

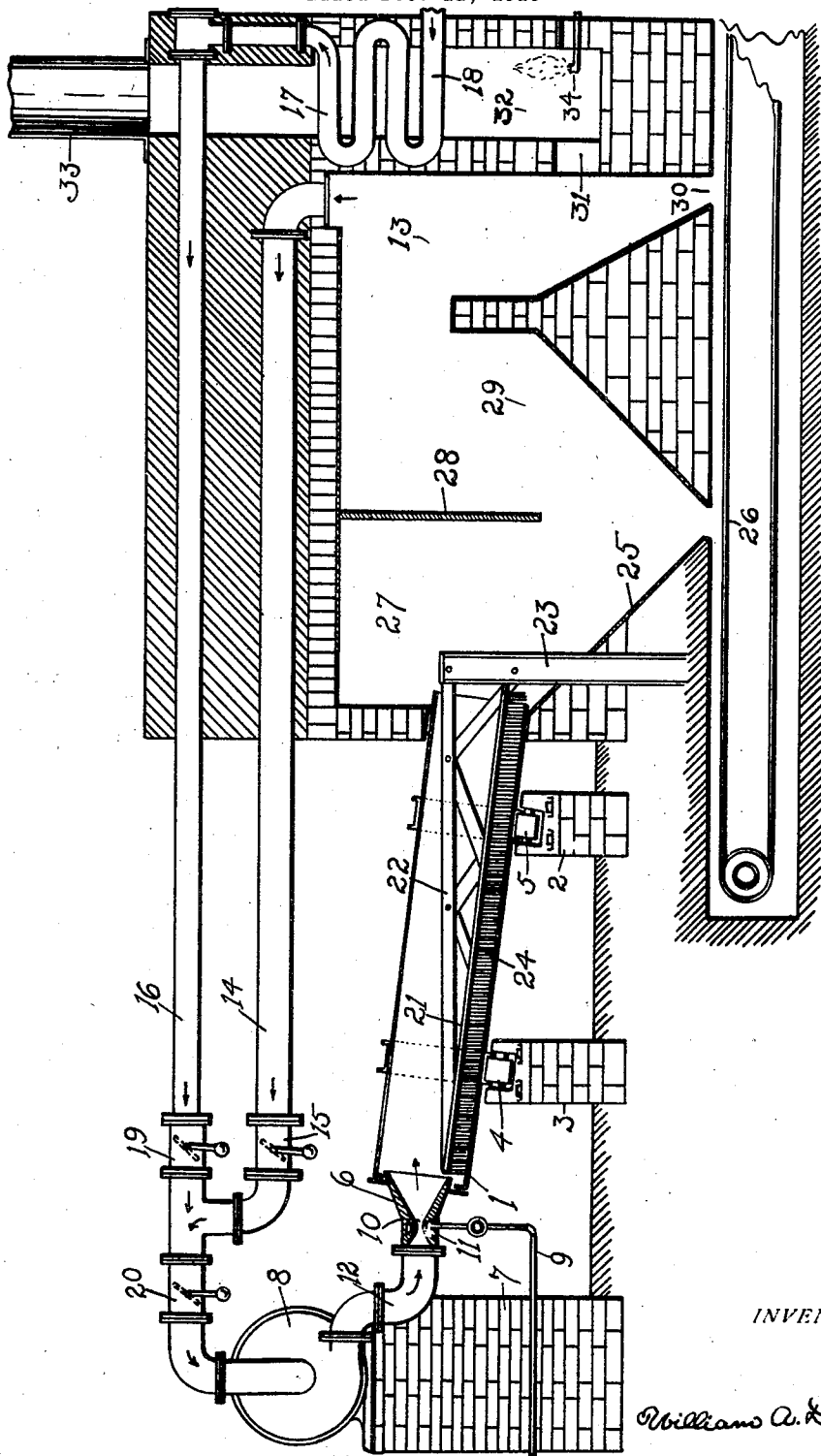
Mar. 13, 1923.

W. A. DARRAH

1,448,655

METHOD OF SELECTIVE OXIDATION AND APPARATUS THEREFOR

Filed Dec. 11, 1919



INVENTOR.

William A. Darrah.

UNITED STATES PATENT OFFICE.

WILLIAM AUSTIN DARRAH, OF CHICAGO, ILLINOIS.

