Aug. 12, 1941. A. H. BATCHELDER 2,252,111

METHOD OF MANUFACTURING ASPHALTS

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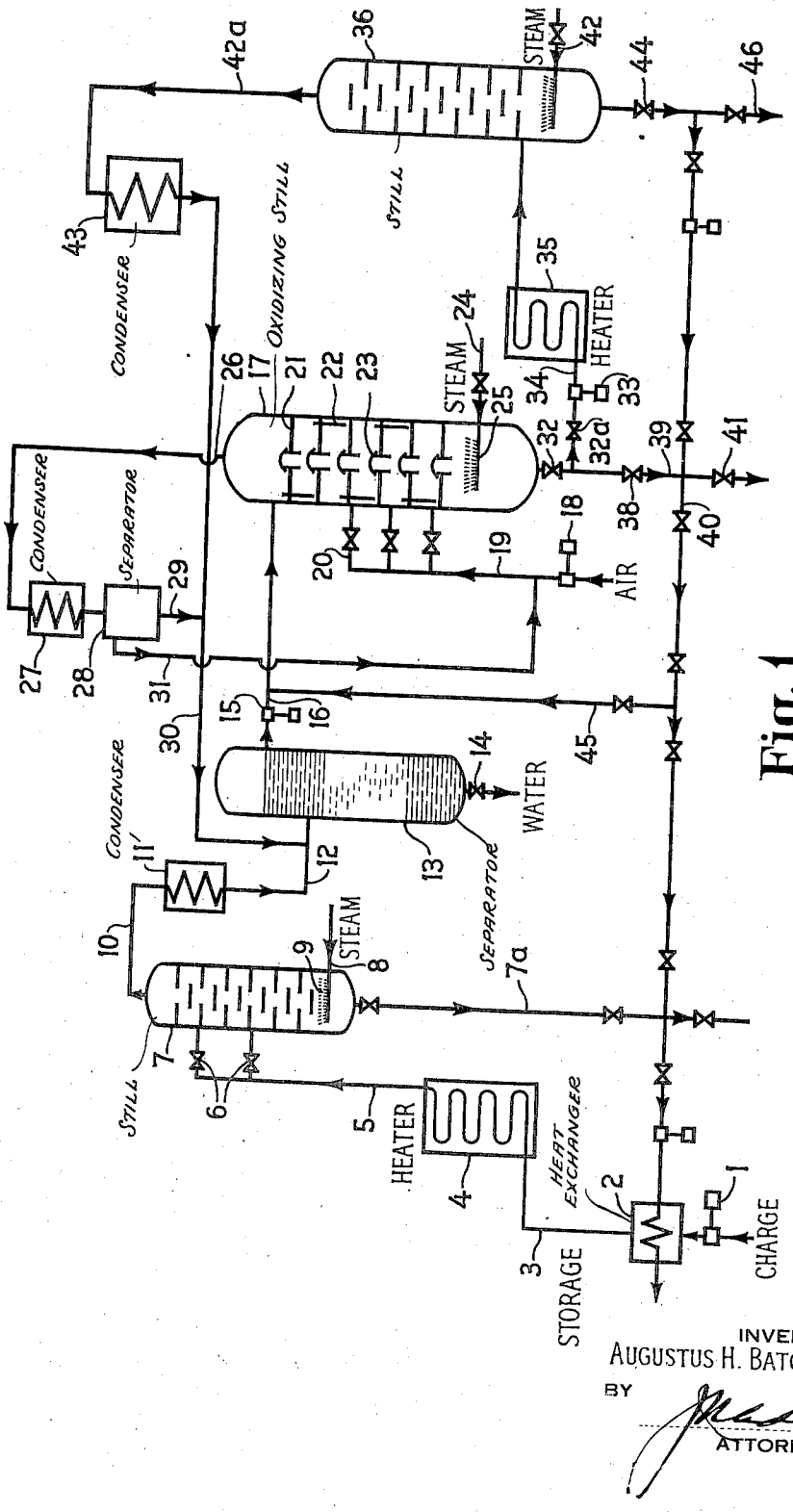


