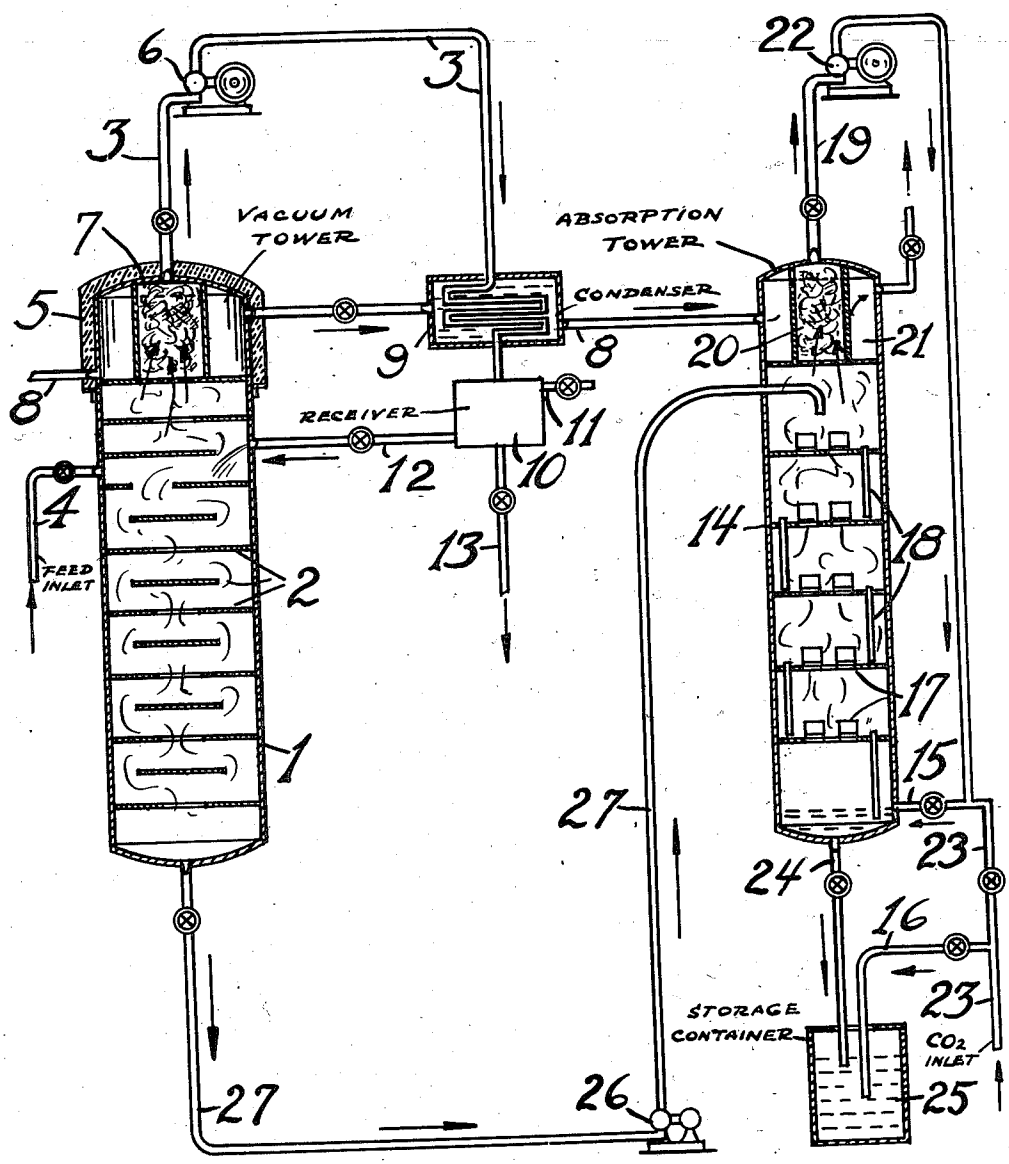
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STABILIZATION AND PROTECTION OF HYDROCARBON COMPOSITIONS

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STABLIZATION AND PROTECTION OF HYDROCARBON COMPOSITIONS

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This invention relates to a method of protecting hydrocarbon compositions, particularly of the nature of light hydrocarbon distillate fuels.

