

May 5, 1964

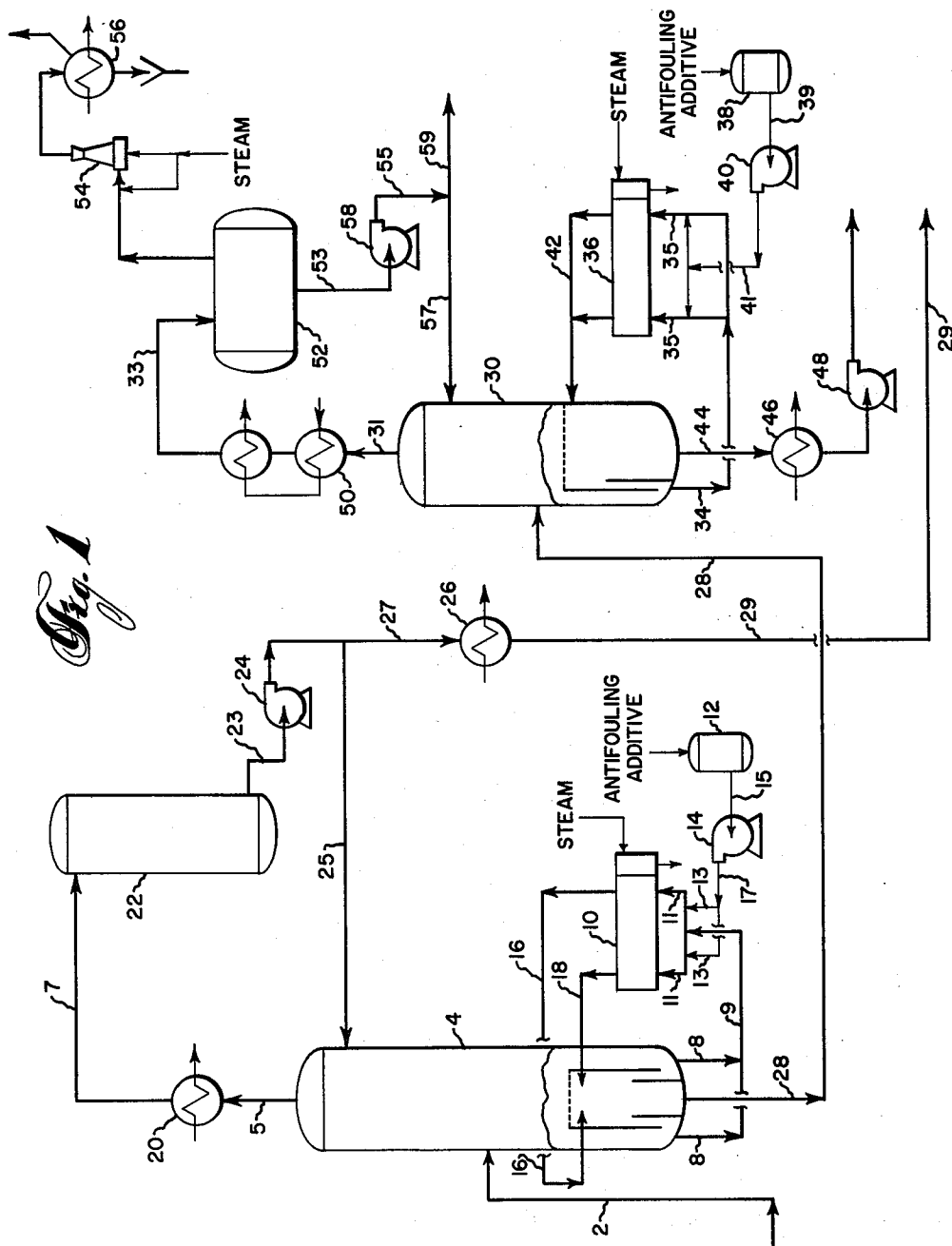
3

C. R. SUMMERS, JR
PROCESS FOR REDUCING FORMATION OF CARBONACEOUS
DEPOSITS ON HEAT TRANSFER SURFACES

3,132,085

Filed Sept. 22, 1960

2 Sheets-Sheet 1



INVENTOR.

CLAUDE R. SUMMERS, JR.

