Feb. 4, 1936. H. C. WEBER 2,029,748

STORAGE OF GASOLINE

Filed March 14, 1932

Fig. 1.

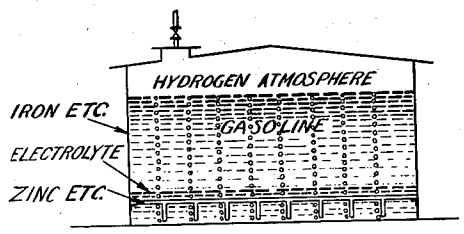


Fig. 2.

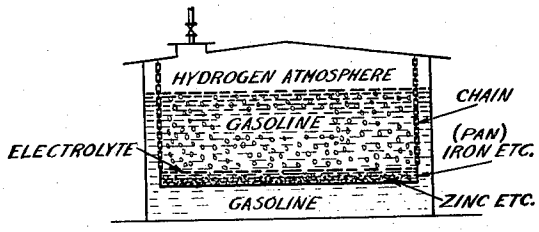


Fig. 3.

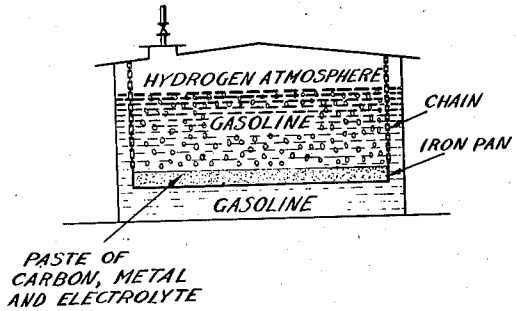


Fig. 4.

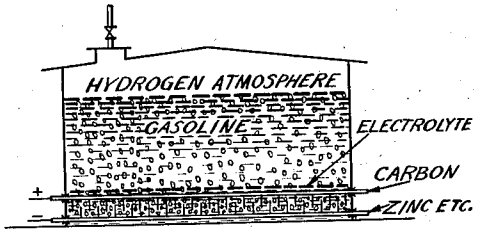


Fig. 5.

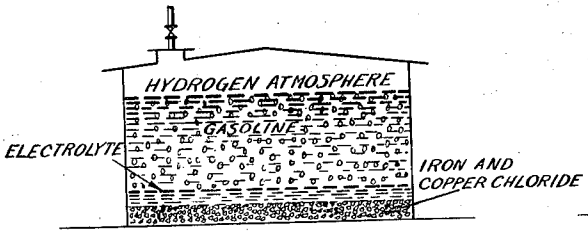
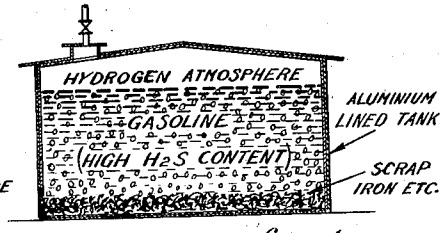


Fig. 6.



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STORAGE OF GASOLINE

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6 Claims. (Cl. 23—239)

This invention relates to the treatment of motor fuel, and refers more particularly to the treatment of motor fuels produced by cracking relatively heavier portions of crude petroleum.

In a more specific sense the invention provides a process or method of treatment whereby the deterioration of gasolines during storage with respect to color, gum content, knock rating, et cetera, may be substantially prevented, the method of treatment disclosed eliminating the principal causes contributing to the deterioration of the properties of the gasoline above mentioned.

Gasolines produced from petroleum, and particularly those produced in cracking the heavier portions thereof, contain constituents in minor percentages which are unstable on standing, particularly in the presence of light and air and at times contact with metallic surfaces which catalyze the reactions. It has been established that the development of color and gums and loss of knock rating suffered by gasolines in storage is due to a large extent to the presence of di and tri olefinic hydrocarbons which have a pronounced tendency to polymerize and form high molecular weight aggregates of a gummy or resinous nature, the initial stage in this gum formation being evidently attributable to the initial formation of peroxides or other oxygen addition compounds. Other components may contribute to the overall result or act to accelerate the reactions of polymerization, such as unstable sulfur compounds either inherent in the raw gasoline or resulting from treatment with sulfuric acid or other chemicals. The net result of these reactions, whatever their exact character may be, is to depreciate the color of the gasoline, increase its gum content and decrease its knock rating and practically all commercial treating processes are aimed at treating out a sufficient amount of the undesirable unstable components to permit storage over several months without rendering the gasoline unsaleable unless retreated.

The accomplishment of this end has thus far been attacked from two general standpoints, the first being to remove the trouble-making components by suitable chemical treatments which are frequently tedious and expensive, and the second to add inhibiting materials to the gasolines which counteract the tendency of the fuel toward deterioration.

