Patented Apr. 15, 1930 1,754,296

UNITED STATES PATENT OFFICE

ALBERT H. ACKERMAN, OF CHICAGO, ILLINOIS, ASSIGNOR TO CATALYTIC CHEMICAL COMPANY, OF DENVER, COLORADO, A CORPORATION OF COLORADO

PROCESS OF ENHANCING THE FLOW OF OILS THROUGH PIPE LINES

No Drawing. Application filed February 16, 1927. Serial No. 168,820.

The present invention relates to a process of treating mineral oils and petroleum products and hydrocarbon products that are to be pumped through pipe lines.

My process is particularly designed for the treatment of petroleum products that are heavy and viscous due to the presence therein of waxes and pitches. The process is also applicable to the treatment of oils containing water in the form of an emulsion.

An object of my invention is to lower the cold-test of mineral oils, petroleum products and similar hydrocarbon products and to lower materially the viscosity of such products so that the same may be more readily pumped through pipe lines and otherwise handled in tanks, tank cars, stills and the like.

Another object of my invention is to provide an improved process for cleaning and keeping clean and unobstructed pipe lines in which waxes and the like accumulate, thereby tending to reduce the flow through the pipe line, as well as to increase the cost of pumping.

While I am aware that natural petroleum oils which are too viscous to be pumped or otherwise handled, and by reason of this have not been used as combustibles, for instance, in oil-fed furnaces in which the fuel oil is pumped to the burners and atomized, have been treated or processed by the simple addition of naphthalene thereto without any further chemical or heat treatment in order to transform the oil into a free flowing fluid or to make it a more mobile liquid at ordinary temperatures so that it can be easily pumped, I am not aware that it has ever been proposed to treat heavy, viscous oil and oil products by a composition of materials as will be described more fully below.

In connection with pipe lines, the crude petroleum may be pumped from the wells to the tank farms or tank farms to the stills. Where the distance from the well to the tank farm is very great, it is customary to have pumping and heating stations at intermediate points as the oil has a tendency to chill and its viscosity increased, causing a deposit of paraffine and other waxes and various products in the pipe lines so that, for example, a six inch pipe line might be so obstructed that it was only equivalent to a two inch pipe. In this instance it is necessary to clean the pipe lines, and in so far as I know, this has never been proposed in the manner in which I have proposed to do it. By the employment of my process and materials used in carrying out the process, not only is the pipe line cleaned, but by the continued use of the materials the pipe line is maintained clean and unobstructed so that there is an immediate saving in pumping and heating expense, and initial equipment is reduced in cost as smaller size pipe lines may be employed.

My treatments or processes may be employed at other steps or points in the flow of the materials between the wells and the market, and has been, for example, found desirable and of value in treating cracker stock either as it comes from the crude stills and prior to entering the cracker, or during the cracking process, as for example, after it has has been subjected to heat in the furnace or heating coils and prior to its admission to the reaction chamber or while in the same or in similar or other apparatus employed in cracking processes.

In the treatment of pipe lines to clean them or to keep them clean, I apply my materials or mixtures to the crude stock as it comes from the well, although the same may be applied in the well or at various points in its flow, as will be hereinafter referred to. For this treatment, I prefer to use a combination of materials that will break up the carbon clusters, waxes, binders, fats, etc., so that the petroleum remains more fluid and does not have a tendency to clog the lines. I have found a very satisfactory mixture to consist of flake naphthalene, anthracene, a combination of alkali which I prefer to make up with caustic soda, sodium phosphate, and ammonium carbonate, together with granulated sugar, oil of mirbane, a phosphate rock or powder or the equivalent, and a limited amount of sulphuric acid. For the phosphate rock, I have secured very satisfactory results using a Florida phosphate rock or powder analyzing approximately as follows: Carbon dioxide, silica, phosphorous pentoxide, lime, alumina (including a trace of ferric oxide

