Patented Nov. 25, 1924. 1,516,756

# UNITED STATES PATENT OFFICE.

HARRY M. WEBER, OF BLOOMFIELD, NEW JERSEY, ASSIGNOR TO ELLIS-FOSTER COMPANY, OF MONTCLAIR, NEW JERSEY, A CORPORATION OF NEW JERSEY.

## PRODUCING AROMATIC SUBSTANCES FROM PETROLEUM.

No Drawing. Application filed May 12, 1922. Serial No. 560,476.

*To all whom it may concern:*

Be it known that I, HARRY M. WEBER, a citizen of the United States, residing at Bloomfield, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Producing Aromatic Substances from Petroleum, of which the following is a specification.

This invention relates to the cracking of heavy petroleum oil and particularly to the cracking of heavy petroleum oil at selective temperatures for the formation of aromatic hydrocarbons and their separation from the cracked petroleum as more fully described in the following specification.

It is well known that small amounts of aromatic hydrocarbons are formed when heavy petroleum oils are cracked at suitable temperatures but heretofore the separation of the aromatic material from the cracked petroleum oil has been difficult and costly. Also the aromatic products obtained have usually been mixtures of two or more compounds.

In the present invention the aromatic hydrocarbons are not only separated easily from the cracked petroleum oils but the products obtained are of greater value. Furthermore the separation is accomplished without materially reducing the gross value of the petroleum hydrocarbons, inasmuch as the petroleum products obtained, while small in quantity have a greater market value. Furthermore by means of the present invention it is possible to control the production of definite compounds within close limits.

I have found that by subjecting heavy petroleum oils to various cracking heats and by subsequently oxidizing the products of the cracking operation by means of air, oxygen, carbon dioxide or other oxidizing gas in the presence of a catalytic agent that the aromatic compounds are almost exclusively oxidized to aromatic acids, aldehydes, anhydrides, etc., which are easily separated, only a small amount of the petroleum compounds being oxidized to carbon dioxide, carbon monoxide and water.

I have also found that by regulating the temperature at which the oil is cracked that it is possible to obtain the selective formation of aromatic hydrocarbons. The temperatures used for these purposes, namely for the selective production of aromatic hydrocarbons, should preferably be moderate temperatures. That is, by cracking petroleum oil at temperatures ranging between 1000 and 1200° F. that the principal aromatic compound formed is benzol or its homologues which may readily be oxidized to maleic acid in the presence of a suitable catalyst. Also that by maintaining the temperature of the cracking chamber between 1200 and 1400° F. that naphthalene is the aromatic that is principally formed and this substance may readily be oxidized to phthalic acid, anhydride, acid aldehyde and aldehyde. The subsequent recovery of the aromatic acid, aldehyde or anhydride material is comparatively simple and pure products are easily obtained.

Maleic acid being readily soluble in water is recovered in aqueous solution by subjecting the products of the oxidizing reaction to sudden chilling by means of a water-cooled condenser or any other suitable means whereby the water which is formed as a by-product of the reaction and also by the oxidation of some of the members of the paraffin series is condensed. The last traces of the maleic acid or anhydride may be recovered by passing the gases through water scrubbing towers. The maleic acid is subsequently recovered by evaporation of the water and crystallization of the maleic acid present. The crude maleic acid obtained in this manner may be purified by any of the well known methods such as sublimation with the formation of the anhydride. On treatment of the anhydride with water and subsequent crystallization the maleic acid is obtained as a clean crystalline product.

Where phthalic acid or anhydride is the main aromatic product of the reaction this may be recovered by any suitable means such as by cooling the gases as they issue from the oxidizing chamber by means of a water-cooled condenser and in this manner obtaining the phthalic acid along with the water formed in the reaction. The phthalic acid and water is collected in any suitable receptacle. Or by passing the hot vapors as they issue from the oxidizing chamber into a comparatively large, air cooled condensing chamber where the formation of needles of phthalic anhydride takes place. The phthalic anhydride may be almost completely recovered by this means but it is usually advisable to cool the gases thoroughly and sub-

sequently scrub them by means of a dilute solution of caustic soda or soda ash whereby the aromatic product is recovered as sodium phthalate and the acid subsequently liberated by treatment with any suitable mineral acid such as sulphuric acid, phosphoric acid etc. The impure acid or anhydride may then be purified by sublimation, crystallization, etc., or used as such.