BY

51
Dana H. H. H.

ATTORNEY

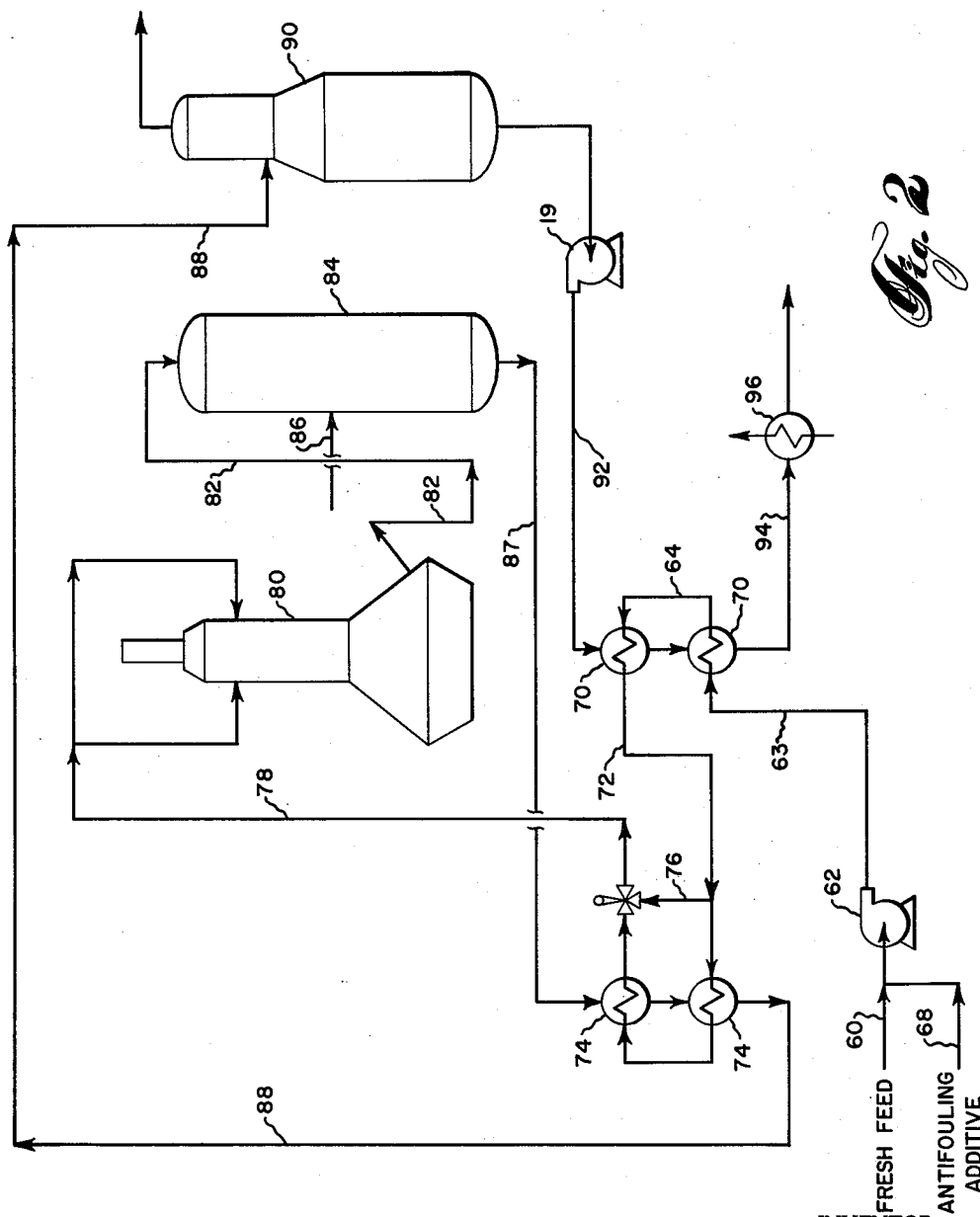
May 5, 1964

C. R. SUMMERS, JR
PROCESS FOR REDUCING FORMATION OF CARBONACEOUS
DEPOSITS ON HEAT TRANSFER SURFACES

3,132,085

Filed Sept. 22, 1960

2 Sheets-Sheet 2



INVENTOR.

CLAUDE R. SUMMERS, JR.

BY

ATTORNEY

1

3,132,085

PROCESS FOR REDUCING FORMATION OF CARBONACEOUS DEPOSITS ON HEAT TRANSFER SURFACES

Claude R. Summers, Jr., Media, Pa., assignor to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

Filed Sept. 22, 1960, Ser. No. 57,740

8 Claims. (Cl. 208-48)

This invention relates to a process for reducing the formation of heat-insulating, carbonaceous deposits on heat transfer surfaces that are contacted with thermally unstable hydrocarbon oils, such as alkylate gasoline, furnace oils, or the like, at temperatures of about 350° F. or more.

The passage of various hydrocarbon oil streams, for example, such as crude or partially refined alkylate gasoline, naphtha reforming feed stocks, virgin furnace oil distillates, light gas oil, thermally cracked gasoline, and the like over the heated metal surfaces of heat transfer equipment such as heat exchangers has been found to result in the deposition of a carbonaceous, coke-like scale upon the surfaces of the heat transfer equipment contacted by the oil streams when the oil streams are maintained in contact with heat transfer surfaces at temperatures of 350° F. or more for a sufficient period of time for thermal degradation of the thermally unstable components of the oil and also thermally accelerated oxidation to occur. These deposits are objectionable not only because they impede the flow of the oil streams through the heat transfer equipment, and consequently through the entire treating unit itself, but also because they greatly reduce the coefficient of heat transfer through the heat transfer surfaces. The reduction in heat transfer can result in insufficient heating of the oil stream by the heat transfer unit, resulting in relatively inefficient operation of processing equipment such as fractionation towers or the like associated with such heat transfer equipment.

To avoid the undesirable results described above, it has frequently been found necessary to shut down units involving fouled heat transfer surfaces substantially before the end of the design onstream period in order to remove the objectionable deposits from the heat exchanger surfaces. As a result of these premature shutdowns, reduced production and increased maintenance costs are experienced.

The present invention relates to a process for reducing formation of carbonaceous deposits on heat transfer surfaces by hydrocarbon oils that are thermally unstable at temperatures of about 350° F. or more, whereby increased efficiency in the operation of heat transfer equipment and processing equipment associated therewith is obtained and whereby maintenance costs and loss-of-use costs for processing equipment resulting from premature cleaning of heat transfer equipment are minimized. It has been found that such reduction of deposits can be obtained by incorporating in the aforementioned oil, prior to contact thereof with hot, heat transfer surfaces, a small amount of a condensation product formed by condensing ammonium hydroxide, formaldehyde, and a monoalkylphenol having from 4 to 12 carbon atoms in the alkyl substituent, at a temperature not exceeding about 200° F., the mole ratio of the formaldehyde and the monoalkylphenol with respect to the ammonium hydroxide being in the range of about 1 to 5:1 and 1 to 4:1, respectively. The oil then can be contacted with a heat transfer surface at a temperature of at least about 350° F. without excessive fouling of said surface. Excellent results have been obtained with condensation products of p-tetramethylbutylphenol, but condensation products derived from other monoalkylphenols also can be used.

