, and to discharge the product through shut-off valve 41 into carrying cans 42, or to a point of direct usage. It will be noted however that the unit is provided with a fitting 44 containing a conventional air-valve, (not shown), to which a hand pump may be coupled or a standard air chuck applied, for the purpose of building up air pressure in the tank 36 to a value of about 2 pounds per square inch which will serve to deliver gasoline through its filters when the autogenous pressure in the tank is insufficient for that purpose.

It will be apparent, of course, that during the operation of the unit, vapor pressure generated in the coil 21 serves to prevent any back flow of gasoline from the condenser 34 towards the separator. When the deleading unit is idle, however, and pressure is built up in tank 36 for delivery purposes, it is necessary that other means be provided for preventing back flow. In the illustrated device this function is performed by check valve 43 which is installed in the condenser line at a point near that at which liquefaction of vapors normally begins.

We prefer to carry out our deleading process under a very low pressure closely approximating atmospheric pressures which, of course, makes for simplicity both in the design and construc-

tion of apparatus in which the process is practiced, as well as to minimize hazards of operation. In the illustrated unit, for example, pump 10 discharges leaded gasoline at a pressure of about 30 pounds per square inch, most of which is lost in overcoming friction in flowmeter 15, in cold side 17 of the exchanger, check valve 20, and the various intervening lines. The pressure maintained in the confined heating zone is of the order of 2 to 5 pounds, being only sufficient to maintain continued flow through heating coil 21, separating chamber 26, hot side 32 of exchanger 18, and through condenser 34. It will be appreciated, however, that the process is not limited to the use of pressure within this stated range, and that where the deleading unit constitutes something in the nature of a permanent installation it may be arranged to operate at such higher or lower pressures as may be found to, promote most efficient operation in the treatment of various types of leaded gasoline.

The illustrated deleading apparatus has been designed primarily as a mobile and self-contained unit which may be mounted upon a two-wheeled trailer for transportation into the field with army supply troops. Its various parts have been arranged, therefore, with a view towards maximum simplicity, ruggedness and independence of outside facitities. The unit accordingly includes a tank 50 into which leaded gasoline may be dumped in small quantities for the purpose of accumulating a minimum inlet charge for pump 10. It will be understood, of course, that this tank is primarily intended for use when the leaded gasoline is vailable only in small unit containers such as a standard five-gallon G. I. can, and that under normal operating conditions gasoline will be drawn from one or more standard drums such as those shown at 12.

The heating equipment for coil 21, and for the preheating of separator 26, is also of the simplest and most readily available kind. Thus burner 22 is a standard army field kitchen gasoline burning unit, while preheater 31 is nothing more than the head of a standard gasoline blow torch, both of which are arranged to be supplied with gasoline from tank 52 through line 53 by air pressure maintained in reservoirs 55 and 56. The use of two reservoirs with a reducing valve 58 between them is again an incident arising out of intended field operation of the unit. Thus air may be pumped manually into reservoir 55 by the use of a conventional hand pump coupled to valve unit 57, until the pressure therein is raised to 60 or more pounds per sq. in. This high pressure air then flows through automatic reducing valve 58 to maintain a substantially constant pressure of 40 pounds per square inch in the second reservoir 56, an arrangement which of course makes intermittent hand pumping possible while maintaining a constant pressure on the gas supply line.

It is to be noted that ethyl gasoline has no advantage over straight gasoline as a fuel for this kind of burning equipment. In fact, its use frequently gives rise to serious operating problems by reason of the tendency of the ethyl decomposition products to clog up the burner orifices. We prefer therefore to employ straight gasoline in tank 52, which may, of course, be the product produced by the practicing of this invention in the illustrated unit.

It will also be observed that condenser 34 is designed to be cooled by air discharged over its outer surface by fan 59. In the illustrated unit the condenser comprises four substantially standard extended surface units of the kind normally used for steam heating and the like, each of which consists of several rows of interconnected tubes 60 having upstanding fins 61 arranged at closely spaced intervals along their outer surfaces. The mounting of the several units is such that fan 59 discharges air over the condenser tubes in a direction which is generally counter to the flow of gasoline condensate therein, so that the coolest air will be in transfer relation with the coolest gasoline and vice-versa to obtain maximum effectiveness.

The field unit also includes a motor generator unit of the kind widely used by the army signal corps, consisting of a small gasoline engine 63 coupled directly to a 110 volt alternator 64 having an output capacity of about 1000 watts which serves to drive fan motor 64 and pump motor 65, and for the operation of such other auxiliaries as may be required. It has been noted hereinbefore that ethyl gasoline has a very destructive effect upon small engines such as this. We accordingly prefer to use a straight gasoline in the motor generator unit, which may, of course, be the end product of the practicing of this invention in the illustrated unit.

The deleading unit described above has an output capacity of about 30 gallons per hour. In starting up operation, burner 22 and preheating burner 31 are both employed to preheat coil 21 and separator 26 to suitably high temperatures as indicated by thermometers 66 and 67, before a flow of leaded gasoline is established. When in the course of about a half hour's operation, equilibrium conditions are obtained, valve 13 is set to establish a flow of leaded gasoline through the heating coil at about the rate indicated above, as indicated by flowmeter 15; burner 22 is set by an adjustment of its valve 23 to maintain the desired decomposition temperature of from 750° to 850° F. in the oil; and burner 31 for the separator is of course shut off. The several instruments mentioned above, together with a condensate thermometer 68, liquid level gage 69, and the pressure gages 70, 71 and 72, serve to give an indication at all times of vital operating conditions within the unit and accordingly form a basis for suitable adjustment of control valves 13 and 23 so that the deleading process may be carried out most efficiently and effectively. In actual practice we have found that this degree of instrumentation, coupled with the extreme simplicity of the operating controls, suffices to permit the unit to be operated safely and on a continuous field basis by unskilled operators, and that technically trained help is not required.

Having described our invention, what we claim as new is :

1. A portable unit for removing ethyl antiknock compounds from gasoline comprising an inlet for liquid ethyl gasoline, a pump connected to said inlet, a pipe coil defining a heating zone, a first conduit connecting the outlet of said pump with the inlet of said zone, means for regulating the quantity of liquid ethyl gasoline delivered by said pump to said coil, a gasoline burner for heating said coil, means for regulating said burner said pump and burner regulating means serving conjointly to control the temperature in said coil within the range of from 750° F. to 850° F. whereby to vaporize such gasoline and decompose its contained ethyl anti-knock compounds, a centrifugal separator for separating ethyl decomposition products from vapor generated in said coil, a second conduit connecting the outlet of

said coil to the inlet of said separator, a series of interconnected finned tubes serving as a vapor condenser, a fan for discharging air at normal atmospheric temperature over said tubes, a third conduit connecting the outlet of said separator with the inlet of said condenser, and a heat interchanger having its hot side constituting a portion of said third conduit and its cold side constituting a portion of said first conduit.

2. A portable unit for removing ethyl antiknock compounds from gasoline according to claim 1 characterized by a tank for collecting condensate from the outlet of said condenser tubes, and by mechanical filters connected to the outlet from said tank.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
410,067	Bower	Aug. 27, 1889
1,582,407	King	Apr. 27, 1926
1,752,350	Parker	Apr. 1, 1930
1,815,366	Stratford	July 21, 1931
2,127,004	Nelson	Aug. 16, 1938
2,219,101	Finwall	Oct. 22, 1940
2,397,142	Howard	Mar. 26, 1946