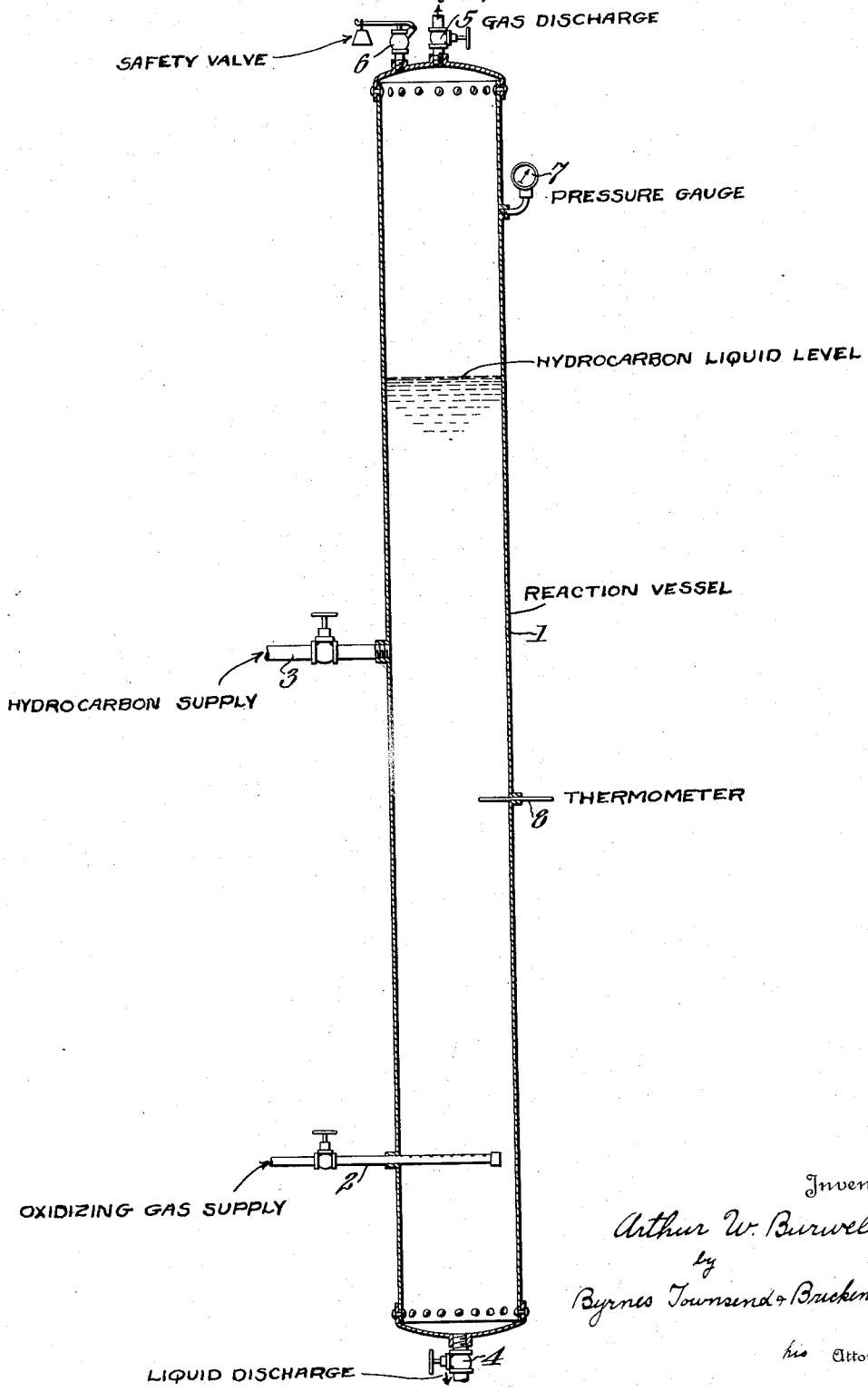
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PROCESS OF MAKING ORGANIC ACIDS FROM PETROLEUM HYDROCARBONS AND PRODUCT

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PROCESS OF MAKING ORGANIC ACIDS FROM PETROLEUM HYDROCARBONS AND PRODUCT.

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This invention relates to an improved process for the controlled oxidation of hydrocarbons and more particularly the hydrocarbons or mixtures thereof occurring in petroleum or distillates or fractions thereof.