As an illustration of method of carrying out the present invention kerosene is cracked at a temperature of 1000° to 1200° F. or 1200 to 1400° F. according to the product desired in an ordinary tube cracking apparatus. The products of the cracking operation are passed through an air-cooled condenser where the less volatile hydrocarbons are condensed. The gaseous and more volatile hydrocarbons are then mixed with two to twenty times their weight of air and passed over a catalyst heated to a suitable temperature by any suitable means where the aromatic hydrocarbons and a small portion of the hydrocarbons of the paraffin series are oxidized. The gases issuing from the catalytic chamber are passed through a water cooled condenser where the water formed by the reaction and most of the maleic acid or phthalic acid formed is condensed and collected in a suitable receptacle. The residual gases are passed through several scrubbing towers where the remainder of the maleic acid or phthalic acid present is washed out.

As the preferred method of carrying out the invention the following examples are given though it is understood that the invention is not limited to these particular methods of operation or the use of the raw material mentioned.

Where maleic acid is the product desired:—Kerosene was passed through a cracking tube maintained at a temperature of 1050° to 1100° F. and the products passed through an air cooled condenser. At this point fifty per cent by volume of the kerosene passed into the cracking tube was recovered. 70 per cent of the recovered oil boiled below 200° C., the remainder boiling between 200° and 280° C. The uncondensed material was then mixed with three and a half to four times its weight of air by means of a Venturi tube and passed over a catalyst consisting of vanadium oxide on pumice. The catalyst was heated by means of a lead bath which was maintained at a temperature of 750° F. The exit gases issued from the catalyst at a temperature of 500° to 600° F. The gases were then passed through a water-cooled condenser where a considerable portion of the maleic acid crystallized out. At this point the water in the gases was also condensed and the volume of water obtained was 12 to 15 per cent of the volume of the kerosene passed into the cracking tube. The gases were then subjected to a water scrubbing process where the remainder of the maleic acid was removed. The yield of maleic acid obtained in this manner was 4.3 per cent by weight of the kerosene passed into the cracking tube.

As the preferred method of carrying out the invention when phthalic acid or anhydride is the desired product the following is cited:—Kerosene was passed into a cracking tube maintained at a temperature of 1250°–1300° F. The products of the cracking operation passed through an air cooled condenser where 61 per cent by volume of the kerosene passed into the cracking tube was recovered. 50 per cent of the recovered oil boiled below 200° C., the remainder boiling between 200° and 270° C. The uncondensed portion of the products of the cracking operation were mixed with four and a half to five times its weight of air by means of a Venturi tube and passed over a catalyst consisting of vanadium oxide on pumice which was heated by means of a lead bath. The lead bath was maintained at a temperature of 750° to 795° F. and the gases issuing from the catalyst were at a temperature of 550° to 650° F. The products of the oxidizing reaction were passed into an air cooled condensing chamber where a considerable portion of the phthalic anhydride formed crystallized on the walls of the chamber. The remainder of the phthalic acid or anhydride in the gases was recovered by passing the warm gases through a water-cooled condenser where a concentrated solution of phthalic acid was obtained. The residual phthalic acid or anhydride was recovered by scrubbing the gases with a ten per cent sodium carbonate solution. The yield of phthalic acid obtained by this process was 2.3 per cent by weight of the total kerosene passed.

Crude oils from any source or any fraction of crude oils such as gas oil, varnish maker's and painter's naphtha, Burton still stock, etc., may be used as the raw material in carrying out the present invention. Variation of the conditions such as temperature of the cracking tube, temperature of the catalytic mass, volume of air mixed with the vapors etc. are also necessary depending upon the raw material used for carrying out the process except within the limits as outlined and also upon the products desired.