2

A specific example of a preferred condensation product is the approximately 1:1.5:1 mole ratio condensation product of ammonium hydroxide, p-tetramethylbutylphenol and formaldehyde. The invention is especially useful in connection with hydrocarbon oils boiling above 100° F. and particularly with hydrocarbon oil distillates, 95 percent of which boils above 150° F., as such oils exhibit relatively less thermal stability than lower boiling oils. A specific example of a hydrocarbon oil with which the invention is useful is the debutanized distillation bottoms obtained from debutanizing crude alkylate gasoline product. Examples of other hydrocarbon oils that are benefited by the present invention are the naphtha or gasoline distillate feed to hydro-reforming units, the gas oil feed to fuel oil hydrogen-treating units, and the fuel feed to combustion gas turbine engines. The condensation products referred to herein are effective when employed in small amounts. Excellent results are normally obtainable by the use of proportions in the range of 1.5 to 35 pounds of condensation product per 1,000 barrels of hydrocarbon oil. However, larger or smaller amounts can be used.

The exact mechanism by which the high temperature deposits with which the present invention is concerned are formed has not been definitely established. It may be that improper control of conditions in some processing step previous to contact of the oil with heat transfer surfaces and/or perhaps incomplete separation of treating reagents promote formation of thermally unstable by-products that, in turn, promote formation of deposits on heat transfer surfaces contacted thereby. Nevertheless, it is emphasized that the deposits with which the present invention is concerned, that is, high temperature deposits, are unlike deposits formed at lower temperatures, that is, storage deposits. Whereas deposits formed in hydrocarbon oils at lower temperatures are normally soft and gummy in nature and contain no components comparable to those obtained during thermal degradation and thermally accelerated oxidation, the high temperature deposits referred to herein are hard, dense, and coke-like in nature and low in ash or metals content and contain components peculiar to thermal degradation and thermally accelerated oxidation reactions. Visual observation using a microscope shows typical deposits to be translucent, reddish-brown materials. Analysis in accordance with the ASTM D893 procedure of a typical deposit removed from the heat transfer surfaces of a debutanizer reboiler of an alkylation unit indicated the deposit to contain 39.22 percent hydrocarbon solvent-soluble material and 60.78 percent material insoluble in pentane, which insoluble material included insoluble resinous material of a tarry or bituminous nature similar to that produced from partial oxidation of crankcase lubricants during service. About 56.66 percent of the material that was insoluble in pentane was also insoluble in benzene. The benzene-insoluble materials include contaminants from external sources together with benzene-insoluble matter similar to that produced by partial oxidation and thermal decomposition of crankcase lubricants during service. Approximately 4.12 percent of the pentane-insoluble material included so-called insoluble resins. About 5.24 percent of the benzene-insoluble material—determined as the sulfated ash residue—included inorganic contaminants from external sources, such as metals and metallic compounds resulting from wear, corrosion, and the like. The distinction between low temperature or storage deposits and the high temperature deposits with which the present invention is concerned is emphasized by the fact that many of the oils that are benefited by the use of the present invention form no deposits whatsoever at temperatures below 350° F., whereas the same oils are found to form heavy heat exchanger deposits when contacted by heat

transfer surfaces at temperatures above 350° F. for periods of time sufficient to permit thermal decomposition to occur. The distinction between deposits with which the present invention is concerned and deposits formed at lower temperatures is further emphasized by the fact that many improvement agents that are effective to reduce deposits formed by hydrocarbon oils at temperatures below 350° F. have no effect whatsoever in reducing deposits formed at higher temperatures.

Referring briefly to the drawings, FIGURE 1 is a simplified flow diagram of a portion of a sulfuric acid alkylation unit embodying the present invention. FIGURE 2 is a simplified flow diagram of a furnace oil hydrogenation unit embodying the process of the present invention.

The condensation products whose use is included by the present invention are preferably prepared by simultaneous reaction of ammonium hydroxide, formaldehyde, and an alkylphenol of the class indicated at a moderately elevated temperature, say, 170° F., but not exceeding about 200° F. The reaction is exothermic, and undesirable by-products are apt to result if the temperature is allowed to become too high. After the condensation is completed, the temperature of the reaction mixture is raised to distill off all water, both that formed during the condensation reaction as well as that added with the reactants. The reactants are preferably employed in the proportions of about one to five moles of formaldehyde, and one to four moles of monoalkylphenol per mole of ammonium hydroxide.

The monoalkylphenols used in preparing the herein-disclosed condensation products have from 4 to 12 carbon atoms in the alkyl substituents. Thus, the alkyl substituents include normal or branched-chain butyl, amyl, hexyl, heptyl, octyl, decyl, and dodecyl radicals. A preferred alkyl substituent is the tetramethylbutyl radical. The monoalkylphenols are preferably obtained by alkylating phenol in known manner, in the presence of concentrated sulfuric acid, with olefins having from 4 to 12 carbon atoms. Olefins such as butene-1, isobutylene, the amylenes, diisobutylene, and triisobutylene are conveniently employed.

Although it is preferred to employ the reactants simultaneously or first to react the alkylphenol and ammonium hydroxide, followed by condensation with formaldehyde, the reaction sequence can be varied with good results. However, when the alkylphenol and formaldehyde are first reacted, a better reaction is effected by employing acidic alkylphenol containing some sulfuric acid alkylation catalyst, since the formaldehyde condensation reaction is facilitated by the presence of an acid or alkaline catalyst. When alkylphenols containing no sulfuric acid are employed, the ammonium hydroxide will catalyze condensation with formaldehyde as long as it is present when the formaldehyde is introduced.

