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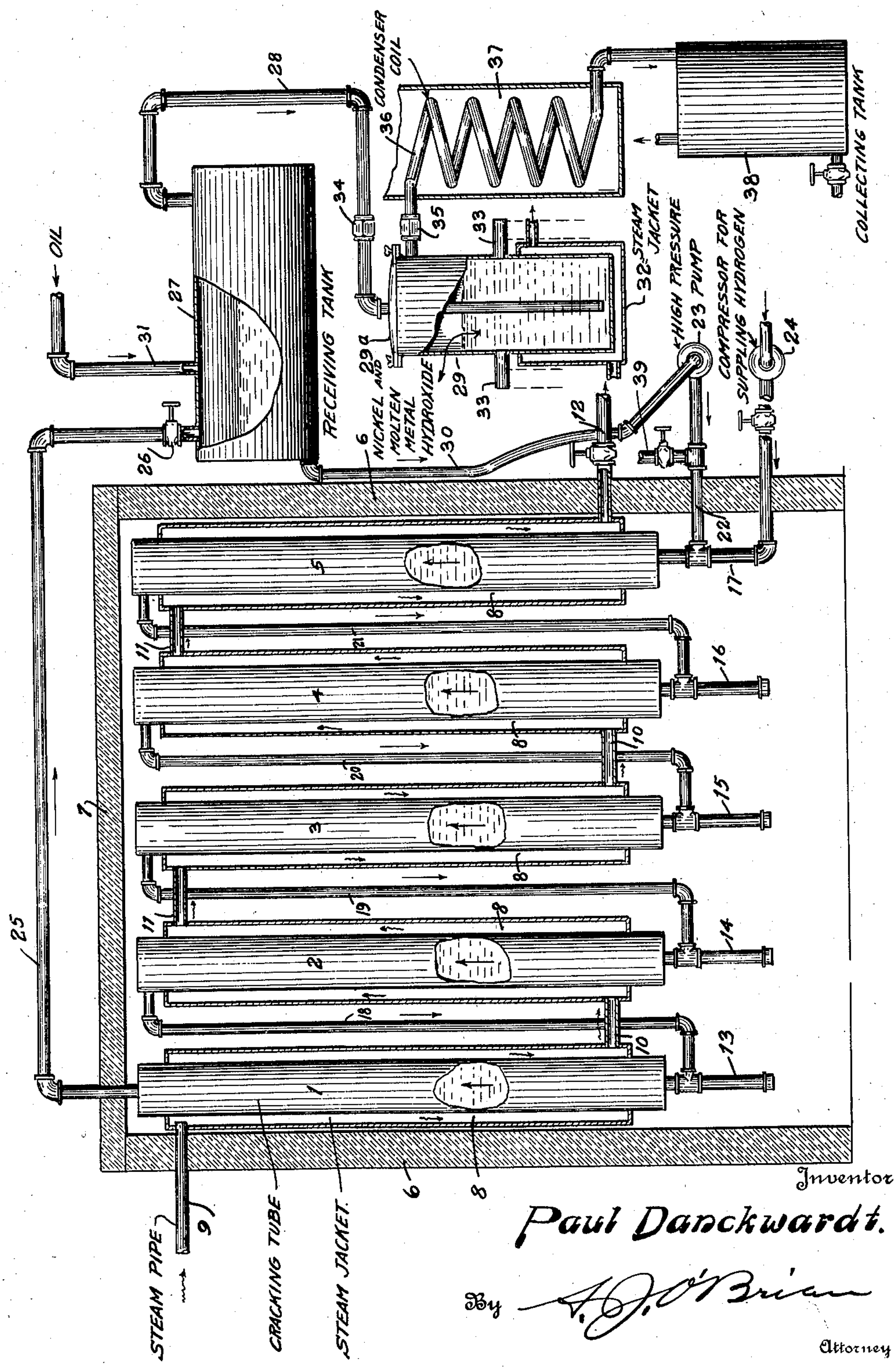

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PROCESS FOR CRACKING OIL.

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It is well known that the products of the cracking processes now employed for the production of gasoline from heavy hydrocarbons have a disagreeable odor and are different in character from gasoline derived from crude oil by distillation carried on at atmospheric pressure.

It is the object of this invention to produce a method whereby a gasoline superior to that obtainable by present cracking methods can be produced.