as iron), magnesia, and fluorine. I prefer the natural phosphate rock rather than a made-up combination of ingredients, and I find that slight variations in the analysis of the rocks do not affect the treatments to any extent. As an illustration, I have secured satisfactory results by the use of 133 lbs. flake naphthalene, 21 lbs. anthracene, 56 lbs. caustic soda, 10 lbs. sodium phosphate, 10 lbs. ammonium carbonate, 20 lbs. granulated sugar, 1 lb. oil of mirbane, ½ lb. sulphuric acid, 3 lbs. phosphate rock, and 2 lbs. of sodium hydroxide. In mixing these, I take first the caustic soda, sodium phosphate and ammonium carbonate, and mix the same with approximately an equal amount of naphthalene, and grind the same thirty minutes in a ball mill, and then add the balance of naphthalene and the proper amounts of anthracene, sodium hydroxide, oil of mirbane and phosphate rock, grinding the desired time, generally a few minutes, say three to five minutes, and then add the granulated sugar and grind that for several minutes. The material is then dumped and packed in airtight metal drums for use.

When used, it is applied to the crude oil in a proportion of about 1 lb. to every 30 bbls. oil, the proportions depending on the particular oil to be treated, which is readily determined by testing. Where tank stock or residuum is treated, I treat in the proportion generally of 1 lb. to 15 bbls. of petroleum, and in instances where there is a very heavy residuum substantially 1 lb. to 8 bbls., it being understood that these proportions may be varied within considerable ranges, this, as before mentioned, being determined by test.

The ½ lb. sulfuric acid mentioned above in connection with formula is employed to treat the 21 lbs. of anthracene before the latter is added to the other ingredients. The acid appears to activate the anthracene or to remove therefrom certain impurities. When pure 85% anthracene is used, this sulfuric acid treatment is not necessary. The second (3 lbs.) of sodium hydroxide specified are used to treat the anthracene which has been subjected to the sulfuric acid treatment, as the final composition is intended to be alkaline. The oil of mirbane can be omitted in some instances from the mixture without affecting its efficacy.

In treating the crude oil or similar hydrocarbon product, the action of the above-mentioned mixture is to increase considerably the fluidity of the oil, to lower its cold test and to cause the liberation and separation of any moisture or water contained therein.

The reagents mentioned may be added to the crude oil at any suitable stage during their handling, either directly as they issue from the well, while in storage, or while being conveyed through pipe lines; and either prior or subsequent to any refining treatment.

In the composition of materials enumerated above, and which is used in carrying out my present invention, the naphthalene and anthracene serve to break down "hydrocarbon clusters" in the oils undergoing treatment, by which term I mean that the heavy waxes and other similar deposits in the oil are rendered soluble and hence the fluidity of the resultant mixture is increased. It is impossible to state exactly the chemical action due to the adding of the caustic soda, sodium phosphate or ammonium carbonate, but these apparently, when added to the petroleum from the well, produce an artificial heat by chemical action and cooperate with the other chemicals in separating the hydrocarbon clusters, the same by chemical action increasing the temperature sufficiently to cause a permanent change of the cold test range of the oils or large bodies of hydrocarbons. These also work with the granulated sugar, it having been found after much experimenting that there was a chemical action creating more fluid substance. Of course, I know that in adding the sugar, I have added a percentage of moisture in itself, and taking the alkalies referred to with the sugar, there is a catalytic action on the hydrocarbon clusters, breaking them and making a more permanent fluid. Presumably the alkali addition breaks up the binders or cuts the binder the same as they would cut fats. By the attack that the combination makes on the binder that holds the clusters together, together with the naphthalene and anthracene which has a milder effect on separating the clusters, the binder is destroyed so that the same is not formed again in the pipe lines or containers so far as the clusters in the paraffine wax, asphalt or tar are concerned. The paraffine wax, tar or asphalt alone may be cut by the caustic soda, ammonium carbonate and granulated sugar mixture, without the presence of carbon in the wax as I have successfully demonstrated this, to wit, by adding the combination to crude oil where it has the presence of a large quantity of gasoline and different groups of oils of low specific gravities. I found that there was a cutting action on the paraffine or wax combination so that they would not adhere at temperatures as low as 45° F., thereby indicating that the cold test is lowered. The phosphate rock appears to act as a clarifying agent, the probability being that inasmuch as it is used in very finely divided condition, it will act as a mild scouring agent upon the walls of the pipe lines without being in sufficiently large particles to cause any obstruction of the valves, pumps, etc. The phosphate rock (calcium phosphate) may be omitted under certain conditions.