In view of the multiple points in the respective molecules at which the reactants may react, it is believed that a mixture of compounds is obtained. The term "condensation product" as used herein is intended to include such mixtures.

The present invention can be employed in connection with any process involving heating of a hydrocarbon oil that normally tends to form deposits when heated to a temperature of about 350° F. or more for a period of time such that thermal decomposition of the oil can occur. Thus, the invention can be used in connection with processes involving heat treatment of a wide variety of hydrocarbon oils, especially hydrocarbon distillates boiling in the gasoline range or higher, including for example distillates such as gasoline, naphtha, jet fuel, gas oil, No. 2 fuel oil, or furnace oil, diesel fuel, lubricating oil, and the like. The invention is especially useful in connection with the heating of such oils by indirect heat transfer from one fluid to another, as opposed to, say, radiant heating, as the time involved in indirect heat trans-

fer is generally relatively greater and as the formation of even a small amount of deposits upon heat transfer surfaces of indirect heat exchangers greatly reduces heat transfer. In addition, formation of deposits in the relatively small fluid passageways on the tube side of such equipment, may appreciably restrict the volume of fluid flow adjacent such surfaces. A specific example of a process that involves heating of a thermally unstable hydrocarbon oil to temperatures above 350° F. by indirect heat exchange with a fluid and that is benefitted by the present invention is the product fractionation section of an alkylation process, for example, the sulfuric acid alkylation of olefins with isoparaffins to produce alkylate gasoline. More particularly, the alkylation of olefins with isoparaffin to produce alkylate gasoline normally involves, among other things, debutanization of the crude alkylate gasoline product, during which the product is contacted with heat transfer surfaces whose temperature is greater than 350° F. for periods of time such that thermal decomposition of the product and deposition of carbonaceous solids may take place on the heat transfer surfaces contacted by the oil. Incorporation in the oil of the anti-fouling agents disclosed herein prior to contact of the oil with the heat transfer surfaces will greatly reduce fouling of such surfaces by solid products of the thermal degradation of the hydrocarbon oil. Although the present invention has been found especially useful in reducing fouling of heat transfer surfaces by crude alkylate gasoline product, the invention can also be used to reduce fouling of heat transfer surfaces contacted with hydrocarbon oils in other processes. For example, the invention can be used to reduce fouling of heat-exchange equipment employed in the preheating of the No. 2 fuel oil feed to a catalytic hydrogen-treating unit. The invention can also be employed in reducing so-called preheater deposits that are formed on heat transfer surfaces of heat-exchange equipment adapted to transfer excess heat from aviation turbine engine lubricants to the fuel prior to combustion of the latter. As will be seen from the experimental results described hereinafter, the herein-disclosed condensation products are not only useful to prevent formation of heat transfer deposits, but also they are useful in effecting removal of preformed deposits.

The herein-disclosed condensation products are useful when incorporated in thermally unstable oils prior to heating the oils by contact with heat transfer surfaces maintained at temperatures of 350° F. or more, usually between about 350° F. and 1200° F., in amounts sufficient to reduce formation of carbonaceous deposits upon heat transfer surfaces. The optimum proportion of condensation product can vary somewhat depending upon the severity of the heat treatment to which the oil is exposed and upon the relative thermal instability of the oil. Excellent results are normally obtained when the condensation products are employed in small amounts. Thus, good results have been obtained by the use of the condensation products in amounts ranging from about 5 to 20 parts per million of oil (about 1.5 to 5 pounds of antifouling agent per 1,000 barrels of hydrocarbon oil), but larger or smaller amounts can be used. For example, there can be used 15 to 35 pounds or more of the condensation products per 1,000 barrels of hydrocarbon oil.

The herein-disclosed condensation products can be incorporated into the thermally unstable oil in any convenient way prior to contact of the oil with the hot heat transfer surfaces. Thus, the condensation products can be incorporated as such directly into the feed to the heat exchangers in which deposits normally are formed. However, in order to facilitate formation of a homogeneous mixture, it is preferred to incorporate a solution of the condensation product in a relatively stable light oil, preferably of similar character to the oil to which the anti-fouling agent is to be added, such as alkylate gasoline, kerosene, or the like, into the feed to the heat exchanger. Where the situation permits, that is, where the oil is

stored prior to contact with heat transfer surfaces, as in the case of aviation turbine engine fuels, the condensation products disclosed herein can be incorporated in the oil to be stabilized during or prior to storage. In such instances, the herein-disclosed condensation products may also improve the storage stability of the hydrocarbon oil, although the property of stabilizing a hydrocarbon oil under storage conditions does not necessarily follow the ability to stabilize at temperatures of 350° F. or more, or vice versa, in view of the difference in reactions that are required to be inhibited in the respective cases.

The herein-disclosed condensation products are especially useful for the purposes described by reason of the fact that they do not appear to survive substantially the contact of the fuel with the hot, heat transfer surfaces, as evidenced by the fact that the final products of processes embodying the present invention exhibit no difference in properties from the products obtained without the use of the antifouling agents.

Referring now in greater detail to FIGURE 1, which is a schematic representation of the debutanizer and rerun sections of a sulfuric acid alkylation unit, numeral 4 refers to a fractionation tower adapted to remove butane from a partly refined, crude alkylate gasoline product obtained by deisobutanizing, or fractionating to remove isobutane, a product obtained by alkylation of olefins, primarily butylene, with isoparaffins, primarily isobutane, in the presence of 98 percent sulfuric acid at a temperature of about 35 to 40° F., decanting and then washing, first with caustic soda and then with water, to neutralize any acid carry-over. Numeral 10 refers to a reboiler or heat exchanger adapted to introduce heat into debutanizer tower 4 whereby proper tower temperatures can be maintained. Numeral 30 refers to a rerun tower adapted to fractionate the deisobutanized and debutanized alkylate into a light alkylate, or alkylate overhead, and a heavy alkylate, or alkylate bottoms.

