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METHOD OF COKING OILS

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Fig. 1.

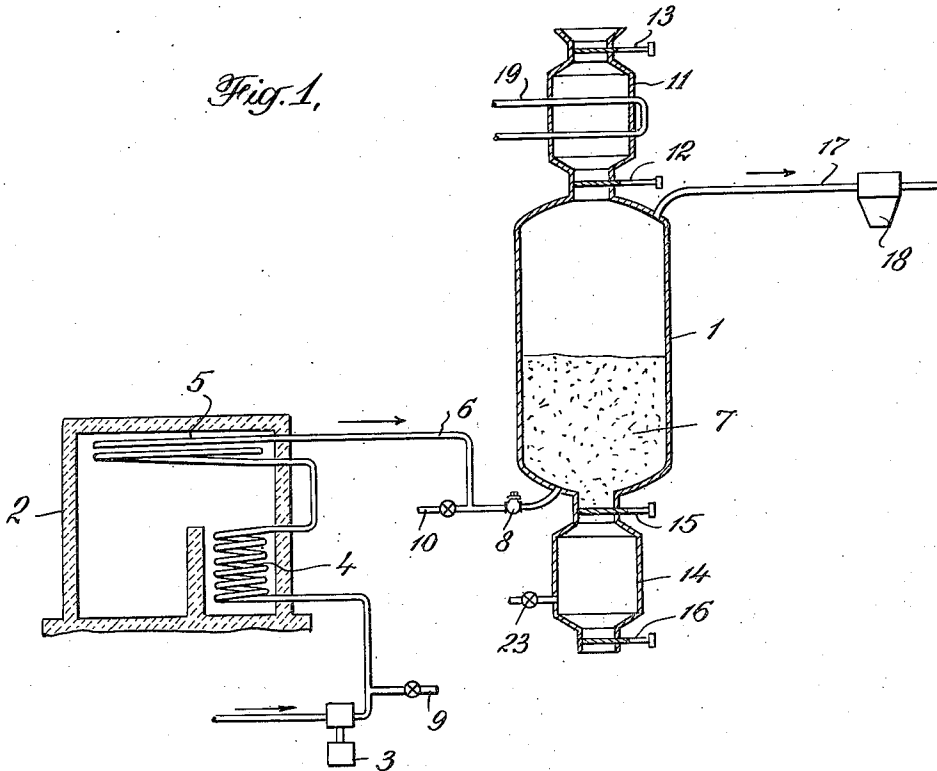
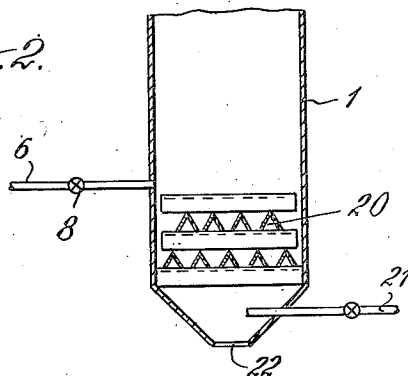


Fig. 2.



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METHOD OF COKING OILS

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3 Claims. (Cl. 196—55)

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This invention is concerned with methods for the coking of mineral oil residues, which have for their object the reduction of a heavy mineral oil fraction to a clean overhead stock, substantially free from constituents having coke forming tendencies under cracking conditions, and a solid carbonaceous residue of the nature of coke.

For many reasons it frequently becomes desirous of separating heavier petroleum oils in such manner. The more usual reason is for the preparation of a charging stock for cracking purposes, in order that, by the prior removal of coke forming bodies, the charge may be more conveniently handled in the cracking process. This is particularly true of vapor phase catalytic processes, wherein the coke forming bodies deposit upon the catalytic material and rapidly decrease its usefulness.

