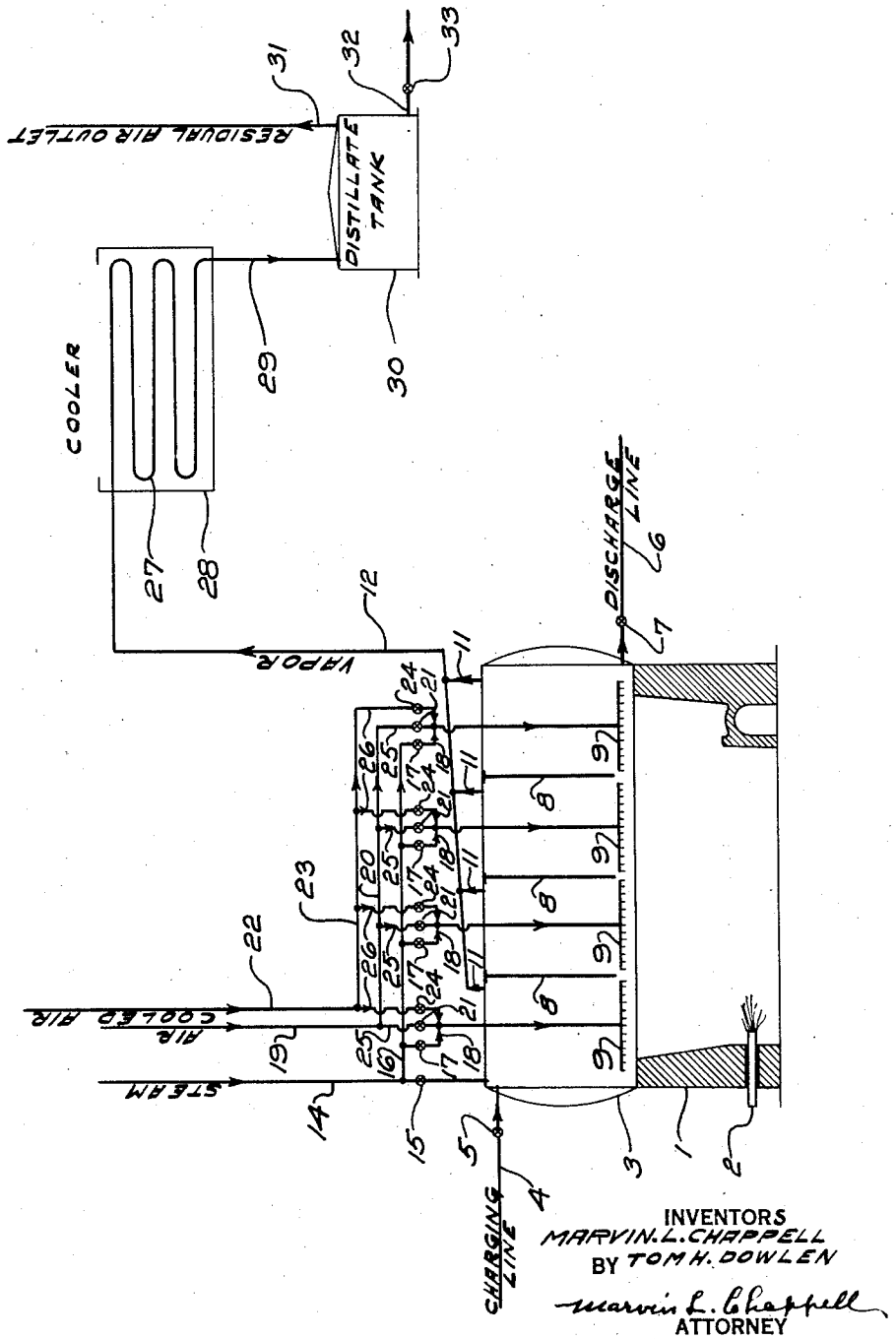
June 28, 1932. M. L. CHAPPELL ET AL 1,865,081

PROCESS OF OXIDIZING OILS

Filed Nov. 26, 1929



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Patented June 28, 1932

1,865,081

UNITED STATES PATENT OFFICE

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PROCESS OF OXIDIZING OILS

Application filed November 26, 1929. Serial No. 409,937.

This invention relates to a process of oxidizing liquids with an aeriform fluid, such as air, oxygen or oxygen bearing gases, either with or without the aid of a catalyst, in which the oxidizing reaction is exothermic.