Fig. 1

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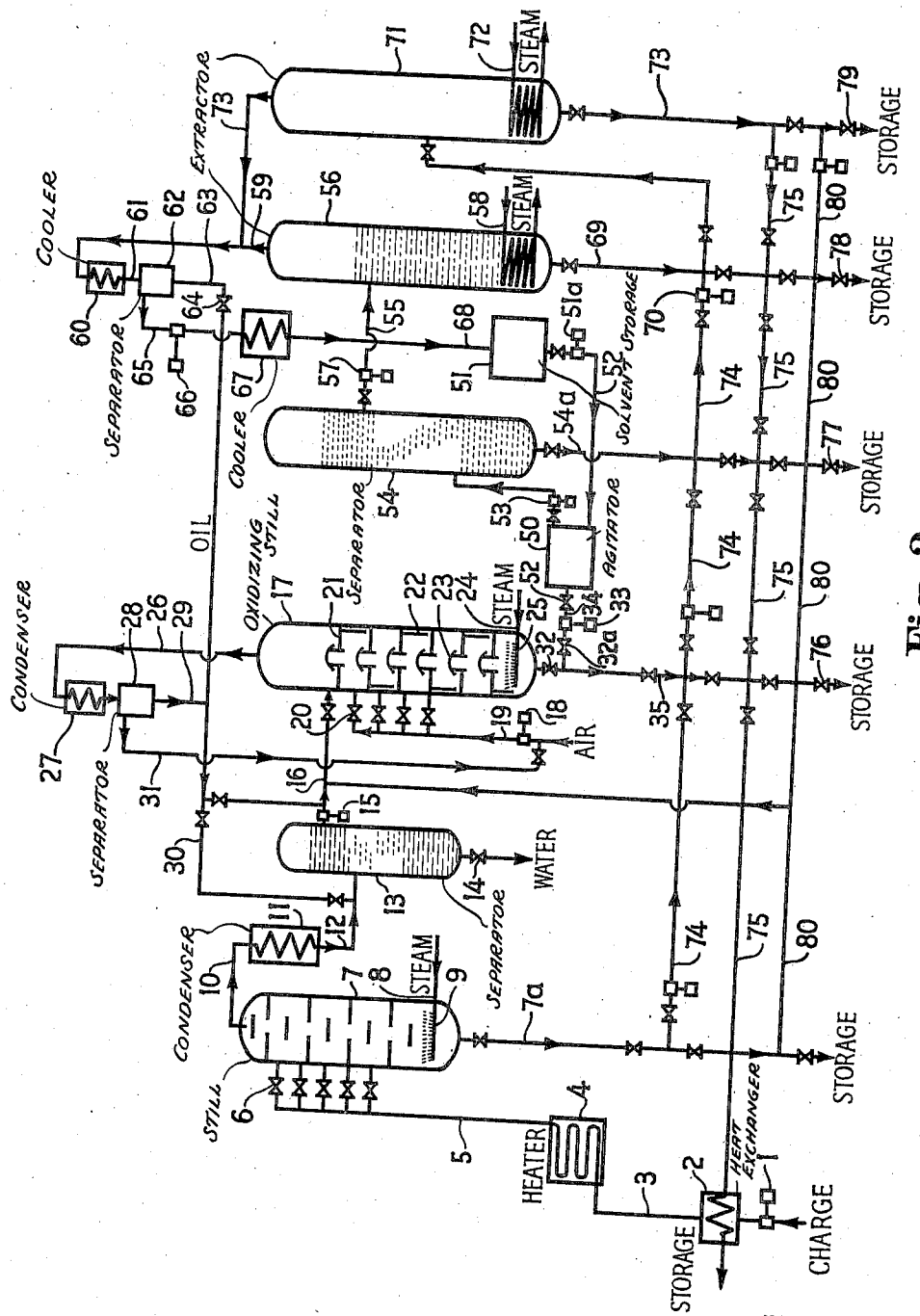


Fig. 2

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2,252,111

METHOD OF MANUFACTURING ASPHALTS

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7 Claims. (Cl. 196—74)

This invention relates to improvements in the manufacture of asphalts.

In general, production of asphalt from petroleum oils is accomplished either by steam distillation of semi-asphaltic or asphaltic petroleums or by air-blowing oils. Each method has its advantages and disadvantages.

The production of asphalt by steam refining, in order to avoid excessive decomposition and cracking of the hydrocarbons, is usually confined to temperatures not exceeding 750° to 800° F. In steam refined asphalts the oily constituents, resins, and asphaltenes are present in substantially the proportions in which they occurred in the crudes. Most of the common asphalts made by this process are deficient in asphaltenes and rich in oily constituents and asphaltic resins.