These improved results are attained by a method in which the cracked vapors and gases are exposed to the action of a nickel catalyzer as they emanate from the cracking still. By this means the unsaturated hydrocarbons and the other ingredients that are responsible for the disagreeable odors and other undesirable qualities, are made to combine with hydrogen, which may be formed from a part of the oil during the cracking process itself, or which may be introduced from an extraneous source. Nickel has long been known as a catalyzer for unsaturated hydrocarbons, but, so far, it has not been employed successfully in a commercial way with mineral oils, for the reason that it soon becomes inactive, a condition referred to by chemists as "poisoned". The inactive or "poisoned" nickel can be revivified, but only by an expensive process, which makes it impracticable.

I obtain my improved results by employing nickel in conjunction with an alkali or alkali earth metal hydroxide, which absorbs the impurities directly from the oil and from the nickel, as will be hereinafter more fully explained.

My process further differs from most other processes of this nature in this, that it employs no direct application of fire to the still and thereby avoids overheating and the consequent production of free carbon.

My process, briefly described, consists in subjecting the oil to a moderate temperature and to high pressures, either with or without the addition of hydrogen, fixed gases or steam from an external source, using as much contact surface as possible for good economy; then bringing the gases and vapors directly into contact with nickel held suspended in molten sodium hydroxide, or first separating the heavier parts of the vapors of distillation by a partial condensation and then passing the remaining light hydrocarbons and the fixed gases through a mixture of molten sodium hydroxide and nickel.

I have found that the effect produced varies somewhat in accordance with which of the above procedures is followed, but not to a great extent. Generally I prefer the second way of working. The temperature of the mixture of nickel and hydroxide must be such that practically no oil can condense while in contact with the molten mass; hence, the vapors that pass through are reacted upon by it, after which they are condensed in water-cooled condensers.

Before describing my process in greater detail, I will now describe the apparatus which I prefer to employ in carrying it out. I may state here, however, that a cracking still such as described and claimed in my copending application (Serial No. 625,697, filed March 17, 1923) or any other of the many pipe stills in common use may be employed.

For the purpose of more clearly describing my invention, I shall have reference to the accompanying drawing, which shows a longitudinal section through the apparatus.

Numerals 1, 2, 3, 4 and 5 designate steel pipes or cracking tubes, which are preferably placed vertically within brick or cement walls 6—6, 7—7. Each cracking tube is surrounded by a jacket 8 of steel tubing. A pipe 9 is connected to the upper end of the jacket surrounding pipe 1 and connects the jacket space with a source of superheated steam. The jackets surrounding pipes 1 and 2 are connected at their lower ends by a pipe 10 and the upper ends of the jackets surrounding pipes 2 and 3 are connected at their upper ends by a pipe 11 and this is continued so that all of the jacket spaces become connected in series. The steam that enters through the pipe 9 flows downwardly through the jacket space about pipe 1 upwardly through the jacket space about pipe 2, etc. and finally leaves the last jacket space through the pipe 12. Extending downwardly from the lower closed ends of the tubes 1 to 5 are pipes 13, 14, 15, 16 and 17 of smaller diameter. These pipes, except pipe 17, have their lower ends closed by caps in the manner shown. Pipes 18, 19, 20 and 21 connect pipes 13, 14, 15 and 16, respectively, with the tops of pipes 2, 3, 4 and 5. A pipe 22 connects the pipe 17 with the high pressure pump 23, while pipe 17 extends to and is connected with the delivery port of the compressor 24 by means of which hydrogen or other gases from an outside source may be supplied if and when desired. From the top of cracking tube 1 a pipe 25, provided with a valve 26, extends to a steel tank 27 which serves as a receiver for all of the oils and vapors coming from the cracking tubes. The tank 27, in addition to serving as a receiver, also serves as a separator. The lighter vapors and gases are carried off through a pipe 28, which connects with and extends into the tank 29, which contains the nickel catalyzer and the hydroxide. The unvaporized oil passes from the tank 27 to the pump 23 through pipe 30. By means of the pump 23 the unvaporized oil that collects in the tank 27 may be forced into and caused to circulate through the cracking tubes in the direction of the arrows. Fresh oil is added to the liquid in tank 27 through a pipe 31. The tank 29, which contains the nickel catalyzer, has its lower end surrounded by a steam jacket 32, which may be connected to the steam supply for heating the contents thereof. In order that the contents of the tank 29 may be dumped, I have provided it with trunnions 33, about which it may be rotated. The tank 29 should be provided with a removable cover 29ᵃ to facilitate the dumping. The pipe 28 and the pipe 36 are provided with couplings or unions 34 and 35, respectively. Pipe 36 forms a condenser coil and is located principally within the tank 37 from which it extends to the collecting tank 38.