More specifically this invention relates to oxidizing oils or oil products such as petroleum oils, petroleum oil residuum, shale oils, animal or vegetable oils, wherein the oxidation action is exothermic and a uniform oxidizing temperature is beneficial or necessary for obtaining the desired product or products, or results in an economical saving of time; such for example as in the oxidation of rape-seed oil or cotton-seed oil, to increase the viscosity, the oxidation or partial oxidation of linseed oil or other like oils either with or without the aid of a catalyst; or in the manufacture of oxidized asphaltic products suitable as a cementing agent for roofing material, battery sealing compounds and for like purposes where an asphaltic cementing agent is required with a relatively high melting point which will be sufficiently ductile and flexible.

In the conventional method of oxidizing oils, or petroleum oil residuum, air or air and steam is introduced into the container holding the oil or residuum, through spray pipes and at the same time the oil is heated to a temperature sufficient to obtain the desired oxidizing reaction. By such methods it is difficult to obtain a uniform product, since a uniform temperature cannot be readily maintained due to the exothermic heat of the oxidizing reaction. The added exothermic heat frequently overheats the oil or asphaltic residuum to a cracking temperature or produces other undesired decomposition reactions. In oxidizing asphaltic residuum with air, overheating produces a product which is more brittle and less ductile than if a regulated uniform oxidizing temperature had been maintained.

Also by the well-known batch still method, the time required to convert a batch of asphaltic residuum into an oxidized product suitable for battery sealing compounds, or for the manufacture of roofing felt, requires approximately 24 hours, while by our invention the reaction is accomplished in about one half the time.

Now, we have discovered an improvement in the art of oxidizing oils and petroleum oil residuum in which the difficulties and various disadvantages before mentioned may be overcome by the use of air, cooled to a temperature sufficient to extract the exothermic heat of the oxidizing reaction, thereby maintaining a substantially uniform temperature at the required degree, this temperature depending upon the oil to be oxidized, the extent of oxidation and the product desired. For example, in oxidizing petroleum asphaltic residuum the temperature may range from approximately 400 to 550 degrees F.; in oxidizing rape-seed oil or cotton-seed oil a temperature ranging from approximately 180 to 300 degrees F. may be employed and in oxidizing linseed oil in the presence of a catalyst such as a manganese salt or compound, a temperature of approximately 180 to 300 degrees F. is employed.

We are aware that cooling jackets through which a cooling liquid flows, surrounding or partly surrounding the container, in which an oxidation action is effected, is well-known in the art for partly extracting the exothermic heat produced from the oxidation of oils. However, such methods are not entirely satisfactory, since the product being oxidized may solidify and coat the inside of the container, thus insulating the inside surface of the container to such an extent that the transmission of heat to the cooling medium is too slow to take away the excess exothermic heat produced, whereby the oil, or residuum may be overheated and undesired decomposition reactions take place.

Briefly stated, our invention comprises continuously commingling an oxidizable oil or an asphaltic residuum at the required oxidizing temperature, with an aeriform fluid containing oxygen, such as air, cooled to such a temperature that the exothermic heat produced by the oxidizing reaction will be continuously and immediately extracted from the body of the oil or residuum, by the cooler residual aeriform fluid leaving the body of oil or residuum.

The use of a cooled aeriform fluid containing oxygen for producing oxidized asphalt, or oxidized oils to increase the viscosity thereof, may be employed by our invention in any batch or continuous system.

An object of the invention is to provide a simple, efficient and economical process or method by which oils, asphaltic residuum or other oxidizable liquids may be converted into desired oxidized products at a minimum production cost and with a minimum consumption of time.

Another object of the invention is to provide an efficient and economical process by which asphaltic residuum may be converted by any continuous or batch system, into oxidized asphaltic products, which will have relatively high melting points, flash and at the same time will be sufficiently ductile and flexible.

Another object of the invention is to provide a simple and efficient process for oxidizing oils or manufacturing oxidized asphaltic products, in which the various characteristics of fluidity or ductility, melting point, flash, etc., required by the different branches of the individual art, may be controlled, separately or in combination with other products, such for example as mixing oxidized asphalt made by this invention with natural asphalt or asphalt made by steam distillation.