The air-blowing of oils for production of asphalt has the opposite effect. Air-blowing is effective for the production of asphaltenes, but such asphaltenes are produced at the expense of the highly desirable asphaltic resins and heavy oils. In general, when hydrocarbon oils are air-blown the constituents are converted first into heavier oils, then to asphaltic resins and finally into asphaltenes. However, in any air-blowing process the three stages are occurring simultaneously; the asphaltic resins are being converted into asphaltenes, the heavy oils into asphaltic resins, and the lighter oils into heavier oils. The three steps cannot be isolated.

The characteristics of steam refined and air-blown asphalts are due, respectively, to a considerable extent to the above described inherent limitations in method of manufacture. Asphaltenes tend to impart hardness and also a high softening point for a given penetration. Asphaltic resins have the effect of imparting ductility and raising the breaking point of asphalt, as well as increasing or prompting the compatibility of oil and asphaltenes.

It is an object of this invention to provide a method of manufacturing asphalt from any given asphaltic or semi-asphaltic oil whereby the percentages of heavy oils, asphaltic resins and asphaltenes of the finished product can be readily controlled.

It is a further object of this invention to produce from any asphaltic or semi-asphaltic oil an asphalt similar to a natural asphalt such as Gilsonite, with and without adding to such asphaltic or semi-asphaltic oil any oil other than that obtainable from such oil.

It is a further object of this invention to provide a method of preparing asphalt from asphaltic or semi-asphaltic oil whereby the asphaltic resins and heavy oils in such asphaltic or semi-asphaltic oil are not converted into asphaltenes but remain as heavy oil and asphaltic resins, while the remainder of such asphaltic or semi-asphaltic oil may be converted into asphaltenes and asphaltic resins. By asphaltic oil, as the term is used herein, is meant not only oil which is asphaltic in its crude state, but also oil which has been made asphaltic by treatment.

It is a further object of this invention to provide a method for the production of asphalt with any desired proportion of oil, asphaltenes, and resins from asphaltic or semi-asphaltic petroleum and residua, tar, distillate or distillable natural or synthetic hydrocarbon oils, waxes, and from residua deficient in, or free from, asphaltenes or resins. It is further contemplated that this process can as well be applied to hydrocarbons or hydrocarbon derivatives which have been modified chemically or physically as by chlorination, oxidation, cracking, or the like. It is evident, too, that the process can be advantageously applied to mixtures of one or more of the above asphaltic or semi-asphaltic residua. It will frequently be expedient to use as charging stock a blend of a relatively paraffinic distillate or residuum either low in or free from asphalt, with asphaltic residuum.

The invention will be understood by reference to the accompanying drawings which show diagrammatically two methods of carrying out this invention.

In Figure 1 the charge, of the nature described above, is passed, by pump 1, through heat exchanger 2, through line 3 to heater 4, whence it passes through line 5 and valves 6 into still 7. In still 7 the charge is topped of that portion of its oily constituents which are desired to be separately oxidized. While the method of topping shown in Figure 1 is by steam, the topping may, of course, be accomplished by subjecting the charge to a partial vacuum or by both steam and vacuum. The temperature in still 7 is as low as is consistent with continuous operation. While continuous operation is deemed preferable, this invention may be practiced by batch operations also. The steam passes into the still through line 8 and is mixed with the charge through steam outlets 9. The extent of such topping will depend on the nature of the charging stock and the nature of the asphalt desired to be manufactured. Anyone familiar with the art of manufacturing asphalts, desiring to practice this invention, will know the necessary ex-

tent of such topping in relation to charging stock and desired product. The overhead passes through line 10 into condenser 11 and from the condenser through line 12 into oil and water separator 13. The water is drawn off through valve 14 and the oil is pumped by means of pump 15 through line 16 into oxidizing still 17 near the top thereof. All of such overhead oil may be passed to oxidizing still 17, or only a portion thereof, such overhead oil having, if so desired, first been treated for extraction and treatment of desirable or undesirable components.