By the term "moderate temperatures" as used in the claims, temperatures such as 1000–1200 degrees F. or 1200–1400 degrees F. which enable the selective control of the hydrocarbons produced by this process, are intended to be covered.

What I claim is:

1. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at moderate

temperatures and subjecting substantially all of the cracked material to oxidizing conditions.

2. The process of producing valuable products from petroleum oil which comprises cracking petroleum oil at moderate temperatures and subsequently subjecting substantially all of the cracked material to oxidizing conditions including a gaseous oxidizing agent in the presence of a catalyst.

3. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at temperatures of 1000 degrees F. to 1400 degrees F. and subjecting substantially all of the resulting cracked products to oxidizing conditions.

4. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at temperatures of 1000 to 1200 degrees F. and subjecting substantially all of the resulting cracked products to oxidizing conditions.

5. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at temperatures of 1000 to 1200 degrees F. and oxidizing the resulting cracked products to form maleic acid.

6. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at moderate temperatures to form aromatic hydrocarbons and then subjecting substantially all of the aromatic hydrocarbons to oxidizing conditions.

7. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at temperatures of 1000 to 1200 degrees F. to form aromatic hydrocarbons containing benzol, and then subjecting substantially all of the aromatic hydrocarbons to oxidizing conditions.

8. The process of producing valuable products from petroleum oils which comprises cracking petroleum oils at temperatures to form aromatic hydrocarbons containing naphthalene, and then oxidizing the aromatic hydrocarbons to form phthalic acid or anhydride.

9. In a process of separating aromatic hydrocarbons from cracked petroleum oil, the step which comprises subjecting substantially all of the aromatic hydrocarbons to oxidizing conditions.

10. In a process of separating aromatic hydrocarbons containing naphthalene from cracked petroleum oil, the step which comprises oxidizing said aromatic hydrocarbons to form products containing phthalic acid or anhydride.

11. In a process of separating aromatic hydrocarbons from cracked petroleum oil containing the same, the step which comprises oxidizing said aromatic hydrocarbons to form products containing acids, anhydrides, aldehydes, and aldehyde acids.

12. In a process of separating aromatic hydrocarbons containing benzol from cracked petroleum, the step which comprises oxidizing the aromatic hydrocarbons to products containing maleic acid.

13. The process of selectively producing aromatic hydrocarbons which comprises moderately cracking petroleum oils.

14. The process of selectively producing aromatic hydrocarbons which comprises cracking petroleum oils at moderate temperatures.

15. The process of selectively producing aromatic hydrocarbons containing benzol which comprises cracking petroleum oils at moderate temperatures to produce aromatic hydrocarbons containing benzol.

16. The process of selectively producing aromatic hydrocarbons containing naphthalene which comprises cracking petroleum oils at moderate temperatures to produce aromatic hydrocarbons containing naphthalene.

17. The process of converting petroleum oils into hydrocarbons such as gasoline and useful products of oxidation which comprises the steps of cracking petroleum, separating heavier portions from the products of cracking and subjecting the remainder to catalytic oxidation to substantially convert aromatic hydrocarbons into organic acids while leaving the aliphatic hydrocarbons substantially unchanged.

18. In the process of cracking petroleum oils the steps of bringing oxygen into contact with cracked products in the presence of a heated catalyst to oxidize aromatic hydrocarbons to useful products of oxidation of a readily separable character and to leave aliphatic hydrocarbons substantially unchanged.

19. In the process of making oxidized products from cracked petroleum oils, the steps which comprise cracking oils to produce mixtures containing aliphatic and aromatic hydrocarbons, and oxidizing the cracked products in the presence of a heated catalyst to oxidize the aromatic hydrocarbons and leave the aliphatic hydrocarbons substantially unchanged, the temperature of the cracking operation being variable to allow the production of different types of oxidized products.

HARRY M. WEBER.