Coking methods in general fall into three types. In the older and obsolete method the whole of the oil to be coked was delivered into a still and coked therein by the application of heat through the still walls. A second method, widely proposed, but little used is that of flowing the oil, unheated or partially heated upon a bed of refractory or other spreading material, such as filter clay or coke and allowing it to distill to dryness thereon. In this method the spreading material is heated either by being placed in a container surrounded by heating gases, or, with the spreading material working slowly down through the container, the coke is burned from it in a lower zone, and the hot gases therefrom pass through and heat the spreading material in the coking zone. The first modification suffers from the severe penalties attendant upon trying to transfer heat in high quantities into a mass of spreading material of low heat transmissive ability. The second suffers from admixture of gases of combustion with the distillates from coking. For these reasons, neither are widely used. The final and most widely used method is that of heating the oil in a flowing stream to such a temperature that it may be flash distilled to dryness, and then passing it to a vapor separating chamber wherein vapors are removed and a coke deposit is built up. Practically all commercially used processes are of this kind, and so operated as to build up a massive coke deposit in spite of the necessity for periodically removing the vaporizer from service to break up and remove the coke. Attempts have been made to achieve spray-coking variations of this to give granular instead of massive coke deposits, with some suc-

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cess but as yet without any wide commercial acceptance.

This invention has for its object the provision of an improved method of coking by the flash vaporization method capable of avoiding entirely the difficulties attendant upon the removal of massive coke deposits from the vaporizing chamber. It has as an additional object the provision of a method wherein the deposit within the chamber is caused to be a relatively free flowing granular mass, not predominantly cokey in nature. It has as a further object the provision of a process wherein the coke, when passing through that adhesive, semi-plastic state characterizing a stage in its formation is kept from contact with the working parts of the equipment and prevented from adhering thereto to be later distilled to a hard highly adherent deposit.

All these and other objects flow from the basic concept of this process which is that of first heating the oil in a flowing stream to a temperature sufficient to insure its distillation to dryness and then introducing it into a bed of refractory granular material in a vaporizer.

This invention may be understood by reference to the drawing attached to this specification, in which Figure 1 shows a set-up of apparatus for the performance of the process as shown in diagram form, and Figure 2 shows certain alternative details. In Figure 1 of this drawing, 1 represents a coking chamber or vaporizer, and 2 a tubular heating furnace. Oil to be coked is introduced by pump 3 to pass through tubes 4 and 5 in furnace 2, wherein it is heated to a coking temperature and from there passes by pipe 6 to vaporizer 1 where it is introduced below the level of a granular packing or spreading material 7. If desirable in order to avoid premature separation of vapors, or for any other purpose, back pressure may be held upon the heating coils 4 and 5 through the agency of valve 8. Steam, in regulated amounts, to assist in the vaporization, may be inserted either through pipe 9 or pipe 10. While vaporizer 1 is shown only partially filled with packing material 7 it will be understood that any level of packing material found desirable may be carried, as later explained. In order to facilitate change of packing material during operations, the vaporizer is fitted above with a charging bin or hopper 11 equipped with slide valves or other suitable closures 12 and 13 whereby access of air to the vaporizer or escape of vapors therefrom during charging operations may be avoided. Similarly, a discharge hopper 14 with closures 15 and 16 is provided at the bottom

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end of vaporizer 1. Alternatively, these hoppers may be omitted, and another vaporizer such as 1 may be provided with alternate use of vaporizer and removal and charge of spreading material in that one not used for vaporization. Vapors are led from vaporizer 1 through pipe 17 to the usual fractionating equipment or to other use, as may be desired.

In Figure 1, the vapors may be separated from any absorbent they may have entrained by a separator 18 inserted in the vapor line, or by a similarly functioning structure placed in the top of chamber 1. In many cases, it may be desirable to heat the absorbent material before introduction to the chamber, and, in such cases, hopper 11 or its equivalent may be provided with tubes 19 through which heat transfer medium at suitable temperature may be passed. In many cases, the material entering hopper 11 will come thereto from a regenerating furnace, and need not be cooled before introduction.

A possible alternative form for the bottom of chamber 1 is shown in Figure 2, wherein the chamber is at least partially filled, from the bottom upward, by a baffling structure, such as the interlaced angle irons 20, through which the absorbent may flow continuously if desired. In such cases, and with continuous flow, it is usually desirable to utilize a steam inlet 21, whereby steam may be introduced to cool, or purge, or blanket the absorbent, which may then be discharged, continuously, if desired, to atmosphere through throat 22.