One of the objects of this invention is to provide a method of preserving stability of the hydrocarbons during storage and use. A further object is to protect highly volatile hydrocarbon compositions against fire hazards.

A substantial removal of air from a hydrocarbon composition followed by saturation of the composition with carbon dioxide under moderate conditions before storing provides a practicable method of insuring protection to the hydrocarbons. When the hydrocarbon compositions are thus treated, they do not have to be kept in any special type of container nor under elevated pressures nor at lowered temperatures to give the desired advantages, but need be handled only with the usual precautions.

When a hydrocarbon composition, such as a motor fuel or even a higher boiling petroleum distillate is exposed to air or oxygen it has a tendency to absorb these oxidizing gases, which when present even in very minute quantities, cause considerable deterioration with resultant acidity formation, gum formation, discoloration, etc. For example, when a 5-gallon case of conventional type used for transporting fuel is filled with gasoline even to full capacity leaving no air space and is tightly capped, a progressive deterioration of the fuel in the container can be detected. Moreover, it is difficult and impracticable to store a highly volatile fuel in any economical type of container without leaving some gas space for expansion. Therefore, ordinarily, the hydrocarbon liquid composition is exposed to oxygen in this gas space. Even those amounts of oxygen which are normally occluded or absorbed in the hydrocarbon oil itself are present in a sufficient amount to give undesirable deterioration.

Hitherto it was found difficult and expensive to remove the air or oxygen which tends to be dissolved or otherwise taken up and retained in the fuel during the refining processes. The hydrocarbon liquids may normally contain as much as 15% by volume of absorbed air, and even with painstaking efforts to saturate the air-containing hydrocarbon liquids with large volumes of carbon dioxide at low temperatures, a point is reached at which the hydrocarbon liquid continues to retain a substantial amount of the absorbed air.

It has now been found possible, in accordance with the present invention, to free the hydrocarbon liquids of the absorbed air by placing the liquids under vacuum with convenient operating conditions, and subsequently while in the deaerated condition to efficiently dissolve into the hydrocarbon liquids gaseous carbon dioxide. In first deaerating the hydrocarbon liquids under vacuum, the amount of absorbed air can be reduced to a mere trace or negligible amount, for example of the order of less than 1% by volume to 0%. In this deaerated condition, the hydrocarbon liquids substantially free of dissolved gas can be readily charged with gaseous carbon dioxide until they contain, under normal conditions, from about 100% to 300% by volume of the carbon dioxide and retain only a negligible amount of air or oxygen. By carrying out this treatment, it was found that the storage stability of a liquid hydrocarbon composition, such as a motor fuel, is greatly improved, even though the liquid is kept in a container at ordinary atmospheric pressure and temperature. The step of first deaerating allows a suitable proportion of the carbon dioxide to be readily dissolved in the hydrocarbon liquid without imparting to the composition an excessive vapor pressure, hence the composition containing the dissolved carbon dioxide is satisfactorily stable under ordinary conditions with the usual type of handling.

It has also been found that the highly volatile hydrocarbon fuels thus treated are highly benefited by a substantial increase in their flash points over a considerable period of time, even if the fuels are placed in a common type of fuel supply tank vented to the atmosphere. This added protection of the fuel is advantageous when the fuel is carried in supply tanks of aircraft or automobiles. Under the conditions that exist when the carbon dioxide is present in the fuel as a result of the treatment herein described, there is no harmful interference with the performance or carbureting of the fuel.

By experimental determinations it was found impractical to dissolve more than 300% by volume of carbon dioxide charged in the deaerated

liquid hydrocarbon composition. More than this proportion requires refrigeration of the composition to low temperatures, and even though an aviation gasoline fuel contained considerably in excess of 300% by volume of carbon dioxide, the fuel showed a low flash point, particularly when the fuel was not first deaerated. For example, an aviation gasoline saturated with carbon dioxide at −22° F. showed a flash point of −35° F. with a closed Tag tester. Numerous other difficulties are encountered in treating and storing a fuel which is not preliminarily deaerated, and which is charged with carbon dioxide at low temperatures, e. g., expensive refrigeration, large waste of carbon dioxide, expensive and complicated equipment for storing, and difficulties in using and supplying such fuels to an internal combustion engine.