METHOD OF SELECTIVE OXIDATION AND APPARATUS THEREFOR.

Application filed December 11, 1919. Serial No. 344,224.

To all whom it may concern:

Be it known that I, WILLIAM AUSTIN DARRAH, a citizen of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a certain new and useful Improvement in Methods of Selective Oxidation and Apparatus Therefor, of which the following is a full, clear, concise, and exact description, reference being had to the accompanying drawings, forming a part of this specification.

This invention relates to methods of partially oxidizing various compounds with a view of producing new materials from various raw materials. This invention is particularly adapted for treating oils, paraffins, methane and similar substances, although it should not be limited to these particular materials.

In the case of fuel oil this invention is particularly adapted to the production of a high grade of lamp black by consuming only a portion of the carbon contents of the oil.

The method here described offers numerous advantages, as will appear in the subsequent description. In producing lamp black from fuel oil or tar residues, it makes possible the efficient transformation of a low grade material into a high quality of lamp black. By this method the losses by oxidation are much smaller than by other methods and practically no labor is required, the process being substantially automatic. Further, the margins of operation are large and it is easy to control the nature of the final product, as will be set forth in the succeeding description. Other advantages of this process will appear in the following specifications.

The description of this method will be confined specifically for purposes of illustration, to the production of lamp black, but it should be understood that this invention is not limited to this field alone, as it is possible to make such products as aldehydes, acetones, alcohols, and other partial oxidation products, without exceeding the scope of this invention, and with relatively little modification in the apparatus.

It is a well known fact that to produce a grade of lamp black or carbon black which will command a high price in the trade, it is necessary that it conform to certain rigid specifications. It is usually required that

the ash content shall be less than 1%, while certain consumers insist on an ash content of less than 0.1%. A good lamp black must be relatively free from oils, tars, or similar materials, which are removed by solution with acetone. The subdivision must be very great. In order to make a product suitable for the ink and rubber trade, it has so far been found necessary to limit consumption to lamp blacks, the ultimate particles of which have a diameter less than one micron. It has also been found necessary to restrict consumption in the rubber and ink trade to a lamp black having the maximum number of fine particles and the minimum number of aggregations of particles. In the case of good grades of carbon black the size of the aggregations averages about 100 microns.

From the above brief description it will be evident that the production of a high grade of lamp black is a matter requiring careful attention, and not an easy end to obtain without the proper apparatus. In addition to the above noted physical characteristics, the color of the black is of considerable importance, many lamp blacks suffering a material reduction in selling price because of the brownish tinge which they display on careful examination.

It has been found impossible to produce a high grade of lamp black or carbon black by grinding any known form of solid carbon. A consideration of the extreme fineness of particles will make the basis of this limitation evident. It has in all cases been found necessary to produce lamp black or carbon black by precipitation of the solid carbon from gases. Precipitation has been accomplished satisfactorily in commercial quantities both by allowing the carbon containing gases to come into contact with a relatively cool solid body, or by cooling the gases by expansion, or other means.

In the case of fuel oil, approximate analysis indicates that it contains about 84% carbon, 15% hydrogen, and a balance of 1% distributed among such gases as oxygen, nitrogen, etc. In the case of natural gas the carbon content is around 70%, the balance being hydrogen, nitrogen and oxygen.

I have found that by mixing the vapor of fuel oil or natural gas with an excess of the products of combustion of the fuel oil or natural gas, and with an amount of

air only sufficient to consume the hydrogen content of the oil or gas, it is possible to produce a high grade of black with an efficiency of recovery hitherto impossible.

5 It appears from my investigations that merely restricting the amount of oxygen is not wholly successful, as other diluting gases materially assist in the production of a high grade of black.

10 In order to obtain the greatest efficiency in the recovery of the carbon content of the raw material, it is preferable that the diluting gases be as largely as practical carbon monoxide and carbon dioxide. It is not ab-

15 solutely essential for the carrying out of this process that such be the case, as a high grade of black may be secured when the diluting gas is wholly nitrogen. A practical

20 means of securing a commercially satisfactory diluting gas, consists in drawing products from the flues, as shown in the drawing, and mixing said combustion products with the incoming air. Another means of ac-

25 complishing the same result would be to pass the incoming air over a glowing bed of coal, charcoal, coke, etc., producing the equivalent of producer gas. It is not essential that the exact amount of oxygen be limited to that quantity theo-