Steam purging or cooling may also be practised in hopper 14 of Figure 1 by means of pipe 23.

The packing or spreading material may be any material of a granular, refractory, nature, preferably fairly free flowing, such as fuller's earth, bauxite, prepared clays, crushed firebrick, crushed pumice, crushed coke of petroleum or coal origin, or similar material. It should be in a form such that it presents a fairly large surface/volume ratio and should be of sufficient size to be free flowing and not too readily suspended in the vapor stream. Fuller's earth of 30-60 mesh size is an exemplary material, as is clay type catalyst in cylindrical pellet from $2\frac{1}{2}$ to 4 mm. in diameter.

In operation, the spreading material becomes heated to the coking temperature upon the entrance of the heated oil stream and the distillation takes place within and upon the surface of the spreading material. The resulting coke is thus deposited within and upon the surface of this material, and a very considerable deposit of coke, to the amount of 25% or more by weight of the spreading material when that material is of a clay nature, for example, may be deposited without any change or loss in the free flowing characteristics of the spreading material.

During the period when the coke undergoing formation is in the adhesive semiplastic stage it is entirely out of contact with any permanently installed portion of the equipment and adherent deposits are not built up thereon. In fact, the passage from liquid phase to coke is so rapid, that there is little opportunity for the formation of any deposits other than those formed in the spreading material.

As an example of the operation of this process, a charge of 17.8° A. P. I. gravity crude residue may be heated to 900° F. and flashed in the presence of about 14% by liquid volume of steam to distill off as an overhead 4.6% of non-condensable gases

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and 85.2% of clean distillate free of material having coke forming tendencies, to leave 10.2 percent of coke, all percentages being by weight. If this operation is so handled according to this invention that the coke is deposited upon fuller's earth, and the amount deposited limited to 10% of coke by weight of the fuller's earth, an amount which will not appreciably change the flow characteristics of the earth, a coking chamber 10 feet in diameter, holding 25 feet of earth, would be sufficient for about four hours operation of a still handling 1000 barrels per stream day. Discharge of the chamber would require a very much shorter time, and higher amounts of coke can be deposited without serious alteration of flow characteristics.

The discharged spreading material may be burned under suitable conditions for the removal of the coke, and returned to the operation. In case the spreading material itself be coke, the discharged material may be used as fuel in other operations, as for example, boiler furnaces or the furnace of this still.

We claim:

1. A method for preparing charging stock for catalytic cracking which comprises heating a petroleum charging stock to a temperature sufficient to cause distillation to coke, introducing said stock into and passing it in counter-current flow through a zone of moving granular contact mass material, maintaining said zone substantially free of combustion supporting gas, and collecting the overhead distillate substantially free of coke-forming constituents so that it may be used as a charging stock in catalytic cracking with greatly reduced catalyst contamination.

2. A method for preparing charging stock for catalytic cracking which comprises heating a petroleum charging stock to a temperature sufficient to cause distillation to coke, introducing said stock into and passing it in countercurrent flow through a zone of moving granular contact mass material, continuously adding granular contact mass material to said zone and withdrawing it therefrom at a rate proportioned to the rate of introduction of charging stock such that the accumulation of coke on the granular contact mass material is never sufficient to substantially change the flow characteristics of said material, maintaining said zone substantially free of combustion supporting gas, and collecting the overhead distillate substantially free of coke-forming constituents so that it may be used as a charging stock in catalytic cracking with greatly reduced catalyst contamination.

3. A method for preparing charging stock for catalytic cracking which comprises heating a petroleum charging stock to a temperature sufficient to cause distillation to coke, introducing said stock into and passing it in counter-current flow through a zone of moving granular contact mass material, continuously adding heated granular contact mass material to said zone and continuously withdrawing granular contact mass material having coke deposited thereon from said zone while maintaining said zone substantially free of combustion supporting gas, and collecting the overhead distillate substantially free of coke-forming constituents so that it may be used as a charging stock in catalytic cracking with greatly reduced catalyst contamination.

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