With the foregoing preliminary explanation the preferred embodiment of our invention will now be more fully explained by reference to the accompanying drawing and for the purpose of simplifying the description, reference will be made to petroleum oil residuum only.

In the drawing, pipe 4, controlled by valve 5, connects oxidizing container 3 near the top to a source of supply of petroleum oil residuum not shown. Container 3 is stationed in the top of furnace 1. Furnace 1 is provided with burner 2 which leads to a source of fuel supply not shown. Pipe 14, controlled by valve 15, is connected to container 3 at the top and leads to a source of steam supply not shown. Pipe 16 connects steam pipe 14 to branch pipes 18. Branch pipes 18, controlled by valves 17, connect pipe 16 to pipes 25. Pipe 20, connects air pipe 19 to branch pipes 25. Air pipe 19 leads to a source of compressed air not shown. Pipe 23, connects cooled air pipe 22 to branch pipes 26. Cooled air pipe 22 leads to a source of cooled compressed air not shown. Branch pipes 26, controlled by valves 24, connect pipe 23 to pipes 25. Pipes 25, controlled by valves 21, extend through the top of container 3 ending in spray pipes 9. Container 3 is provided with baffle plates 8 which divide the container or oxidizing chamber 3 into a plurality of connected compartments. Pipe 6, controlled by valve 7 leads to a storage tank not shown. Pipes 11 connect the compartments of container 3 to vapor outlet pipe 12. Pipe 12 is connected to the cooling coil 27 situated in cooler box 28. Pipe 29 connects cooling coil 27 to the top of distillate tank 30. Pipe 32, controlled by valve 33 leads to a storage not shown. A residual air outlet pipe 31 is connected to the top of distillate tank 30.

The preferred operation of the apparatus just described is as follows:

The oil to be oxidized, such as a petroleum oil residuum, is charged into oxidizing container 3 to any desired level by opening valve 5 in the pipe 4, the pipe 4 leading to a source of supply not shown. The container 3 is provided with a plurality of connected compartments separated by baffle plates 8, each baffle plate having an opening at the bottom, although this opening may be at any place in the baffle plate below the oil level, so that in the continuous operation of the apparatus the oil under oxidation will flow through the compartments and out through discharge line 6, the rate of flow being governed by the rate of oxidation and controlled by regulated openings of valves 5 and 7 in the pipes 4 and 6 to maintain a substantially constant level. When container 3 has been filled to the desired level valve 5 is tentatively closed and the residuum in container 3 is heated to the required oxidizing temperature by burner 2 in the furnace 1, this temperature ranging from approximately 400 to 550 degrees F. for petroleum oil residuum and usually somewhat lower for animal or vegetable oils, the degree of heat depending upon the oil to be oxidized and the product desired. At the beginning of the heating operation of the residuum in oxidizing container 3, as well as during the oxidation operation, a small amount of steam is preferably continuously introduced into the top of each compartment of oxidizing container 3, from steam pipe 14 by a regulated opening of valve 15, to prevent explosive or burning mixtures from forming in the top of container 3. In the drawing only one pipe connection is shown for introducing steam into the top of the compartments of container 3 and it is to be understood that steam pipe 14 has branch pipe connections (not shown) to the other compartments.

It is desirable during this preliminary heating operation to introduce regulated quantities of air into each compartment of the oxidizing container 3, the rate of flow being substantially the same as during the oxidizing operation. The quantity of air employed to agitate the petroleum oil residuum during the preliminary heating and oxidation operation may vary through a wide range. Preferably approximately 1400 cubic feet of air per minute for each 600 barrels of residuum under treatment is employed. The introduction of air into the compartments of container 3 is carried out by regu-

lated openings of valves 21 in the branch pipes 25, branch pipes 25 being connected to pipe 20. Pipe 20 is connected to air pipe 19, which leads to a source of air not shown.

The air passing through pipes 25 and out through the spray pipes 9 into the compartments of oxidizing container 3 is usually equally proportioned, although equally proportioned amounts of air are not absolutely essential for each compartment, and in certain cases more air may be introduced into the last compartment or compartments to obtain the required oxidation.

If desired, steam may be introduced into the compartments of container 3 along with the air during the preliminary heating operation to free the residuum of volatile hydrocarbons and water, or steam may be introduced at intervals or continuously during the oxidation operation. The introduction of steam into the residuum is carried out by regulated openings of valves 17 in the branch pipes 18. The branch pipes 18 are connected to pipe 16. Pipe 16 is connected to steam pipe 14.