As the oil passes down through oxidizing still 17 it is intimately mixed with air or other oxidizing gas which is pumped by means of pump 18 through line 19 and conduits 20. Oxidizing still 17 comprises a column containing a series of plates 21 and down-flow pipes 22 and bubble caps 23. The heated stream of oil gradually descends through still 17 by gravity, and forms a separate pool of liquid on every tray 21 before overflowing into the down-flow pipes 22. The oxidizing gas rises within still 17, through bubble caps 23, in counterflow to the liquefied overhead. Still 17 is shown to be equipped at the bottom thereof with means for the injection of steam through line 24 and steam vents 25. The steam entering through line 24 first passes through the oxidized material which will have accumulated at the bottom of still 17 and will then pass up the still in counterflow to the descending oil. The use of the steam in conjunction with the oxidizing gases has the advantage of reducing the oxidized asphalt accumulating at the bottom of the still and in further removing undesired higher boiling components. Of course, if it is desired, the oxidizing gas pumped through line 19 may be mixed with other gases such as chlorine to hasten the process of oxidation. The air-blowing is usually accomplished at from 400 to 600° F. at the rate of about 30 to 60 cubic feet of air per minute per ton of asphalt, depending upon the nature of the material being oxidized. The length of blowing time varies from 9 to 18 hours usually, also depending upon the type of material. The charge undergoing oxidation may vary in volatility from a light gas oil to a high flash distillate. Since the purpose of the air-blowing is the conversion of the overhead from still 7 into asphaltenes and asphaltic resins, it will be apparent that the step of air-blowing will vary with the overhead.

In the practice of this method a large percentage of the asphaltenes, asphaltic resins and some heavy oils in the charging stock which emerge from heater 4 will have remained at the bottom of still 7 whence they are withdrawn through line 7a. Hence the desirable asphaltic resins and heavy oils contained in the charging stock are not lost by being converted into asphaltenes, as is usually the case in the production of air-blown asphalts. The air-blowing which occurs in the oxidizing still 17 will be continued longer and be more extensive than would be necessary had the charging stock passing through heater 4 been blown immediately before being topped. In general also, the extent of air-blowing and the temperature of air-blowing will, of course, depend upon the nature of the product desired to be produced in the air-blowing still.

The air may either be blown through still 17 under pressure or be sucked through by subjecting the contents of the still to a partial vacuum. As shown in Figure 1, the air is blown.

The overhead from the oxidizing still 17, which will be comprised of oil vapors, oxidizing gases, and water vapors, passes by means of line 26 to condenser 27 where the oil vapors from still 17 are condensed, along with the water vapors, and pass together with the oxidizing gases emerging from still 17 into the gas and oil separator 28. The condensed oil and water vapors emerge from the bottom of separator 28 into line 29 and to line 30 and separator 13. This oil is withdrawn, along with fresh oil from still 7, and passed to oxidizing still 17 for further oxidation, by way of separator 13.

The air which emerged from oxidizing still 17 is passed from the top of gas and oil separator 28 into line 31, from which it is forced by pump 18, together with necessary fresh air, back to oxidizing still 17.

The oxidized oil having accumulated at the bottom of still 17, is drawn off through valves 32 and 32a into line 34 and by pump 33 is passed through heater 35 to still 36 for further separation of any entrained unoxidized oil.

In some cases, however, depending upon the nature of the charging stock, treatment rendered prior to withdrawal from still 17, and product desired from still 17, the oil remaining at the bottom of oxidizing still 17 will not be desired to be further separated from the asphaltenes and asphaltic resins with which it is mixed. In such case said oil, asphaltenes and asphaltic resins may be passed through valve 38 through line 39 to line 40, back to storage or drawn off through valve 41 for segregation.

However, if the contents drawn off from the bottom of asphalt still 17 are passed through heater 35 to still 36, the contents of still 36 are subjected to steam entering still 36 through line 42 with the result that the contents of still 36 are further stripped of undesired oil content. The vapors from such treatment pass through line 42a to condenser 43 where they are liquefied and passed through line 30 to the separator 13 from which they may be recycled to oxidizing still 17 for further oxidation. Asphaltenes and asphaltic resins and other contents not passed off through line 42a, accumulating at the bottom of still 36, are drawn off through valve 44 into line 40 where they are then pumped to storage or through line 45 back to line 16 for further oxidation if desired. If it is desired to segregate the accumulation at the bottom of still 36, such bottoms may be drawn off through valved line 46.