I have found that by the oxidation of petroleum hydrocarbons under properly controlled conditions valuable organic acid products, including both simple carboxylic acids and hydroxy carboxylic acids, may be economically prepared in commercial quantities. Reference is made particularly to the treatment of so-called petroleum hydrocarbons, since petroleum oil is the principal source of such hydrocarbons at the present time. The invention, however, includes the treatment of hydrocarbons such as those occurring in petroleum, regardless of the source from which they are obtained. It is noted in this connection that petroleum is a rather heterogeneous material, some of it containing principally paraffin hydrocarbons, while petroleum from other sources contains a relatively large proportion of cyclic or aromatic hydrocarbons or naphthenes, and still other supplies of petroleum contain both the paraffin and the aromatic hydrocarbons in substantial but varying proportions. All of such hydrocarbons or mixtures may be treated in accordance with my invention with the production of organic acid products, the chemical composition and physical properties of which bear a direct relation to the composition of the hydrocarbon or mixture of hydrocarbons from which they are made.

The process consists generally in oxidizing the hydrocarbons or mixtures thereof, including both light and heavy petroleum distillates in the liquid phase.

A feature of the invention is the production from certain hydrocarbons of organic acids which are solids at normal atmospheric temperatures. A further feature of the invention is the production of organic acids which correspond with or bear a direct relation to the hydrocarbons from which they are derived.

The invention will be described hereinafter by reference to the accompanying drawing which illustrates one form of apparatus suitable for carrying out the oxidation process.

Referring to the drawing, 1 is an upright cylindrical reaction vessel which may be, for example, about 17 inches in diameter and about 16 feet in height. The vessel 1 may be made of any suitable material such as iron, but preferably is made of or lined with material which is resistant to the corrosive action of the reaction mixture. An iron vessel lined with aluminum gives good results, the aluminum being very little attacked. Suitable means, not illustrated, such as a jacket surrounding the vessel or pipe coils within the vessel are provided for heating and cooling the contents thereof. At a short distance above the bottom of the vessel 1 is an air spray pipe 2. The spray pipe 2 is positioned above the bottom of the vessel in order to provide a dead space or trap therebelow, the purpose of which will be explained hereinafter. 3, 4 and 5 are a valved hydrocarbon supply pipe, a liquid discharge pipe and a gas discharge pipe, respectively. 6 is a safety valve, 7 a pressure gauge and 8 a thermometer.

The process is carried out in the apparatus illustrated as follows:

A petroleum hydrocarbon oil, such as for example a distillate from Pennsylvania crude oil measuring 42° Bé. is charged into the vessel 1 up to two or three feet, more or less, from the top of the vessel, a small amount of an oxidizing catalyst such as a compound of manganese, copper or iron, say manganese stearate, amounting to about 0.1 percent of the weight of the oil is added and the mixture heated up to a temperature in the neighborhood of 120° C. or higher, say about 135–140° C., and an oxidizing gas, preferably air, is supplied through the spray pipe 2. Gases are permitted to accumulate in the vessel until the desired pressure is reached, and the pressure is then maintained or regulated by controlling the discharge of gases through the valved outlet pipe 5. The pressure may vary considerably, say from 250 to 320 pounds per square inch. The preferred pressure will depend upon a number of conditions, including the temperature maintained, the kind of hydrocarbon mixture under treatment, the rate of air supply and, if oxygen-enriched air is used, upon the richness of the oxygen supply. The kind of apparatus, that is, its heat dissipating

characteristics, and the extent to which the batch of hydrocarbon has been oxidized at any particular moment also have a bearing upon the other reaction conditions. It may be explained here that it is preferred to carry out the oxidation process under such conditions that the reaction is substantially self-sustaining. When using apparatus such as that illustrated and described, the vessel 1 having its walls freely exposed to the surrounding atmosphere, that is, unjacketed and uninsulated, and using a hydrocarbon mixture such as that referred to with a catalyst and air as the source of oxygen supplied as rapidly as may be without causing the body of hydrocarbon to froth or foam to such an extent as to flow through the outlet pipe 5, the reaction is self-sustaining at a temperature of about 135–140° C. and at a pressure of about 290–300 pounds per square inch. The reaction conditions may be varied. For instance, it is not essential that the process be carried out under self-sustaining conditions. Heat may be be supplied from an external source in order to maintain the desired reaction temperature. Or the reaction vessel may be insulated. Or if the temperature of the reaction mixture tends to rise, cooling may be resorted to. The rate of reaction may be increased by increasing the air supply or the richness of the oxygen supply or the pressure or the temperature. Oxidation apparently takes place at all temperatures, very slowly at low temperatures and more rapidly at higher temperatures. Therefore, while I prefer to carry out the process at a temperature at which the reaction rate is fairly rapid and the reaction self-sustaining, say 120° C. or higher, it is to be understood that the invention includes the employment of all suitable temperatures at which oxidation takes place.