It has also been determined that the persistence of the carbon dioxide in the fuel stably dissolved therein remains at nearly a constant level even with a reduction of pressure at high altitudes as in aviation service. The carbon dioxide concentration in the fuel tends to decrease only silghtly with altitude, because with the increase in altitude, there is a lowering of temperature which compensates for the reduction in pressure. With the lowering of the temperature the carbon dioxide concentration tends to increase while with decrease in pressure the carbon dioxide concentration tends to decrease. This is illustrated in the following table:

TABLE I

Effect of altitude on CO_2 solubility in gasoline

Elevation	Solubility of CO_2 in gasoline
	G./liter
Sea level	4.55
5,000 feet	4.30
10,000	4.26
20,000	4.24

It is to be noted that the net effect of the change of altitude is that the concentration of the carbon dioxide remains nearly constant. Accordingly, the carburetor and fuel induction means of the engine do not need alteration in adjustment after they have been set for the carbon dioxide protective fuel herein indicated.

A method by which a hydrocarbon composition is satisfactorily deaerated and treated with carbon dioxide will be described by reference to the accompanying drawing. The drawing shows a diagrammatic view in elevation and cross section of apparatus suitably used for the method.

Referring to the drawing, 1 indicates a vacuum or deaerating tower. This tower may be constructed similarly to conventional dephlegmating towers in refiniery equipment. In the tower may be disposed baffle plates 2, as shown, for the purpose of preventing entrainment of hydrocarbon oil in the gases removed overhead through line 3 and of extending the surface of the oil so as to facilitate the disengagement of the air. The fuel to be treated is passed in near the top of the tower by line 4.

At the top of the tower 1 is provided a cooling means 5 in the form of a condenser or jacket to chill the gaseous fluids as they are withdrawn from the tower through packing 7. The cooling medium in the cooling means may be a slurry of solid carbon dioxide, or any other material which has a low temperature, e. g. cold brine, or even cold water. The cooling medium is conducted through the unit by pipe 8. It is, however, desirable to have the gases passing the cooling means reduced to a fairly low temperature to prevent passage of light hydrocarbon vapors from the oil overhead. Of course, less cooling is required if the oil treated has low volatility, as this cooler is only to insure condensation of any hydrocarbons which might tend to boil under the reduced pressure. The overhead line 3 from the deaerating tower, is evacuated by means of a vacuum pump 6. For extra precaution in eliminating any loss of hydrocarbon vapors, the gaseous fluids may be passed by the vacuum pump on the pressure side into a heat exchange condenser 9 in which overhead vapors of normally liquid hydrocarbons are condensed under pressure at low temperatures, so that a further separation of gases from condensible vapors is obtained, the gases being withdrawn from the receiver 10 by line 11. Any condensate formed in condenser 9 and collected in receiver 10 may be recycled to tower 1 by line 12, or be withdrawn from the system through valved outlet 13.

From a point near the bottom of tower 1, the deaerated hydrocarbon oil is made to pass by pump 26 through line 27 to enter the upper part of the absorption tower 14. Near the bottom of the absorption tower carbon dioxide gas is fed by line 15 to pass countercurrently to the stream of the hydrocarbon oil as it descends through the tower. Baffle plates 17 provided with bell caps and down corners 18 are disposed in tower 14 to aid in bringing about intimate contact between the carbon dioxide gas and the hydrocarbon oil so as to facilitate the absorption. The unabsorbed carbon dioxide gas withdrawn from the tower by line 19 through packing 20 in a cooler 21 may be recycled to the inlet line 15 by means of the compressor 22. A supply of fresh carbon dioxide is led in by line 23.

The fuel saturated with the carbon dioxide is withdrawn from the tower by valved outlet 24 which acts as a line for charging a container 25 in which the oil is to be stored.

The storage container or packing case to be filled with the treated oil is preferably first filled with carbon dioxide, injected by valve controlled line 16 from supply line 23, so that this gas displaces all air from the container, and in turn, the carbon dioxide is displaced by the treated fuel as it is charged into the container. After the container is filled to the desired level, it may be capped or hermetically sealed; or it may be left open to atmospheric pressure through a suitable small vent.