It will be apparent that the bottoms from stills 7, 17 and 36 may all be returned to oxidizing still 17 for further oxidation if it is so desired. Likewise it will be seen that any given volume of the original charging stock after having been treated, as above described, may be reassembled. Such reassembled material may possess all the asphaltenes, asphaltic resins and heavy oils of the original charging stock plus new asphaltenes and asphaltic resins created by oxidation of the overhead which had been separated from the original charging stock. The characteristics of the final asphaltic product can be altered at will by the amounts of the asphaltenes, asphaltic resins and fresh charging stock which are added to the bottoms withdrawn from still 7 or to other stock. Anyone skilled in the art of manufacturing asphalts, with the aid of this specification, will understand the circumstances and amounts

of commingling to produce his desired asphaltic product.

In the practice of the invention as described above, if at any time the product produced is found to be deficient in asphaltic resins and overly rich in asphaltenes, such difficulty can be overcome by commingling with such product over-rich in asphaltenes a steam refined asphalt, because, as already pointed out, steam refined asphalts tend to have a high asphaltic resins to asphaltenes ratio. Of course, it is possible, by the apparatus shown in Figure 1, to obtain steam refined asphalts by omitting the oxidation step.

In Figure 2 the process described is essentially the same as that illustrated in Figure 1 except that a different method is described for separating the oil from the asphaltenes and asphaltic resins generated in oxidizing still 17. The numbers from 1 to 34, inclusive, in Figure 2 represent equipment having the same function and corresponding to equipment similarly numbered in Figure 1.

When the accumulation at the bottom of oxidizing still 17 is withdrawn through valved line 34, instead of passing to a still, as to still 36 in Figure 1, the withdrawn material, consisting mainly of asphaltic resins, asphaltenes, and some oil which did not go over from still 17 as overhead, is pumped to agitator 50. Agitator 50 is fed from solvent storage 51, through pump 51a and line 52, with an appropriate hydrocarbon solvent which will precipitate the asphaltenes and asphaltic resins and dissolve most of the entrained oily constituents which have been withdrawn from oxidizing still 17. Solvents best adapted to perform this function are liquefied normally gaseous hydrocarbons, such as butane, isobutane, ethane and propane. Such light hydrocarbons may be liquefied in the conventional manner by compression and cooling in storage and pressure chambers. A pressure of 125 lbs. per square inch at 75° F. is sufficient to reduce such hydrocarbons to a liquid state. Agitator 50 is equipped with means intimately to effect mixture of the flow from line 34 with the solvent, the agitation being such that asphaltenes and asphaltic resins are not permitted to settle in agitator 50. The mixture containing solvent, oil, asphaltic resins and asphaltenes is pumped by pump 53 to separator 54. In such separator the solution of solvent and oil will rise to the top thereof and the asphaltic resins and asphaltenes will be precipitated to the bottom. The solution of oil and solvent is passed through line 55 to extractor 56 by pump 57. Upon the application of heat through steam coil 58, the solution of oil and solvent is vaporized and passes through line 59 to cooler 60 where the oil vapors are condensed and pass through line 61 to separator 62, thence into line 63 and past valve 64 back to separator 13 from which they may be drawn for further oxidation. The solvent vapors having been uncondensed by cooler 60, pass from the top of separator 62 through line 65 to pump 66, where they are raised to pressure, and cooled in cooler 67 whereby they are again liquefied and pass through line 68 back to solvent storage.

The asphaltenes and asphaltic resins which may not have been completely precipitated by the solvent in separator 54 will accumulate at the bottom of extractor 56 from which they may be withdrawn through line 69 and pumped by pump 70 to extractor 71. The application of heat through closed steam coil 72 in extractor 71 will cause oil and any entrained solvent in such asphaltenes and asphaltic resins to be evaporated and to pass from extractor 71 through line 73 to cooler 60 and separator 62 where such vapors receive the same treatment received by vapors from extractor 56. The asphaltenes and asphaltic resins accumulating at the bottom of extractor 71 may then be withdrawn at the bottom through line 73.