During the oxidizing treatment, as is stated above, gases collecting in the upper end of the vessel 1 are released through the pipe 5. These gases contain practically no oxygen, a small amount of carbon dioxid varying from say 1½ percent at the beginning of the treatment of a batch of hydrocarbon to say 7½ percent near the end of the treatment, and varying quantities of volatile acids. The amount of carbon dioxide formed apparently depends somewhat upon the amount of gas space in the vessel 1 above the level of the liquid, the greater the space the greater the quantity of carbon dioxid produced, presumably by the oxidation of volatile acids in this space. The volatile acids passing off with the exit gases include a relatively large proportion of formic acid, amounting to say 5 percent of the batch of hydrocarbons, and about 5% of other volatile acids including acetic and propionic acids. These acids are formed in part from corresponding hydrocarbons in the charge and apparently in part from hydrocarbons of higher molecular weight which are broken down to hydrocarbons of less molecular weight during the process. Even when the charge is substantially free of methane a relatively large quantity of formic acid is produced.

The passage of air is continued until the desired degree of oxidation of the charge is obtained, for instance, until the oxidation is substantially complete, which condition is indicated when a sample of the charge is substantially completely saponifiable. The oxidation may readily be carried to the point in many instances at which only about 1 percent of the charge remains unsaponifiable.

At the beginning of the oxidation process a portion of the mixed hydrocarbons are quickly oxidized, forming a product which is insoluble in the remaining hydrocarbons. If at this point the injection of air is discontinued and the charge permitted to settle the insoluble product may be drawn off. This product is a dark-colored mass, insoluble in petroleum, acid in nature and shows properties of resins and drying oils, and apparently is a material which may be used as a substitute for resins such as shellac and drying oils such as linseed oil.

The oxidation is then resumed and as the oxidation proceeds an aqueous liquid highly charged with coloring matter and water-soluble acids amounting to as high as 30 percent of the liquid collects in the dead space below the air pipe 2. This liquid is withdrawn from time to time during the process. By removing the highly colored liquid from the bottom of the vessel 1 during the oxidation process it is found that the final product produced in the vessel 1 will have a much lighter color and less odor than when the highly colored aqueous liquid collecting in the bottom of the vessel 1 is allowed to remain therein.

The acid product left in the vessel 1 after the completion of the oxidation may be refined by the usual methods, for instance, by filtration thru charcoal, crystallization, distillation, extraction and the like. A suitable procedure is to treat the oxidation product with a solution of caustic soda and separate the resulting aqueous solution of the sodium salts of the acids from any unsaponifiable matter and then liberate the free acids from their sodium salts by means of a strong mineral acid such as sulfuric.

The product ordinarily comprises a mixture of simple carboxylic acids and hydroxy acids which may be separated for instance by treating the mixture with a petroleum distillate, thus dissolving the simple acids and leaving the hydroxy acids as undissolved residue. Or the hydroxy acids and simple acids may be separated by treatment with strong sulfuric

acid which dissolves the hydroxy acids but not the simple acids.

The kind of acids produced, that is, simple acids or hydroxy acids, depends upon the nature of the hydrocarbon treated and the extent to which the oxidation is carried. For instance, by the oxidation of a distillate from crude oil obtained from the Bradford field containing mainly the normal paraffin hydrocarbons, a product consisting principally of solid white carboxylic acids of high molecular weight and having all of the characteristics of normal fatty acids is obtained, while from petroleum hydrocarbons obtained from the lower district of Pennsylvania comprising a relatively large proportion of cyclic hydrocarbons, a product containing some hydroxy acids and relatively large quantities of acids which appear to be formed from iso-paraffins and which are readily converted into hydroxy acids by further oxidation, is obtained. The oxidation of the non-crystalline portion of crude oil from the lower district of Pennsylvania, such as is found in lubricating oils made from distillates which have been freed from wax and finally reduced to give oils of high viscosity and low cold test, gives practically nothing but highly hydroxylated acids which are insoluble in petroleum, soluble in alcohol, and have the characteristics of shellac.