30 retically required to consume the hydrogen present. While probably this would be the theoretical amount, I have found that 50% to 75% more oxygen produces a higher grade of black, although it results in a somewhat lower carbon recovery. For practical conditions, I have found

35 that the total amount of gas necessary should be approximately equal to the total amount of air which would ordinarily be required to give complete combustion to the oil or gas used. In other words, approxi-

40 mately 1500 cu. ft. of gas (total inert gases and air) is a commercially satisfactory quantity for the consumption of one gallon of fuel oil. It should be understood that I do not wish to be restricted to this figure, as I have found wide variations possible without seriously influencing the quality of the prod-

45 uct. The particular design of apparatus undoubtedly has a very important bearing on the quantity of gases employed in the partial oxidation process. Too little diluting gases results in a black containing large quantities of oily matter, some grit, and having a brownish shade. In the case of natural gas an equivalent amount of total gases (8000 cu. ft. per 1000 cu. ft. of natu-

50 ral gas) gives satisfactory results. I have found that best results are secured when the above mentioned 1500 cu. ft. of gases are divided in the ratio of about one part air and two parts flue gases. This ratio is also subject to considerable variation

55 without seriously affecting the results pro-

duced. As a general rule, it is possible to use less diluting gases in the case of natural gas than in the case where fuel oil is employed.

In the case of fuel oil it is desirable to have the air and diluting gases both heated to a temperature ranging from 700° F. to 800° F. Similar treatment in the case of natural gas produces excellent results but it is possible to secure satisfactory results with somewhat lower gas temperatures in case natural gas is employed.

In case it is desired to precipitate the carbon upon a cold surface, as shown in the attached drawing, the best results are usually obtained when the temperature of the surface is approximately 300° F.

It will be evident that the temperature of the precipitating surface can readily be controlled in the case of the apparatus shown in the attached drawing, by regulating the amount of fuel which is consumed in a given period. Since the radiation from the precipitating surface is approximately a constant quantity, the consumption of fuel will control its temperature.

Referring to the drawing, Figure 1 indicates a sectional elevation through one form of apparatus designed to carry out the process of this invention. It should be understood that Figure 1 is purely schematic, being intended for purposes of illustration only, many obvious modifications being required to conform to local practical conditions.

In the drawing (1) refers to a rotating cylinder or drum mounted upon supports (2) and (3) in such manner that it can revolve upon rollers (4) and (5). Rotation may be produced by any convenient mechanical driving means.

A venturi shaped burner (6) is mounted upon a stationary support (7) which also carries blower (8). A pipe (9) serves to bring natural gas or fuel oil (or other fuel) to burner (6).

Burner (6) is provided with a narrow throat (10) surrounded by a channel of torous form through which the fuel is introduced into the burner (6), by way of port (11).

Burner (6) is connected to blower (8) by pipe (12). The blower is connected to the flue passage (13) by pipe (14) in which is inserted butterfly valve (15). Pipe (16) connects blower (8) with air heater (17) which secures outside air through inlet (18). Butterfly valve (19) regulates the flow of air thru pipe (16).

A butterfly valve (20) is inserted between blower (8) and the union of pipes (14) and (16) in order that the total amount of gas delivered to burner (6) may be under control.

Rotating cylinder (1), which may well be

made of metal, is provided internally with an arm (21) supported by bracket (22) mounted upon upright channel (23). A series of carbon removing devices (24) is fastened to bracket (21) and serves to remove the deposit of carbon as the drum rotates. The said carbon removing devices may be in the form of wire brushes, chains, or other equivalent means. I may even fasten a series of chains longitudinally to the inner surface of rotating cylinder (1) and by providing sufficient looseness in said chains, cause them to brush the carbon deposit from the walls of the drum as the device is rotated. Many other equivalent means will be apparent.

Drum (1) is shown slightly inclined in order that as the carbon is brushed from the surface by rotation it will slide down toward the lower end of the drum and be directed by inclined surface (25) to conveyor (26) which serves to carry it to the storage bin or any other desired point.

The warm gases leaving drum (1) usually carry appreciable amounts of carbon in suspension. These gases on entering chamber (27) are materially decreased in speed, with the result that a portion of the carbon falls to the bottom of chamber (27) and passes on to conveyor.