In a specific instance deisobutanized alkylate gasoline product is introduced into debutanizer tower 4 by way of line 2 at a temperature of about 207° F. The butane contained in the deisobutanized alkylate is separated from the alkylate product by fractionation through the tower trays, not shown. The butane separated passes overhead from the tower at a temperature of about 122° F. and at a pressure of about 58 p.s.i.g. through line 5, overhead condenser 20 and line 7, to debutanizer reflux drum 22 where liquefied butane is collected for reflux to debutanizer tower 4. The liquid reflux in drum 22 is at a temperature of 105° F. and at a pressure of 54 p.s.i.g. Reflux butane is withdrawn from drum 22 through line 23 by discharge reflux pump 24 and delivered to the upper portion of tower 4 through line 25 at a pressure of 126 p.s.i.g. The butane obtained from drum 22 that is not returned to the tower as reflux through line 25 is directed out of the system by way of line 27, condenser 26, and line 29 to storage.

Debutanized alkylate collects as distillation bottoms in the lower portion of the debutanizer tower 4. Debutanized alkylate is withdrawn from the bottom of tower 4 by way of lines 8 and 9 and lines 11 into debutanizer reboiler 10, which is a typical shell-and-tube-type heat exchanger bundle that is supplied with 12,000 pounds per hour of superheated steam at 175 p.s.i.g. and at approximately 440° F. Just prior to introduction of the debutanized alkylate bottoms into reboiler 10, antifouling agent is incorporated therein by injection into lines 11 of antifouling agent obtained from tank 12, line 15, proportioning pump 14 and lines 17 and 13. Antifouling agent is introduced into the alkylate bottoms in the proportion of about 33 parts per million or about 9 pounds of agent (33 percent solution) per 1,000 barrels of debutanized alkylate.

The antifouling agent injected into lines 11 is a condensation product prepared by charging 200 parts by weight of p-tetramethylbutylphenol to a closed kettle,

melting this material at about 140 to 150° F., and pumping 61 parts by weight of ammonium hydroxide—containing 29.4 percent ammonia—and 130 parts by weight of a 37 percent aqueous solution of formaldehyde into the kettle, with agitation of the mixture and while maintaining the temperature at about 160° to 170° F. The mole ratio of reactants in this instance is one mole of octylphenol and 1.5 moles of formaldehyde per mole of ammonia. The temperature is allowed to rise to 180° F. and 100 parts by weight of kerosene are added. The temperature of the reaction mixture is then raised to 280° F. to remove water. After releasing the pressure in the reaction system, the system is then placed under vacuum for a half-hour, cooled to 180° F. and 150 additional parts by weight of kerosene are added. The product is then stirred for one hour and 192 additional parts by weight of kerosene are added with further agitation. The total of 442 parts of kerosene added to the reaction product is sufficient to produce a 33 percent concentrate of the condensation product. A kerosene concentrate prepared as described had the following properties:

Gravity, ° API	29.3
Viscosity, SUV, 210° F	38.9
Flash, O.C., ° F	150
Fire, O.C., ° F	160
Pour, ° F	-50
Color, ASTM D1500	13.5
Sulfur, percent	0.08
Nitrogen, percent	1.03
Neutralization value	1.84
pH value	8.6
Ash, percent	0.007

Continuing with the description of a specific operation in the apparatus shown in FIGURE 1, debutanized alkylate bottoms containing the antifouling agent is contacted with the hot, heat transfer surfaces, which in this instance comprise the shell side of the heat exchanger tube bundle, for a period of time sufficient to elevate the temperature of the alkylate bottoms to about 292° F. Although the temperature of the alkylate removed from the reboiler 10 is only 292° F., it will be appreciated that the material actually contacted with the heat exchanger surfaces will approximate the temperature of the steam introduced into the heat exchanger, that is, 440° F. The heated debutanized alkylate, partly in vapor form, is fed back into debutanizer tower 4 by way of lines 16 and 18. The vapor portion of the heated alkylate product passes through the liquid contained on the upper surface of a perforated fractionating tray, not numbered, into the fractionating section of the tower, and the liquid portion of the heated alkylate bottoms is returned to the lower portion of the debutanizer tower 4.

Debutanized alkylate bottoms are withdrawn through the bottom of tower 4 by way of line 28 at a temperature of about 288° F. and this stream is introduced into the center portion of rerun column 30. The temperature of the alkylate product at the middle of column 30 is about 208° F. and the pressure of the system at this point is maintained at 18 inches Hg absolute. Within the rerun tower 30, deisobutanized and debutanized alkylate is fractionated into a light alkylate stream and a heavy alkylate stream.

Light alkylate product passes overhead from the rerun tower 30 through line 31 and through rerun overhead condenser 50, where the product is at least partially condensed. Cooled and condensed alkylate overhead then passes through line 33 into rerun reflux drum 52 which is maintained at a pressure of 13.2 inches Hg through operation of steam ejector 54. Steam ejector 54 is operated by passing therethrough steam at 175 p.s.i.g. Steam and vapors exhausted from the rerun reflux drum 52 are passed through ejector condenser 56, where the vapors and the portion of the steam are condensed. Condensate

is discarded, and the remaining uncondensed steam is vented to the atmosphere.

Light alkylate is withdrawn from reflux drum 52 through line 53 by means of discharge-reflux pump 58. Light alkylate passes from pump 58 into line 55 from which a portion is directed as reflux at a temperature of 94° F. and at a pressure of 242 p.s.i.g., through line 57 to the upper portion of rerun column 30 as reflux. The remainder of the light alkylate is passed to storage by way of line 59.