The asphaltenes and asphaltic resins withdrawn from still 7, oxidizing still 17, separator 54, and extractor 56, through lines 7a, 35, 54a and 69, respectively, may, either separately or jointly, be pumped through line 74 to extractor 71 for the removal of any additional oil content remaining therein which is not desired; or such asphaltenes and asphaltic resins and any desired entrained oil may be pumped through line 75 to storage. Line 75 is appropriately valved to permit the combination of any two or more of the bottoms from still 7, oxidizing still 17, separator 54 and extractors 56 and 71. If desired, such bottoms may be separately withdrawn at valves or may pass together through line 80 to storage.

Thus it will be seen from the above described method that the main function of the operation is the oxidation and creation of asphaltenes and asphaltic resins solely from certain fractions of the original charging stock. Substantially all of the asphaltic resins which existed in the original charging stock have been maintained and the method of oxidation described above has not resulted in the destruction of such asphaltic resins. The original asphaltenes and asphaltic resins of the charging stock are maintained together with the desirable heavy oil. To such concentrations may be added, as the process continues, any desired portions of asphaltenes and asphaltic resins, all obtained, if so desired, by the treatment of the original charging stock. It will be seen that the method described is entirely free from the limitations imposed by the nature of the processes of making steam refined or oxidized asphalt. It is possible by the method described to produce an asphalt from any given charging stock having any desired percentage of asphaltenes, asphaltic resins and heavy oils.

While the character of the invention has been described in detail this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. Likewise, the drawings are to be regarded as diagrammatical, no attempt having been made to show all the many details such as pumps, valves, pressure control devices and the like. It will be apparent to those skilled in the art that numerous modifications and variations may be adopted in the apparatus and method of the invention which is of the scope of the appended claims.

I claim:

1. The method of manufacturing an asphalt from a charging stock containing asphaltenes, oily constituents, and asphaltic resins, substantially without converting such asphaltic resins into asphaltenes, comprising separating oily constituents from the asphaltic resins and asphaltenes and separately airblowing said oily constituents, whereby additional asphaltenes are formed without converting the asphaltic resins in the charging stock to asphaltenes, commingling said additional asphaltenes with asphaltenes and asphaltic resins obtained from the charging stock without airblowing.

2. The method of manufacturing an asphalt

from a charging stock containing oil, asphaltenes and asphaltic resins without conversion of said asphaltic resins, which comprises distilling oil from said charging stock, air-blowing resulting distillate for the production of asphaltenes, commingling said air-blown distillate with a selective solvent which dissolves substantially all of the oil remaining in said air-blown distillate and precipitates substantially all the asphaltenes and asphaltic resins in such air-blown distillate, separating the solution of oil and solvent from asphaltenes and asphaltic resins, commingling said last mentioned asphaltenes and asphaltic resins with asphaltic resins and asphaltenes obtained from the charging stock without air-blowing.

3. The method of manufacturing an asphalt from a charging stock containing oil, asphaltenes and asphaltic resins without conversion of said asphaltic resins in said charging stock, which comprises distilling oil from the charging stock, air-blowing resulting distillate for the production of asphaltenes, separating oil from such air-blown distillate by distilling resulting air-blown distillate, commingling asphaltenes and asphaltic resins obtained by the air-blowing with asphaltic resins and asphaltenes obtained from the charging stock without air-blowing.

4. The method of manufacturing an asphalt comprising separating oily constituents from a charging stock containing asphaltenes, oily constituents, and asphaltic resins, air-blowing said separated oily constituents, commingling resulting oxidized material with the charging stock remaining after separation of said oily constituents.

5. The method of producing an asphalt from a charging stock containing oil, asphaltenes, and asphaltic resins, which comprises separating oil from the charging stock, producing additional asphaltenes from said separated oil, by air-blowing, commingling such additional asphaltenes with asphaltenes and asphaltic resins obtained from the charging stock.

6. The method of producing an asphalt from a charging stock containing oil, asphaltenes, and asphaltic resins, which comprises separating oil from the charging stock, producing additional asphaltic resins from said separated oil by air-blowing, commingling such additional asphaltic resins with asphaltenes and asphaltic resins obtained from the charging stock.

7. The method of manufacturing an asphalt from a charging stock containing oily constituents and asphaltic resins, which comprises separating a portion of oily constituents from a charging stock while leaving a portion therein, producing asphaltenes and asphaltic resins from separated oily constituents by air-blowing, and mixing asphaltenes and asphaltic resins so produced with charging stock remaining after separation of said oily constituents.

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