In the drawing, I have shown only five cracking tubes, but any number may be used and they may be connected in series as shown or in parallel or in parallel groups of series connected tubes.

The larger the number of tubes, the better will the heat from the superheated steam be utilized and the more quickly will the cracking proceed. It will be noted that the steam in the jacket spaces flows in the opposite direction from the oil in the cracking tubes. This allows the oil to be heated gradually and permits an efficient utilization of the heat. As the temperature to which the oil is raised is low (not over 800° F.) very little carbon is formed and for this reason, cleaning out is seldom required. It may be necessary, however, from time to time to remove the caps at the ends of pipes 13—16 one at a time and blow or wash the tubes out by means of steam, which may be connected at the pipe 39, which branches from the pipe 22. Thermometers and pressure gages may be connected wherever desired, but as this does not involve invention, they have not been shown.

In carrying out my process by means of the above described apparatus, I fill tank 27 about two-thirds (⅔) full of oil and start the pump 23 with valve 26 partly open. Steam, superheated to a temperature of 1000–1100° F., is now turned into the jackets, flowing in through pipe 9 and leaving through pipe 12. The valve in pipe 12 is adjusted so that the steam, just before it leaves the outlet pipe, is under a pressure of 200 pounds per square inch, or more if the process is to be carried out at higher pressures, and at a temperature somewhat above the boiling point of water at that pressure so that no condensation of steam will take place. If these directions are observed the steam escaping from the pipe 12 may be used for other purposes, such as for driving engines or for heating. The pump 23 is operated at such a speed that the oil escaping from the top of the cracking tube 1 will have a temperature of not more than 800° F. Valve 26 is now closed to such an extent that the pressure of the oil within the cracking tubes is somewhere between 400 to 1000 pounds per square inch. The exact pressure to be used must be determined by trial, as it will differ for different grades of oil. In order that none of the pipes shall be subjected to excessive strain, I aim to keep the steam pressure within the jackets about one-half as great as the pressure of the oil within the cracking tubes. In this way the outer walls of the steam jacket are subjected to strains due to the steam pressure alone, while the walls of the cracking tubes are subjected to both an inner and an outer pressure and the strains are therefore due to the difference of these opposing pressures. If the steam pressure is one-half as great as the oil pressure, then the walls of the cracking tubes and of the steam jacket are subjected to the same effective pressures. By this means the danger of rupture is greatly reduced.

During the operation of my process there is a continuous stream of oil, vapor and gas entering the tank 27. After passing the valve 26, the pressure to which the gases and vapors are subjected, is greatly decreased whereby the heavier parts will be separated out. The lighter parts will not condense in the tank 27, but will travel through the pipe 28 into the container 29 where they will be liberated near the bottom and will bubble upwardly through the molten mixture of sodium hydroxide in which the nickel catalyzer, either in the form of powder, wire, or cuttings, is suspended. Before starting the operation the contents of the tank 29 is heated by steam to such a temperature that it will melt. After the gases have started to flow from the tank 27 into tank 29 the sodium hydroxide is kept molten and fluid by heat from the vapors alone.

Sodium hydroxide melts at about 210° C. when perfectly dehydrated and at a lower temperature when it contains some water. I have found that a small amount of water does no harm to the action of the nickel. If, however, the oil contains any carbonic acid or forms it upon decomposition, the hydroxide becomes gradually less fluid as carbonates are formed. When this occurs the charge must finally be dumped and replaced by a new one. The time of usefulness of a charge can be prolonged somewhat by using mechanical stirrers. It is, however, better practice to provide two tanks 29 and connections by means of which the gases may be diverted into the reserve tank whenever the hydroxide in the first tank becomes too hard. This makes it possible to dump and recharge one tank at a time without interrupting the operation.

The hydroxide that has become useless may be regenerated by leaching the charge with water, filtering and treating the filtrate with caustic lime. In this way a solution of fresh sodium hydroxide, is obtained, which, upon evaporation, yields dry hydroxide. When the dry hydroxide thus formed is mixed with nickel and melted down in one of the containers 29 by the application of steam to the heating jacket, the mixture is ready for use.