The present process is distinct from these two general methods stated, and in one specific embodiment consists in providing a reducing atmosphere in contact with stored gasolines, thus eliminating the principal cause of deterioration.

It is preferred to employ hydrogen as a reducing atmosphere, and the invention further comprises the generation of hydrogen in contact with the gasoline, this being possible of accomplishment by a number of methods which may readily be applied in practice. To illustrate some of the methods which may be employed, the attached drawing has been provided which indicates six methods of generating hydrogen, though other methods than the ones shown may be employed as the invention is broad in this respect.

Referring to Fig. 1 of the drawing, a simple electrolytic method of generating hydrogen is shown. A solution of an electrolyte is maintained below the surface of the gasoline in a storage tank and a zinc frame or grid of suitable type is supported in the electrolyte so that an electric couple is set up between the two metals of different position in the electro-chemical series, this resulting in the generation of hydrogen at the surface of the iron, which return serves the two-fold purpose of providing a reducing atmosphere for the gasoline and preventing corrosion of the iron. The latter may comprise various solutions of inorganic acids, bases or salts and may, for example, be a simple solution of sodium chloride, caustic soda or even the natural brine separated from crude oil. The strength of the electrolyte, the amount of zinc used and the efficiency of contact may be readily adjusted so that hydrogen is generated at a moderately slow rate and no removal of spent materials is needed until the gasoline is removed for sale.

In Fig. 2 a modification of the method employed in Fig. 1 is shown, the electrolysis for the generation of hydrogen being conducted in a pan or series of pans suspended in the gasoline at a point near the bottom of the tank, this method allowing the introduction of new electrolytic materials without removing the gasoline from the tank.

In Fig. 3 a pan is again employed which may contain materials similar to those employed in so-called dry cells, hydrogen being generated until the materials are spent at which time the pan may be raised and the fresh charge introduced.

In Fig. 4 a system of hydrogen generation is shown which employs an outside electromotive force to decompose an electrolyte to produce reducing gases. A positive electromotive force is impressed on a carbon or iron electrode of suitable design immersed in an electrolyte and insulated from the tank proper, the current passing to a second electrode of similar design and similarly insulated, placed in opposite relationship

thereto. Assuming that the essential reaction is the decomposition of the water in the electrolyte, the net result will be the release of hydrogen on the second electrode and oxygen on the carbon or other electrode which will result in the formation of oxides so that the reducing atmosphere in this case will consist of hydrogen or a mixture of the various gases evolved.

Fig. 5 shows a convenient method of slowly generating hydrogen from water or aqueous electrolytes by the interaction of iron therewith, the rate of reaction being controllably accelerated by incorporating small amounts of copper chloride with the iron particles. This method is of simple and ready application and results in the gradual formation of iron oxide with the simultaneous liberation of equivalent amounts of hydrogen to effect the results desired.

Fig. 6 shows a method of generating hydrogen somewhat different than the five preceding in that use is made of the sulfur which may be present in some gasolines, particularly those resulting from the cracking of high sulfur charging stocks to produce the necessary amount of hydrogen. By employing an aluminum lined tank which is resistant to the corrosive action of hydrogen sulfide and homologous sulfur compounds, scrap iron may be added to the gasoline to react slowly with the sulfur compounds with the formation of iron sulfides and the liberation of gaseous hydrogen, the efficiency of the reaction being somewhat promoted by the contact of the iron with the aluminum lining, although the conductivity of the gasoline is of a low value.

The foregoing examples of methods for producing reducing atmospheres essential to the preservation of desirable properties in gasoline are merely illustrative of many different methods that may be employed. The rate of generation of the gas may be controlled in a variety of ways, and in general will be maintained only at a point sufficient to prevent the depreciation of properties in any particular gasoline being stored. It has been found that with gasolines of fairly good stability that the amount of hydrogen necessary is very small, and in some cases it is sufficient merely to provide enough for the initial displacement of oxidizing gases in the storage tank, while in others the generation of hydrogen must be maintained at a higher rate to insure effective inhibiting action.

The particular method of hydrogen generation employed and the rate of generation will also depend on a number of other factors such as the temperature of storage and the relative amounts of unsaturated and sulfur compounds present in the gasoline, etcetera. It will be noted that the tanks shown in the drawing are provided with a vent for the release of excess gas pressure so that they will not be subjected to unsafe internal pressures. Automatic release devices or "breathing" systems may be employed and if necessary the evolved gases may be subjected to absorption to recover gasoline constituents although in many cases the process has the added advantage of producing a gradual stabilization or weathering so that the gasoline is thus further improved.