The waste gases pass from chamber (27) around deflector (28) to chamber (29) and thence to flue (13). It has been my experience that some portions of carbon will deposit on the walls of chamber (29) and flue (13) so that provision has been made by outlet (30) to allow this material to pass to conveyor (26).

Flue gases then continue through port (31) into the base of chimney (32) from which they circulate over air heaters (17) and finally pass up stack (33). An auxiliary burner (34) is provided in the base of stack (32) in order to insure that the temperature of the incoming air in heaters (17) shall be sufficiently high.

The operation of this device will be evident from the construction described above and the description given in this specification. Operation may be briefly outlined as follows:

The mixture of heated flue gases and air is forced by blower (8) through venturi throat (10). The rapid increase in velocity caused by the contraction of the throat creates a materially reduced pressure at that point. The entering oil or gas to be carbonized, is preheated by circulating through torous (7), and on entering the rapidly moving gas current immediately flashes into a true vapor due both to the reduced pressure, the increased temperature, and the large amount of diluting gases.

It will be noted from this description that a mixture of vaporized oil, diluting gases,

and insufficient air for complete combustion, are very thoroughly mixed and superheated. Under these conditions the mixture will immediately undergo carbonization as soon as the speed is reduced. The result is a yellow, carbon-depositing flame in drum (1). This flame on coming into contact with the relatively cool metal surface, deposits the greater portion of its carbon at this place, and by maintaining the temperature of this surface at the proper value, the carbon thus formed is of a dense black variety, quite free from materials soluble in acetone and free from grit.

By using this process it is possible in the case of natural gas to obtain a far higher recovery than by any of the commercial methods now employed. When properly controlled, the quality of the material is equal to the best carbon black.

It will be obvious that many of the mechanical arrangements here described may be substituted by other mechanical devices without departing from the method which forms the basis of this invention. The devices shown, however, represent one arrangement which has proven satisfactory in practice.

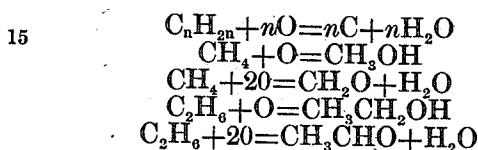
In order to clearly set forth the basis of this invention, it should be pointed out that the function of the diluting or inert gases is at least two-fold. In other words, by providing a large body of gases whose temperature must be raised before the temperature of the flame can reach high values, I am providing a means of controlling the maximum flame temperature. It is a well known fact that high temperatures have a decided tendency to cause grit or adamantite carbon which is very undesirable in either lamp black or carbon black. The presence of the diluting gases make the formation of this undesirable product impossible. The diluting gases also serve to prevent the oxidation of the carbon when the said diluting gases contain large quantities of the oxides of carbon. The effect in this case will be evident from a consideration of the fundamental principles of the mass action law, on the principle that the accumulation of the products of any reversible reaction tends to prevent the progress of the said reaction. The presence, therefore, of the oxides of carbon tends to reduce the oxidation of the carbon of the hydrocarbon, and tends to increase the oxidation of the hydrogen content of the hydrocarbon.

The diluting gases also materially assist in the thorough vaporization of the hydrocarbon and reduce the possibility of any subsequent condensation of the hydrocarbon. The effect of this action is to cause the resultant carbon deposit to be relatively free from oils or other soluble materials.

One advantage of the diluting gases re-

sults from the fact that by controlling the temperature it is possible to keep the flame temperature at such a value that the water vapor formed by the reaction does not attack the carbon set free. It is a well known fact that at elevated temperatures water vapor will oxidize carbon with a formation of carbon monoxide (some carbon dioxide) and the liberation of hydrogen.

The following equations will exemplify the class of reactions which it is possible to carry out by the method which forms the basis of this invention:



It will be understood that any or all of the above re-actions may take place with the formation of carbon monoxide and hydrogen, as outlined above, and that under such conditions the valuable products of the reaction would be the gases which would be collected from stack (33) in any suitable manner. Obviously, these gases may be used for fuel purposes, if so desired.

While the above description has been confined largely to the specific term "oxidation" it should be kept in mind that the term "oxidation" or combination is not restricted to the addition of oxygen to various compounds but may be applied with equal correctness to the addition of chlorine, sulphur, sulphuric acid, nitric acid, or any other radicles. The basis of this invention therefore, should not be restricted to oxygen compounds alone.