The reaction, as far as the oil is concerned, which takes place in the catalytic cell or the tank 29 that contains the hydroxide and nickel, consists very probably of a simple addition of hydrogen to the unsaturated hydrocarbons, which have been formed by the heat treatment. This is perhaps accompanied by a regrouping of the molecules of certain parts of the oil. This is indicated by the fact that the amount of light hydrocarbons formed by the catalytic treatment exceeds that formed when the catalyzer is not used, so much that it can hardly be explained by the fact alone that the unsaturates are changed into saturates.

In other processes, using nickel as a catalyzer, it was found that the nickel soon lost its efficacy. In my method it does not. I may explain this on the theory that the molten alkali is continually decomposing the layers of inactive substances formed on the surface of the nickel or that it prevents its formation by absorbing the substances which "poison" the nickel when no hydroxide is used.

The vapors which leave the catalytic cell, pass through the condenser coil 36 where they are condensed and flow thence to the reservoir 38 where the condensate collects as a sweet smelling, clear liquid, practically identical with natural gasoline.

As fast as the liquid in tank 27 is decreasing during the operation of the process, fresh oil is introduced through pipe 31. If this oil contains natural gasoline, the latter will be evaporated by the heat of the oil and vapors in the tank as they come from the cranking tubes. This gasoline will therefore not pass through the cracking tubes where it might be partly destroyed.

Although I have referred specifically to sodium hydroxide, other oxides and hydroxides of the alkali or alkali-earth metals may be used. In case alkali-earth compounds or mixtures of these with compounds of the alkali metals are used, it will be necessary to granulate them or to form balls containing nickel and to pass the vapors through the granules or over the surface of the granules or balls as such mixtures cannot be rendered fluid.

I have also tried to substitute for the nickel other metals such as iron, manganese, copper, zinc and aluminum and have found that some reactions take place which are similar to those that take place with nickel. When the oxides of the other metals were employed, some of them were reduced and acted the same as the metals, others dissolved in the hydroxide, except when calcium hydrate was used, which seemed to form a hard mass with them. Iron and copper and their oxides seem to come nearest to nickel in their catalytic action.

The introduction of hydrogen or hydrogen containing gases during the process, by means of the compressor 24, is not absolutely necessary, as with most oils sufficient hydrogen is formed by the cracking. The use of hydrogen is, however, of considerable advantage when working under high pressure, when it seems to take part in the cracking of the oil and almost entirely prevents the formation of carbon. The same applies to the use of steam, which, when introduced with the oil during the cracking phase, appears to supply hydrogen.

Having now described my invention, what I claim is:

1. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in passing the vapors and gases from a cracking still through a mixture of molten sodium hydroxide and nickel.

2. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in passing the vapors and gases from a cracking still through a mixture of molten alkali metal hydroxide and nickel.

3. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in passing the vapors and gases from a cracking still into intimate contact with a mixture composed of molten sodium hydroxide and nickel.

4. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in submitting the hydrocarbons to a temperature and pressure high enough to cause the hy-

drocarbons to disintegrate partially, bringing the products formed into intimate contact with nickel and molten sodium hydroxide, and condensing the light hydrocarbon vapors.

5. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in cracking the hydrocarbons at a temperature not to exceed 800° F. and under a pressure of 400–1000 pounds per square inch, passing the vapors and gases formed through molten sodium hydroxide in which metallic nickel is suspended, and condensing the vapors.

6. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in cracking the hydrocarbons at a temperature not to exceed 800° F. and under a pressure of 400–1000 pounds per square inch, passing the vapors and gases formed through molten alkali metal hydroxide in which metallic nickel is suspended, and then condensing the vapors.

7. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in cracking the hydrocarbons at a temperature not to exceed 800° F. and under a pressure of 400–1000 pounds per square inch, passing the vapors and gases formed into intimate contact with molten sodium hydroxide in which metallic nickel is suspended, and then condensing the vapors.

8. The process of producing hydrocarbons of low boiling points from hydrocarbons of higher boiling points, which consists in cracking the hydrocarbons at a temperature not to exceed 800° F. and under a pressure of 400–1000 pounds per square inch, introducing hydrogen, passing the vapors and gases formed into intimate contact with molten sodium hydroxide in which metallic nickel is suspended, and then condensing the vapors.

In testimony whereof I affix my signature.

PAUL DANCKWARDT.