When the petroleum oil residuum has attained a temperature at which it is desired to carry out the oxidizing operation, such for example as 480 degrees F., burner 2 in the furnace 1 is shut off to such an extent that there will be substantially no further transmission of heat to container 3, and at the same time cooled air preferably approximately at 10° F. from pipe 22 is introduced into each compartment of container 3 along with the air coming through pipe 19, the cooled air, which may be at any desired temperature lower than atmospheric (50° F. to 0° F. or lower), being in quantities sufficient to extract the excess exothermic heat produced by the oxidizing reaction.

The cooled air, or cooled aeriform fluid containing oxygen, employed in the oxidizing operation, may be obtained by any refrigeration or cooling method, such for example as passing air through a brine solution cooled to 10 F. by an ammonia or sulphur dioxide refrigerating system or by any of the well-known multiple compression, cooling and expansion systems for cooling or liquefying air.

The introduction of cooled air into the compartments of container 3 along with the air coming through pipe 19, is carried out by regulated openings of valves 24 in the branch pipes 26. Branch pipes 26 are connected to pipe 23 and pipe 23 is connected to cooled air pipe 22. At the same time the valves 21 which control the flow of air passing through pipe 19 may be closed to such a degree that the total volume of air agitating the petroleum oil residuum in the container 3 will remain substantially constant. Valve 5 is now opened to such a degree as to admit a regulated flow of the petroleum oil residuum to be oxidized, the rate of flow being governed by the rate of oxidation. At the same time valve 7 is opened sufficiently to permit a regulated flow of the oxidized residuum to pass into discharge line 6, in order to maintain a constant level in container 3. From discharge pipe 6 the oxidized residuum passes into a storage tank not shown and it may be partly cooled before passing into the storage tank.

The residual air, steam, volatile oil and gaseous products of the oxidizing reaction pass out of the various compartments of oxidizing container 3 through pipes 11 into pipe 12 and then through cooler coil 27, stationed in the cooler box 28, whereby the condensable hydrocarbons and steam are liquefied and pass from cooler coil 27, together with the residual air and gaseous products, through pipe 29 into distillate tank 30. In distillate tank 30 the residual air and gaseous products separate from the condensed liquid products and pass out of the system through the residual air outlet pipe 31. From distillate tank 30, the condensed oil and water may be conducted to a storage not shown through the pipe 32 controlled by valve 30.

The operation of our invention in batch lots, is carried out substantially the same as in the continuous system just described with the exception that the petroleum oil residuum is not permitted to flow through the compartments of container 3, during the oxidizing operation, valves 5 and 7 remaining closed. Also the use of cool air is usually discontinued during the latter part of the oxidizing operation and heat applied by burner 2 to maintain the required constant elevated oxidizing temperature for completing the oxidizing reaction. The application of heat to container 3 and the discontinued use of cooled air is usually necessary when the petroleum oil residuum has been oxidized to such a degree that it has a melting point of approximately 260° F. to obtain an oxidized product having a higher melting point. Instead of applying heat to container 3 by burner 2, when the petroleum oil residuum under oxidation has an approximate melting point of 260° F., hot air may be employed to finish the oxidation operation, introduced through the pipe 19 and branch pipes 25 which end in spray pipes 9.

The operation of this invention may be carried out under super-atmospheric pressure or under pressure less than atmospheric, depending upon the oil to be oxidized and the product desired. For example, in the manufacture of high melting point oxidized asphalt from a petroleum oil or petroleum oil residuum containing a high percentage of relatively low boiling hydrocarbons, the oxidizing operation as heretofore described, may be conducted under vacuum ranging from 755 to 5 mm. of mercury or less, absolute pressure, and in the production of oxidized asphaltic products from low Baumé gravity

petroleum residuum, which contains substantially no relatively low boiling hydrocarbons, the oxidizing operations may be conducted at atmospheric pressure or at higher pressure.

While the process herein described is well adapted for carrying out the objects of the present invention, it is to be understood that various modifications and changes may be made without departing from the spirit of the invention, such for example as the employment of a plurality of connected oxidizing containers, and the invention includes all such changes and modifications as come within the scope of the appended claims.