A portion of the heavy alkylate at the bottom of rerun tower 30 is withdrawn by way of line 34 and introduced into rerun reboiler 36 by way of lines 35. Just prior to introduction of the heavy alkylate into reboiler 36, anti-fouling agent is withdrawn from tank 33 through line 39 by means of proportioning pump 40 and introduced through line 41 into lines 35 in the proportion of about 23 parts per million or about six pounds of antifouling agent (33 percent solution) per 1,000 barrels of heavy alkylate. The antifouling agent in tank 33 in this instance is the same as that described above as being withdrawn from tank 12.

Within the reboiler 36 the inhibited heavy alkylate bottoms is heated to an outlet temperature of 352° F. by contact with the shell side of the heat exchanger tubes. The heat exchanger tubes are heated by passage there-through of 3,750 pounds per hour of 650 p.s.i.g. steam at a temperature of about 460° F. The heated heavy alkylate is returned to tower 30 by way of line 42. Vaporized heavy alkylate passes upwardly through the perforations of a fractionation tray, not numbered, to the fractionation section of rerun column 30. The unvaporized portion of the heavy alkylate is returned to the bottom of the tower 30. Heavy alkylate is withdrawn from the system by way of line 44 at a temperature of about 337° F. from which it is passed through rerun bottoms cooler 46 having an outlet temperature of about 79° F. The alkylate bottoms product is removed to storage by discharge bottoms pump 48 at a pressure of 78 p.s.i.g.

In order to determine the effect of incorporating the herein-disclosed antifouling agents in the thermally unstable oils that are in contact with heat transfer surfaces maintained at temperatures above 350° F., the antifouling agent described above was injected into the debutanizer reboiler bottoms of a sulfuric acid alkylation unit operated as described above, in the proportion of nine pounds of antifouling agent (33 percent solution) per 1,000 barrels bottoms, and the debutanizer bottoms temperature was observed over a period of 20 weeks. The observed temperatures were then compared with the corresponding temperatures over a similar test period during which no antifouling agent was employed. The temperature of the debutanizer bottoms stream is an indication of the extent to which fouling has taken place on the heat transfer surfaces of the debutanizer reboiler. As fouling of the heat transfer surfaces progresses, the amount of heat transfer will be reduced, whereby the temperature of the debutanizer bottoms stream will become lower. At the time the uninhibited test run was begun, the temperature of the debutanizer bottoms stream was about 293° F. After slightly more than 14 weeks, during which approximately 5,000 barrels per day of olefin-isoparaffin feed were charged to the unit, the temperature of the debutanizer bottoms stream had declined to about 270° F. At this time the unit feed was decreased to 2,000 barrels per day of olefin-isoparaffin charge for reasons having nothing to do with the test. After slightly more than five and one-half additional weeks, or a total of 20 weeks in all, the temperature of the debutanizer stream had further declined to about 253° F. Thus, during the entire 20-week period the temperature of the debutanizer bottoms stream declined from about 293° to about 253° F. or about 40°.

At the conclusion of the 20-week test period, without intermediate cleaning of the heat exchanger surfaces, nine pounds of the antifouling agent described above in con-

nection with the apparatus shown in FIGURE 1 per 1,000 barrels of debutanizer bottoms was added to the bottoms stream withdrawn from the debutanizer tower prior to passage of the latter through the debutanizer reboiler for an additional 20-week period. After an induction period of about eight weeks during which the temperature of the debutanizer bottoms stream further declined from 253° F. to 234° F., the temperature of the debutanizer bottoms stream began to increase and at the end of the 20-week period the temperature of this stream was found to be 290° F., or in other words, nearly as great as the 293° F. temperature 40 weeks previous.

Referring now to FIGURE 2 in detail, numerals 60 to 80 indicate the feed preheat system of a hydrogen treating unit for desulfurization and mild hydrogenation of No. 2 fuel oil distillate. Numeral 84 indicates a fixed bed catalytic hydrogenation reactor and numeral 90 indicates a separator for separating gaseous and liquid products obtained from hydrogenation reactor 84.

In a specific operation, a partly unsaturated, sulfur-containing No. 2 fuel oil distillate is introduced into the system by way of line 60, pump 62, and line 63. The anti-fouling agent hereinabove-described is injected into line 60 by way of line 68 in the proportion of about 15 parts per million or about five pounds (33 percent solution) per 1,000 barrels of feed. The mixture of feed and anti-fouling agent passes into line 63 at a temperature of about 107° F. and at a pressure of about 800 p.s.i.g. Line 63 directs the feed through the tube side of fresh feed-hydrogen treated oil product heat exchanger 70. This exchanger, as illustrated, consists of two shell-and-tube-type heat exchangers, connected by line 64, functioning as one unit. The temperature of the preheated feed is about 435° F. at the outlet of exchanger 70. The preheated feed passes from exchanger 70 through line 72, through the tube side of reactor effluent-fresh feed exchangers 74, which exchangers are provided with bypass 76, and the feed is then directed through line 78 at a temperature of 500° F. and at a pressure of about 510 p.s.i.g. to feed-recycle gas furnace 80. The heated feed passes from heater 80 via line 82 to reactor 84 which contains a fixed bed of a suitable hydrogenation catalyst supported upon an inert carrier and which is operated at an average temperature of about 667° F. and at a pressure of about 600 p.s.i.g. Hydrogen is supplied to reactor 84 at about 455 p.s.i.g. through line 86. The hydrogenated oil product is withdrawn from reactor 84 by way of line 87 at a temperature of about 581° F. and passed through the shell side of heat exchangers 74 in which the product stream is cooled to 477° F. The cooled product passes through line 88 to separator 90, which operates at a temperature of about 400° F. and at a pressure of about 15 p.s.i.g. Unreacted hydrogen and some hydrogenated product pass out of overhead separator 90 to a reflux drum, not shown, for collection and separation. The separator bottoms are withdrawn from separator 90 by discharge pump 19 through line 92 to the fresh feed-hydrogen treated oil product exchangers 70. The separator bottoms pass through the exchangers 70 on the shell side and are at a temperature of about 297° F. at the outlet of the exchanger. Hydrogenated product then passes through line 94 into cooler 96 and thence, at a temperature of about 112° F., to storage.