In the step of deaerating the hydrocarbon liquid, the vacuum or reduced pressure to which the liquid is subjected depends to some extent on the efficiency of the deaerating apparatus, i. e. such factors as the time in which the liquid is subjected to the vacuum, and the extent to which the liquid is agitated and spread out to give greater liquid-gas interphase area. The reduction of pressure also depends to some extent on the temperature of the hydrocarbon liquid, for at higher temperatures more air can be disengaged with less reduction in pressure. However, as a practical matter, the temperature should not be very high, for it becomes more difficult with increase in temperature to cool the overhead gases and to prevent loss of volatile normally-liquid hydrocarbons. Conditions in the vacuum tower found to be suitable for obtaining efficient deaerating of aviation gasolines are tempera-

tures in the range of 40° F. to 100° F. and a subatmospheric pressure of 2 to 200 millimeters of mercury absolute, more preferably 55–75° F. and 25 to 100 mm. Hg absolute.

In the absorption tower, the temperature of the liquid contacted with the carbon dioxide is suitably at about ordinary atmosphere or room temperature, for it is preferred not to have the liquid highly supersaturated with carbon dioxide nor too cold when it is being charged into the container. A suitable temperature range for the absorption is about 40° F. to about 70° F. The pressure in the absorber may be approximately atmospheric or superatmospheric up to about 5 atmospheres.

In the preferred embodiment described, the deaerating step is carried out with very little expense. The carbon dioxide absorption step also has a high efficiency, for it permits the carbon dioxide to be recycled without deleterious contamination by oxygen and the absorption process has a high efficiency due to the intimate contact of the carbon dioxide with the hydrocarbon liquid. The operation described also permits the hydrocarbon liquid to be treated with very little or substantially no loss of normally liquid hydrocarbons, even when these hydrocarbons are highly volatile, as for example, a gasoline fuel having an initial boiling point of about 100° F.

To demonstrate the effectiveness of the present method for imparting to a volatile gasoline a safety fuel flash point, analytical determinations were made on a sample of a regular aviation gasoline before and after being subjected to the described treatment of deaerating and saturating with carbon dioxide. Tests were made by the A. S. T. M. method with both a closed flash point tester and a Tag open flash point tester. The boiling ranges and octane numbers of the treated and untreated gasoline were as follows:

TABLE II

Inspection of clear aviation gasoline

	Untreated	Deaerated and saturated with CO_2
Octane number	74.0	73.8
Gravity, °A. P. I.	64.2	63.9
Distillation:		
I. B. P. °F.	117	113
140°	4.0	4.0
158	21.0	21.0
212	82.0	82.0
284	98.0	98.0
F. B. P. degrees	291	289
Recov.	98.5	98.0
Residue	1.1	1.2

The distillation characteristics of the motor fuel were not appreciably changed. It was demonstrated, however, that the flash point of the fuel was greatly elevated, as is shown in the following data:

TABLE III

	Aviation gasoline	Aviation gasoline deaerated and saturated with carbon dioxide
Flash point (tag closed tester).	°F. −10	Did not "flash" up to 140° F. Vapors burned outside opening from about 70° to 140° F. Burned above tester at 150° F.

Similarly, a kerosene distillate of standard specification was treated and tested for flash point in comparison with the flash point tests of a sample of the untreated kerosene to obtain the following data:

TABLE IV

Flash point °F.	Kerosene	Kerosene deaerated and saturated with carbon dioxide
Tag closed tester	127	136
Tag open tester	145	160

While it can be readily understood that the method of treating hydrocarbon liquids that has been described is applicable to all types of liquid hydrocarbon refinery products, it is of particular benefit for treatment of motor fuel distillates such as gasoline, kerosene, Diesel fuels, and heating oils. It may also be used in protecting viscous liquid to solid hydrocarbon products which are susceptible to oxidation.

One of the highest advantages of the present invention is that it provides a protected hydrocarbon composition which is substantially free from deleterious absorbed oxygen and containing absorbed carbon dioxide in suitable and adequate amounts incorporated into the oil by absorption without excessive cooling or supersaturation so that the treated composition can be readily and safely stored in ordinary containers under normal conditions.