What we claim is:

1. A process of oxidizing asphaltic oils, comprising, maintaining a supply of asphaltic oil in a container provided with a plurality of distinct but connected compartments through which the asphaltic oil continually passes, at an oxidizing temperature, continuously introducing and commingling regulated streams of cooled air with the oil in each compartment of the container, continuously withdrawing the residual air and volatile oil products from each compartment of the container, continuously introducing a regulated stream of asphaltic oil into the first compartment of the container, continuously extracting the heat of the oxidizing reaction by regulating the temperature of the cooled introduced air, and discharging the oxidized oil from the system.

2. A process of oxidizing asphaltic oils, comprising, maintaining a supply of asphaltic oil in a container with a plurality of distinct but connected compartments through which the asphaltic oil continuously passes at an elevated oxidizing temperature, continuously introducing a regulated stream of asphaltic oil into the first compartment of the container, continuously introducing an individual supply of cooled air into each compartment of the container at a temperature sufficient to extract the exothermic heat of the oxidizing reaction, continuously withdrawing the residual air and volatile oil products from each compartment of the container, and discharging the oxidized product from the system.

3. A process of oxidizing asphaltic oils, comprising, maintaining a supply of asphaltic oil in a container provided with a plurality of distinct but connected compartments through which the asphaltic oil continuously passes at temperatures of approximately 400 to 550 degrees F., continuously introducing a regulated stream of asphaltic oil into the first compartment of the container, continuously introducing and commingling regulated streams of cooled air with the asphaltic oil in each compartment of the container at a temperature and in quantities sufficient to extract the exothermic heat of the oxidizing reaction, continuously withdrawing the residual air and volatile oil products from each compartment of the container, and discharging oxidized asphaltic oil from the system.

4. A process of oxidizing asphaltic oils, comprising, maintaining a supply of asphaltic oil in a container provided with a plurality of distinct but connected compartments through which the asphaltic oil continuously passes, at an elevated oxidizing temperature, continuously introducing a regulated stream of asphaltic oil into the first compartment of the container, continuously introducing regulated streams of air, cooled to a temperature sufficient to extract the exothermic heat of the oxidizing reaction, into the supply of asphaltic oil in each compartment, continuously withdrawing the residual air and volatile oil products from each compartment of the container and finally discharging the oxidized oil from the system.

5. A process of oxidizing asphaltic oils, comprising, maintaining a supply of asphaltic oil in a container provided with a plurality of distinct but connected compartments through which the asphaltic oil continuously passes, maintaining the supply of asphaltic oil at a temperature of approximately 480 degrees F., continuously introducing a regulated stream of asphaltic oil into the first compartment of the container, continuously introducing and commingling regulated streams of cooled air with the asphaltic oil in each compartment of the container, continuously withdrawing the residual air and volatile oil products from each compartment of the container, and discharging the oxidized asphaltic oil from the system.

6. A process of producing oxidized asphalt, comprising, continuously introducing and passing petroleum oil residuum through a series of distinct but connected compartments in a container holding a bulk supply of petroleum oil residuum, maintaining the bulk supply of petroleum oil residuum at an elevated oxidizing temperature, introducing separately regulated streams of cooled air into each compartment of the container, continuously separating and withdrawing the residual air and volatile oil products from the residuum undergoing oxidation, continuously extracting from the residuum undergoing oxidation the excess heat produced by the oxidation reaction by regulating the temperature of the cooled air, maintaining the temperature of the residuum and the time of passage through the connected compartments so that the residuum will be oxidized to the required degree and then passing the oxidized residuum out of the system.

7. A process of forming oxidized asphalt, comprising continuously introducing and passing petroleum oil residuum in a regulated stream flow through a series of distinct but connected compartments in a container hold-

ing a bulk supply of petroleum oil residuum, maintaining the bulk supply of petroleum oil residuum at a temperature of approximately 400 to 550 degrees F., introducing and commingling separately regulated streams of air, cooled to a temperature of approximately 10 degrees F., with the petroleum oil residuum in each compartment of the container, continuously separating and withdrawing the residual air and volatile products from the residuum undergoing oxidation in each compartment of said container, continuously extracting from the residuum the excess heat produced by the oxidation reaction by regulating the quantity of introduced cooled air, maintaining the temperature of the residuum and time of passage through the connected compartments so that the residuum will be oxidized to the required degree and continuously passing the oxidized residuum out of the system.

In testimony whereof we affix our signatures.

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