It will be understood that the combination of chlorine, sulphur radicals, or similar substances may be substituted in place of oxygen and similar equipment may be used.

Having now fully described my invention, what I claim as new and wish to secure by Letters Patent is as follows:—

I claim:

1. The method of partially oxidizing substances, which consists in vaporizing the substance to be oxidized, mixing the vapor thus produced with preheated diluting gases and insufficient air for complete burning said mixture combustion, and collecting the products of the reaction.

2. The method of partially oxidizing substances which consists in mixing the substance to be oxidized in gaseous form with preheated diluting gases and heated air, burning said mixture in a closed chamber and collecting the products of the reaction.

3. The method of selectively oxidizing substances by mixing the said substance in gaseous form with a small amount of oxygen and a quantity of the oxidized product of the constituent of said compound

which it is desired to protect and burning said mixture.

4. The method of oxidizing hydrocarbons which consists in mixing said hydrocarbon in gaseous form with a heated mixture of an oxide of carbon and insufficient oxygen for complete combustion, and controlling the temperature of the reaction by the quantity and temperature of the added gases.

5. The method of separating carbon from hydrocarbons by mixing the said hydrocarbon in gaseous form with heated diluting gases and insufficient heated oxygen for complete combustion of the hydrocarbon and finally collecting the solid carbon formed by the reaction upon surfaces which are cooler than the flame.

6. The method of separating carbon from hydrocarbons by mixing said hydrocarbon in gaseous form with heated products of combustion and insufficient heated air for complete combustion, causing said combustion to take place in a closed chamber and collecting the products of the reaction, on a cooling surface.

7. The method of producing lampblack which consists in adding to a hydrocarbon in gaseous form insufficient heated air for complete combustion said heated air being previously mixed with heated flue gases, and collecting the resulting carbon on a cooling surface.

8. The method of producing lampblack which consists in heating a hydrocarbon, adding said heated hydrocarbon to a stream of heated flue gases and air under reduced pressure, and collecting the resulting carbon.

9. As a product of manufacture, a form of carbon precipitated from a hydrocarbon by heating to a controlled temperature a mixture of said hydrocarbon, heated flue gases, and insufficient oxygen for complete combustion.

10. The method of oxidizing a hydrocarbon which consists in mixing said hydrocarbon in gaseous form with insufficient oxygen for complete combustion and controlling the temperature of the reaction.

11. The method of oxidizing a hydrocarbon in gaseous form with insufficient oxygen for complete combustion, and controlling the temperature of the reaction by adding a given amount of diluting gases at a controlled temperature.

12. The method of oxidizing a hydrocarbon in gaseous form with insufficient oxygen for complete combustion, and controlling the temperature of the reaction by adding a controlled amount of diluting gases at a controlled temperature, said diluting gases containing some of the products of said oxidation.

13. An apparatus for producing lamp black, consisting of a gas mixing device, a combustion chamber in which hydrocarbons

may be added to gas mixed in said gas mixing device, an enclosed surface for collecting the resultant carbon, and a duct for removing the products of combustion.

5 14. An apparatus for producing carbon, consisting of a gas mixing device, a combustion chamber in which hydrocarbons may be added to gas mixed in said gas mixing device, an enclosed surface for collecting the
10 resultant carbon, means for removing said carbon from the device, and a duct for removing the products of combustion.

15 15. The method of partially oxidizing hydrocarbons, which consists in introducing the substance to be partially oxidized, into a rapidly moving current of preheated gases containing insufficient oxygen for complete combustion, the pressure of the gases being lower at the point of introduction of the
20 hydrocarbon than at any other point in the system.

16. The process of partially oxidizing

hydrocarbons, which consists in introducing the hydrocarbon to be partially oxidized, into a moving stream of heated products of combustion and air under reduced pressure. 25

17. The process of partially oxidizing hydrocarbons, which consists in introducing the material to be partially oxidized, into a moving stream of heated products of combustion and air, said heated products being expanded to occupy a materially greater volume than under atmospheric conditions of pressure and temperature. 30

18. The process of partially oxidizing hydrocarbons, which consists in introducing the hydrocarbon to be partially oxidized, into a moving stream of expanded products of combustion and air. 35

In witness whereof, I hereunto subscribe my name this fourth day of December, A. D. 40 1919.

WILLIAM AUSTIN DARRAH.