In pipe line stock coming from wells, and storage tank, none of the waxes or the like therein contained have been subjected to any heat treatment. Moreover, in the pipe lines,

or crude oil from the well, all of the various waxes and fats, tars, asphalts, etc., as well as impurities, are in the crude oil. The composition of materials for treating the crude oil must therefore perform an additional function or functions in more or less breaking down these waxes, fats or the like, so that the clusters therein may be treated. The breaking down of the clusters in the pipe lines may not be complete, depending on the nature of the crude oil, its source, etc. Also in the various processes following, or in the various refinery treatments, the carbons may re-clusters so that breaking down of clusters in the crude oil may not be permanent or sufficient for all of the later products.

As before mentioned, the employment of my compounds and processes at any step improves the efficiency of succeeding treatments or processes and apparatus so that even though I prefer to treat the petroleum in succeeding refinery steps, the refining processes are improved by preceding treatments so that there is a general improvement at all points between the crude in the well and the products to be marketed.

In using my composition of materials to remove paraffine from pipe lines, a very interesting experiment was made on a 6-inch pipe line 53 miles long. Examination at a number of points disclosed that the line was choked with paraffine until it had only about two inches clear inside diameter. In making the experiment, 59,000 barrels of oil in tanks at the field end of the line were treated with the chemical-composition of this invention. This required 2850 pounds of the chemical, and required 72 hours of time. The oil was drawn from the big tanks through a series of 5000 and 10,000-barrel tanks, where my composition was applied and the oil returned to storage tanks until ready for use. When all the oil had been treated, it was started through the line, and at the end of about 10 days all the treated oil had been pumped into it. A close examination was then made at numerous points all along the line, and the inside of the pipe was found to have been absolutely cleaned of all paraffine accumulation. The line has been in operation for a considerable time and has not paraffined since that time.

Having thus described my invention, it is obvious that in view of the many varied conditions under which petroleum and their products are treated and the various processes and the varied apparatus employed in refining and treating them, as well as the varied characteristics of the petroleums and their products, that considerable variation may be made from the above disclosure without departing from the spirit of my invention as set forth in the appended claims, which should be construed accordingly.

I claim:

1. In a process for removing deposits from pipe lines used for conveying crude oil, the step of passing through the lines a composition comprising naphthalene, anthracene, alkalies and sugar dissolved in oil that is being pumped through the lines.

2. In a process for removing deposits from pipe lines used for conveying crude oil, the step of passing through the lines a composition comprising naphthalene, anthracene, alkalies, sugar and phosphate rock dissolved in oil that is being pumped through the lines.

3. In a process for removing deposits from pipe lines used for conveying crude oil, the step of passing through the lines a composition comprising naphthalene, anthracene, sodium hydroxide, sugar and phosphate rock dissolved in oil that is being pumped through the lines.

4. In a process for removing deposits from pipe lines used for conveying crude oils, the step of passing through the lines a composition comprising naphthalene, anthracene, sodium hydroxide, sodium phosphate, sugar and phosphate rock dissolved in oil that is being pumped through the lines.

5. In a process for removing deposits from pipe lines used for conveying crude oils, the step of passing through the lines a composition comprising naphthalene, anthracene, sodium hydroxide, ammonium carbonate, sodium phosphate, sugar, and phosphate rock dissolved in oil that is being pumped through the lines.

In witness whereof, I have hereunto subscribed my name.

ALBERT H. ACKERMAN.