The safety aviation fuel made possible by the present invention considerably reduces the fire hazard incident to forced landings should gasoline be spilled over hot engine parts. It is well recognized that fire following an airplane accident is a frequent cause of the resultant fatalities, a condition avoided by the present invention. In addition, military aviation gasoline treated as described would be less vulnerable in the face of enemy attack.

In treating aviation fuels by the present method, it was found that they were converted into excellent safety fuels having substantially unchanged volatility and anti-knock characteristics without imparting to the fuels excessive vapor pressure properties, which would be undesirable in causing vapor lock. Safety fuel compositions thus provided preferably have boiling ranges substantially within the range of 100° F. to 350° F., boiling off at least 50% at normal pressure up to about 212° F., and have satisfactory low Reid vapor pressures in the range of about 7 to 8.5 pounds per square inch at 100° F. These treated safety fuels are made substantially free of deleterious oxygen by the deaeration and contain sufficient stably dissolved carbon dioxide, in a proportion of 100% to 300% by volume under normal conditions, to elevate the flash point of the fuel to as high as 150° F. and to ordinarily maintain the flash point above 70° F. for a long period, as determined with a Tagliabue closed flash point tester.

It is not intended that the invention be limited by the specific examples and embodiments given for the purposes of illustration, for a number of modifications come within the spirit and scope of the invention as set forth in the appended claims.

I claim:

1. A safety motor fuel composition of high oxidation resistance and high flash point which comprises a gasoline hydrocarbon boiling substantially within the range of 100° F. to 350° F.

substantially free from molecular oxygen and containing carbon dioxide in an amount above 100% by volume at about atmospheric temperature and pressure sufficient to give the composition a flash point of the order of 70° F. to 150° F. while the fuel composition containing the dissolved carbon dioxide has a Reid vapor pressure below 8.5 pounds per square inch at 100° F.

2. A motor fuel composition of high oxidation resistance and high flash point, which comprises a gasoline hydrocarbon fuel deaerated to reduce its air content to a negligible amount, and containing dissolved carbon dioxide in a proportion of about 100% to about 300% by volume under atmospheric conditions of temperature and pressure.

3. The method of improving a safety motor fuel composition to increase its resistance to oxidation and elevate its flash point, which comprises subjecting a highly volatile gasoline hydrocarbon composition of which at least 50% boils off at 212° F. to a subatmospheric pressure under conditions to substantially deaerate said composition, and dissolving into said deaerated composition under approximately atmospheric temperature and pressure gaseous carbon dioxide until said composition contains from about 100% to 300% by volume of dissolved carbon dioxide.

4. The method as described in claim 3 in which said hydrocarbon composition is deaerated at an absolute pressure in the range of from about 2 to 200 millimeters of mercury and a temperature in the range of from about 40° F. to about 100° F.

5. A method of treating a hydrocarbon distillate product to stabilize and protect the product during storage, which comprises applying to said hydrocarbon distillate product a subatmospheric pressure under conditions to disengage substantially all absorbed air, and thereafter intimately contacting the thus deaerated hydrocarbon product with a stream of gaseous carbon dioxide at about atmospheric temperature and pressure until said hydrocarbon product contains from about 100% to 300% by volume of dissolved carbon dioxide.

6. The method as described in claim 5, in which said deaerated hydrocarbon product is intimately contacted with a stream of gaseous carbon dioxide to cause absorption of the carbon dioxide by the hydrocarbon product, and unabsorbed carbon dioxide from said stream substantially free of oxygen is recycled into contact with the deaerated hydrocarbon product.

7. In the refining of a liquid hydrocarbon product susceptible to deterioration by oxidation, a step in the treatment which comprises subjecting the hydrocarbon product to a degasifying treatment under reduced pressure for removing substantially all normally gaseous substances including air absorbed and occluded in said liquid product, then substantially saturating the degasified liquid hydrocarbon product with carbon dioxide under approximately atmospheric temperature and pressure until at least about 100% by volume of carbon dioxide is dissolved in the liquid hydrocarbon, loss of any normally liquid hydrocarbons volatilized during the process being prevented by condensation.

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