In order further to demonstrate the effectiveness of the present invention, test runs were carried out in a commercial hydrogen treating unit for desulfurizing and stabilizing No. 2 fuel oil distillate. In the presently described tests similarly as in those described previously, the temperature of the stream from the reactor effluent-fresh feed exchanger was first measured during a period of 20 weeks in which no antifouling agent was employed. The temperature of the feed stream removed from the reactor effluent-fresh feed exchanger is an indication of the degree to which fouling has occurred on the heat transfer surfaces both in the reactor effluent-fresh feed exchanger and in

the fresh feed-hydrogen treated oil product exchanger. For purposes of comparison, the temperature of the stream was later measured during another 20-week period. During the period the antifouling agent described in connection with the operation of the apparatus illustrated in FIGURE 2 was introduced into the unit feed prior to introduction of the latter into the fresh feed-hydrogen treated oil product exchanger, as illustrated in FIGURE 2, in the amount of five pounds of antifouling agent (33 percent solution) per 1,000 barrels of No. 2 fuel oil distillate charge. At the beginning of the first test period the temperature of the reactor effluent-fresh feed exchanger stream was about 426° F. After 20 weeks of operation the temperature of this stream had declined to about 353° F., a decrease of about 73° F. During the inhibited test run, the temperature of the reactor effluent-fresh feed exchanger stream at the beginning of the test was about 467° F. After 20 weeks of operation the temperature of this stream had declined only to about 436° F., or a reduction of only 31° F. Thus, notwithstanding that the inhibited test run was carried out at a higher temperature, the decline in temperature resulting from fouling of the heat transfer surfaces was less than one-half that encountered in the uninhibited test run.

In order further to demonstrate the effectiveness of the present invention, aviation turbine engine fuels to which an antifouling agent of the kind disclosed herein had been added in varying amounts were subjected to the conditions of the CFR fuel coker test procedure, described under the designation ASTM D1660 in the ASTM Standards on Petroleum Products and Lubricants, December 1959. The test procedure is designed to simulate the conditions occurring in some aviation turbine engines wherein the engine fuel is used as a heat sink to absorb heat accumulated by the engine lubricant during operation of the engine. Heat is transferred from the engine lubricant to the fuel by means of a heat exchanger. When the heat transfer surfaces of the fuel preheater become fouled due to deposits formed from the fuel, heat transfer becomes less efficient and cooling of engine lubricant is retarded. More particularly, the test is carried out by delivering fuel at a predetermined rate to a preheater section which simulates the hot fuel line sections of the engine as typified by the engine fuel-lubricating oil cooler. The extent of fouling of heat transfer surfaces in the preheater section is determined by inspection and is used in an index of the high temperature stability of the aviation turbine fuel in the heat exchanger section of an aviation turbine engine. Preheater deposits are rated according to the following scale: 0=no visible deposits; 1=visible haze or dulling, but no visible color; 2=barely visible discoloration; 3=light tan to peacock stain; 4=heavier than 3. Average preheater deposit rating is obtained by individually rating small sections of the preheater tube and then averaging all of the sectioned ratings. The preheated fuel passes from the preheater section through a heated filter section which represents the nozzle area or small passages in the vicinity of the combustion zone of the engine where fuel degradation products may become trapped. A precision, sintered, stainless steel filter is located in the heated filter section of the test apparatus to trap fuel degradation products formed during the test. The amount of the accumulation of deposits in the filter is measured by the increase in the pressure drop across the test filter. The test is normally conducted for 300 minutes or until the pressure drop across the filter exceeds 25 inches Hg, with a fuel delivery rate of six pounds per hour, a preheater temperature of 400° F. and a filter temperature of 500° F.

During the uninhibited test run it was found that the pressure differential drop across the filter reached 25 inches Hg after only 29 minutes, at which time the average preheater deposit rating was 0.6. Since the inhibited test runs were carried out for the full 300 minute-test period, the uninhibited test run was repeated with the

filter removed for the full test period to obtain an adequate basis for comparison of the extent of fouling taking place on the heat transfer surfaces of the preheater section of the test apparatus over the full test period.

- 5 The fuel employed in the test was a JP-5 aviation turbine engine fuel having the following properties.

Gravity, ° API	41.6
Viscosity, kinematic, cs., -30° F.	9.97
Flash, P-M, ° F.	148
Freezing point, ° F.	-62
Sulfur, percent	0.04
Corrosion test, MIL-F-5624	1
Existent gum, mg./100 ml.	2
Accelerated gum, mg./100 ml.	2
15 Aniline point, ° F.	140.8
Olefins, vol. percent	1
Aromatic content, vol. percent	18
Saturates, vol. percent	81
Heat of combustion, B.t.u./lb., net	18,526
20 Ash, percent	0.001
Smoke point, MIL-F-5624, mm.	21
Distillation, kerosene, ° F.:	
Over point	352
End point	496
25 10% evap. at	376
20% evap. at	386
50% evap. at	410
90% evap. at	464
Percent evap. at 400° F.	38

- 30 The antifouling agent employed was the 1:1.5:1 mole ratio ammonium hydroxide-formaldehyde-octylphenol condensation product described in connection with the description of the operation of the apparatus shown in FIGURE 1.