As an example of the results which may be obtained by the application of the process, the case of storage of a gasoline made by cracking heavy Mid-Continent residuum may be cited. To sufficiently stabilize the gasoline produced from the process so that it may be stored for two months without undue depreciation in properties may necessitate the use of 8 to 10 pounds of 66° Bé. sulfuric acid per barrel of gasoline. By maintaining a reducing atmosphere in the gasoline, the amount of acid necessary for producing a saleable product before and after storage may be reduced to four pounds per barrel.

The following tabulation shows in column 1 the properties of the gasoline from the fractionator of the process prior to chemical treatment; column 2 shows the properties after treatment with ten pounds per barrel of sulfuric acid; column 2A shows the properties of this treated gasoline after two months' storage; column 3 shows the properties after treatment with four pounds of acid and column 3A shows the properties which this treated gasoline may have after storage during the slow generation of hydrogen beneath its surface.

	1	2	2A	3	3A
Gravity, °A. P. I.	56.1	56.2	55.8	56.3	56
End point, °F.	410	415	417	412	411
Color, Saybolt	10	+30	23	29	28
Gums, copper dish	340	20	55	30	25
Total sulfur, per cent	0.28	0.11	0.11	0.13	0.12
Octane number	76	71	69	74	74

Consideration of the figures in the preceding tabulation will make the advantages of the process readily apparent. It will be observed that while the color produced in the ten pound acid treatment was +30, that the color dropped after two months' storage to 23, the gum content rising at the same time from 20 to 55 mgs. Furthermore, the relatively heavy acid treatment reduced the octane number 4%, this dropping still further on storage to a final value of 69%.

The lighter acid treatment producing the gasoline having properties shown in column 3 produced a 29 color which was slightly below the color resulting from a ten pound treatment, which, however, dropped only one point after two months' storage so that the final value was five points higher than the color of the ten pound treated gasoline after a similar period of storage. The lighter acid treatment had noticeably less effect upon the octane number, the value of 74% undergoing no further change upon storage in the reducing atmosphere. The gum content underwent substantially no change.

The preceding description of the invention and the examples of results obtainable by its use will serve to define its character and show its advantages, but neither is to be construed as imposing limitations thereon.

By the term "electrolytic means" as used in the specification and claims is meant a process which not only includes the use of electric current for generating hydrogen, but also the use of metals or other substances in conjunction with a medium whereby a difference in electromotive potential exists between two or more of the substances, and as a result hydrogen is generated.

The expression "storage over prolonged time periods", used in the claims, is intended to differentiate from the customary refining of oil wherein the time of contact between the oil and refining agents in treating apparatus is only of relatively short duration as compared with the customary long time periods during which oil is kept in storage vessels while awaiting disposal.

I claim as my invention:

1. The method of preventing deterioration of gasoline containing gum and color forming constituents during storage thereof over prolonged time periods, which comprises generating nas-

cent hydrogen beneath the surface of the gasoline in storage, permitting the hydrogen to freely contact with the gasoline, and maintaining an atmosphere of the hydrogen above the surface of the gasoline during the storage period to prevent access of oxidizing gases to the gasoline.

2. In the storage over prolonged time periods of gasoline containing gum and color forming constituents, the method which comprises generating nascent hydrogen beneath the surface of the gasoline in the storage vessel, permitting the hydrogen to freely contact with the gasoline, and maintaining an atmosphere of the hydrogen in the vessel above the surface of the gasoline during the storage period to prevent access of oxidizing gases to the gasoline.

3. The method of preventing deterioration of gasoline containing gum and color forming constituents during storage thereof over prolonged time periods, which comprises storing the gasoline in the presence of electrolytic hydrogen-generating means immersed in the body of gasoline, electrolytically generating hydrogen during storage, permitting the hydrogen to freely contact with the gasoline, and maintaining an atmosphere of the hydrogen above the surface of the gasoline.

4. In the storage over prolonged time periods of gasoline containing sulphur compounds and gum and color forming constituents, the method which comprises reacting upon the sulphur compounds to form hydrogen during storage, permitting the hydrogen to freely contact with the gasoline, and maintaining an atmosphere of the hydrogen above the surface of the gasoline.

5. In the storage over prolonged time periods of gasoline containing sulphur compounds and gum and color forming constituents, the method which comprises adding iron to the gasoline and reacting the same with the sulphur compounds to form hydrogen during storage, permitting the hydrogen to freely contact with the gasoline, and maintaining an atmosphere of the hydrogen above the surface of the gasoline.

6. In the storage over prolonged time periods of gasoline containing sulphur compounds and gum and color forming constituents, the method which comprises adding iron to the gasoline and reacting the same in the presence of aluminum with the sulphur compounds to form hydrogen during storage, permitting the hydrogen to freely contact with the gasoline, and maintaining an atmosphere of the hydrogen above the surface of the gasoline.

HAROLD C. WEBER.