As a general rule the farther the oxidation is carried, the greater is the proportion of hydroxy acids in the product. This may be due to the conversion of simple acids to hydroxy acids during the treatment or to the fact that the hydrocarbons which give hydroxy acids oxidize more slowly than those hydrocarbons which give simple acids. It is noteworthy in this connection that the different kinds of hydrocarbons present in a petroleum distillate undergo selective oxidation. The first to oxidize are those which may be separated from the distillate by treatment with fuming sulfuric acid or liquid sulfur dioxid in accordance with the known refining methods. The oxidized product of these hydrocarbons is insoluble in the remainder of the distillate and may be separated before the oxidation is continued, as is described above. The next portion of the distillate to oxidize is that portion which, as is described above, collects at the bottom of the vessel 1 along with water formed by the oxidation and may be withdrawn and thus separated from the remainder of the distillate.

When the oxidation of a batch of mixed hydrocarbons such as a petroleum distillate is carried substantially to completion, then the kind of acids produced must depend mainly upon the nature of the hydrocarbons in the distillate. If it is desired to produce only or mainly simple acids from a distillate which by complete oxidation gives more or less of the hydroxy acids, the formation of hydroxy acids may be very substantially limited by oxidizing only a small portion of the distillate, say 20 percent, separating the resulting acids and then repeating the treatment of the residual portion of the distillate. By proceeding in this manner less hydroxy acids are formed than when the oxidation of a batch of distillate is completed in a single operating stage.

The results produced by the treatment of different distillates is illustrated by the following:—

(1) Oxidation of 42° Bé. distillate from Pennsylvania crude oil.

The products are, about 5 percent of formic acid, 5 percent of acids from $C_7H_{14}O_2$ to $C_{12}H_{24}O_2$, and 90 to 95 percent of acids having an average molecular weight above 300, being liquid in the mixed state and having a specific gravity greater than 1.

(2) Oxidation of 30–35° Bé. distillate from Pennsylvania crude oil.

The products are, about 5 percent of formic acid, 5 per cent of other volatile acids and 95 to 100 percent of acids having an average molecular weight above 345, a specific gravity less than 1, solid at 10° C. and partly crystallized at 20° C.

(3) Oxidation of wax melting at 50–51° C. from Pennsylvania crude oil.

The products are, about 5–10 percent formic acid, 5–10 percent of other volatile acids and 100–110 percent acids which are solid or semisolid at ordinary temperature and resemble bees wax in appearance and odor and have a melting point of 45° C. and a specific gravity less than 1.

In the foregoing illustrations the products are calculated upon the weight of the hydrocarbon mixture treated.

The process of my invention is simple and inexpensive and does not involve the use of either complicated apparatus or expensive materials. It is applicable to the petroleum oils and distillates which are readily obtainable in large quantities and produces good yields. There is very little loss either by way of destructive oxidation or unconsumed material. The products of course are of commercial utility.

This application is a continuation in part of my application, Serial No. 588,073, filed September 13, 1922.

I claim:

1. Process which comprises contacting an oxidizing gas with a normally liquid petroleum hydrocarbon mixture in liquid phase at a temperature above 100° C. and at a pressure greater than atmospheric pressure but not substantially above about 320 pounds per square inch, producing thereby oxidation products including water-insoluble heavy organic acids which are insoluble in the hydrocarbon mixture, separating the insoluble

acids, and thereafter during the further treatment of the hydrocarbon mixture with oxidizing gas separating aqueous liquid therefrom.

2. Process which comprises contacting an oxidizing gas with a normally liquid petroleum hydrocarbon mixture in liquid phase at a temperature above 100° C. and at a pressure greater than atmospheric pressure but substantially not above about 320 pounds per square inch until the formation therein of products insoluble in said hydrocarbon mixture substantially ceases, separating said insoluble products, continuing the treatment of the hydrocarbon mixture with the oxidizing gas and separating therefrom the resulting aqueous liquid.

3. Process as defined in claim 1 in which the pressure greater than atmospheric pressure is from 250 to 320 pounds per square inch.

4. Process which comprises contacting an oxidizing gas with a normally liquid petroleum hydrocarbon mixture in liquid phase at a temperature above 100° C. and at a pressure greater than atmospheric pressure but substantially not above about 320 pounds per square inch, separating the resulting insoluble material from the liquid, continuing the treatment of the liquid with the oxidizing gas, separating the resulting aqueous liquid therefrom, and further continuing the treatment of the liquid with the oxidizing gas.

5. Process as defined in claim 1, in which the normally liquid petroleum hydrocarbon mixture is contacted with oxidizing gas in the presence of a compound of manganese soluble in said hydrocarbon mixture.

In testimony whereof, I affix my signature.

ARTHUR W. BURWELL.