- 35 The results of the above-described tests were as follows:

Table

40 Composition	A	B	C	D
Make-Up, Vol. Percent:				
JP-5 Jet Engine Fuel	100	100	100	100
Additive Added, Lb./1,000 Bbl. 1:1.5:				
45 Mole Ratio Ammonium Hydroxide-Formaldehyde Octylphenol Condensation Product (33 Percent Solution)		20	30	50
Inspection:				
Thermal Stability Test—				
Time to Reach a Pressure Drop of 25 In. Hg, Min.	29	300	300	300
Average Preheater Deposit Rating	0.6	1.5	1.5	1.5
Pressure Drop at End of Test, In. Hg.	25	0.6	0	0
50 Test with Filter Removed, Average Preheater Deposit Rating	2.4			

- From the results presented in the foregoing table it will be seen that addition of antifouling agents of the class disclosed herein to uninhibited jet fuel in proportions of 20 to 50 pounds (33 percent active component) per 1,000 barrels of fuel reduced the average preheater deposit rating, that is, fouling of heat transfer surfaces in the preheater section, from 2.4 to 1.5. The results of the foregoing tests also demonstrate that the herein-disclosed antifouling agents possess detergent characteristics, since the use of the herein-disclosed materials prevent filter plugging over the full 300 minutes of the test; whereas the uninhibited fuel causes filter plugging after only 29 minutes.

- 65 The above-described embodiments are illustrative only and similar benefits also can be obtained by the use of the herein-disclosed antifouling agents in other thermally unstable hydrocarbon oils prior to contact with heat transfer surfaces at temperatures of 350° F. or more. For example, good results can be obtained by incorporating the herein-disclosed condensation products in thermally unstable naphtha reforming stocks, furnace oil, gas oil, thermally cracked gasoline, and lubricating stocks, in the proportion disclosed, prior to heating to temperatures of

350° F. or more. Similarly, the invention is not limited to the use of the 1:1.5:1 mole ratio ammonium hydroxide-formaldehyde-octylphenol condensation product employed in the specific embodiment. Thus, good results can be obtained by the use of condensation products obtained by 5 condensing at a temperature not exceeding 200° F. of the 1:2:2, 1:1:4, 1:4:1, or 1:5:4 mole ratio condensation products of ammonium hydroxide, formaldehyde, and alkylphenols such as isobutylphenol, diisobutylphenol, and triisobutylphenol.

The terms "No. 2 fuel oil" and "gasoline" are defined in ASTM Specifications D396, D439, and D910. Jet fuels, i.e., aviation grade turbine engine fuels are defined in the following specifications: MIL-J-5161E, MIL-J-5624D, MIL-F-25656, MIL-F-25524A, MIL-F-25558B, 15 MIL-R-25576B and American Airlines Spec. No. M6-4A.

Many modifications and variations as herein described will suggest themselves to those skilled in the art, and resort may be had to such modifications and variations without departing from the spirit and scope of the invention. Accordingly, only such limitations should be imposed as are indicated in the claims appended hereto.

I claim:

1. A process for reducing formation of carbonaceous deposits by thermally unstable hydrocarbon oils on hot, heat transfer surfaces contacted thereby comprising incorporating in a hydrocarbon oil that normally forms deposits upon hot, heat transfer surfaces prior to contact with said heat transfer surfaces a small amount, sufficient to reduce deposit formation, of a condensation product 30 formed from ammonium hydroxide, formaldehyde, and a monoalkylphenol having from 4 to 12 carbon atoms in the alkyl substituent, at a temperature not exceeding about 200° F., the mole ratio of the formaldehyde and the

monoalkylphenol with respect to the ammonium hydroxide being in the range of about 1 to 5:1 and 1 to 4:1, respectively, and then heating the oil by contact with a heat transfer surface at a temperature in excess of about 350° F.

2. The process of claim 1 where the temperature of the heat transfer surface with which the oil is contacted is about 350° F. to 1200° F.

3. The process of claim 1 where said small amount is about 1.5 to 35 pounds of said condensation product per 1,000 barrels of hydrocarbon oil.

4. The process of claim 1 where the monoalkylphenol is tetramethylbutylphenol and the mole ratio of the formaldehyde and the tetramethylbutylphenol with respect to the ammonium hydroxide is about 1.5:1 and about 1:1, respectively.

5. The process of claim 1 where the hydrocarbon oil is a debutanized alkylate gasoline distillation residue.

6. The process of claim 1 where the hydrocarbon oil is a heavy alkylate gasoline distillation residue boiling above about 325° F.

7. The process of claim 1 where the hydrocarbon oil is a distillate fuel oil.

8. The process of claim 1 where the hydrocarbon oil is an aviation turbine engine fuel.

References Cited in the file of this patent

UNITED STATES PATENTS

1,844,475	Morrell et al. -----	Feb. 9, 1932
2,019,559	Burke -----	Nov. 5, 1935
2,099,350	Stoesser -----	Nov. 16, 1937
2,453,850	Mikeska et al. -----	Nov. 16, 1948
2,940,922	Carl et al. -----	June 14, 1960

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,132,085

May 5, 1964

Claude R. Summers, Jr.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, in the table, under the heading "Composition", line 3 thereof, for "1:1.5:." read -- 1:1.5:1 --.

Signed and sealed this 8th day of September 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,132,085

May 5, 1964

Claude R. Summers, Jr.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, in the table, under the heading "Composition", line 3 thereof, for "1:1.5:." read -- 1:1.5:1 --.

Signed and sealed this 8th day of September 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents