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2,953,514

METHOD OF REDUCING HEAT EXCHANGER FOULING

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2 Sheets-Sheet 1

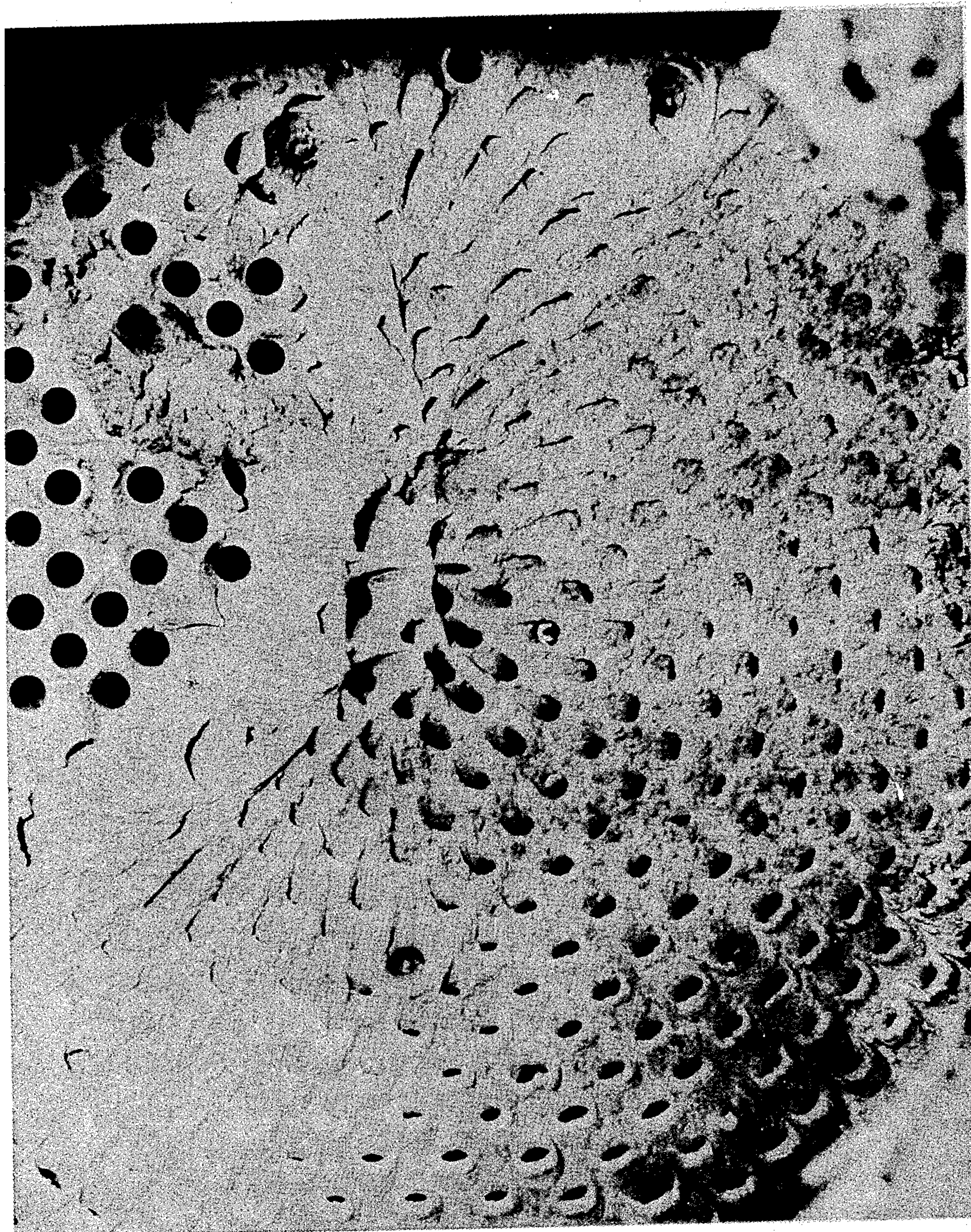


FIG. 1

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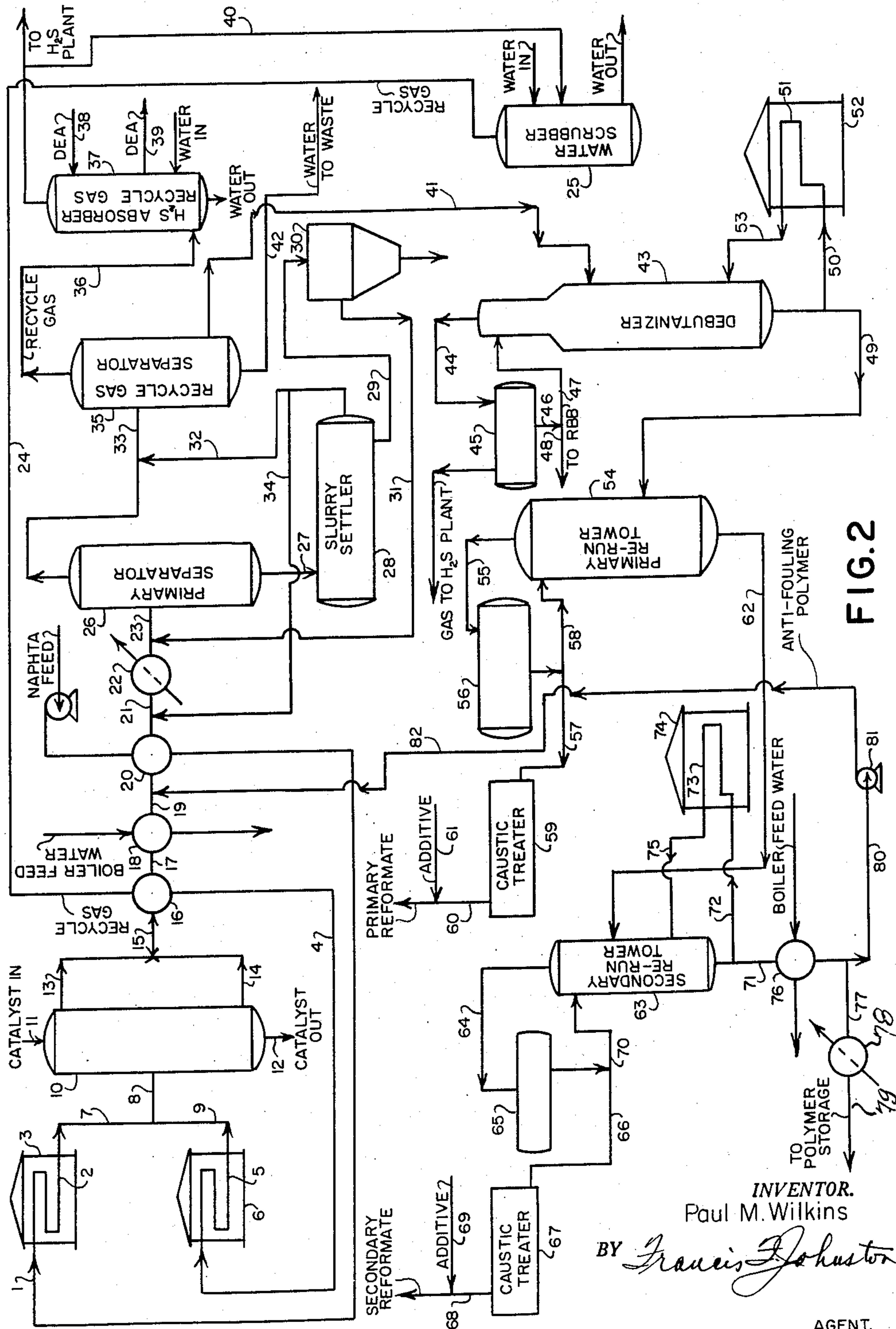
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2 Sheets-Sheet 2



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METHOD OF REDUCING HEAT EXCHANGER FOULING

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5 Claims. (Cl. 208—95)

The present invention relates to heat exchanger fouling and, more particularly, to the fouling of heat exchangers wherein heat exchange relationship is established between a reformed naphtha on the tube side of the heat exchanger and another fluid, for example, charge naphtha on the shell side of the heat exchanger.

For economical operation of any hydrocarbon conversion taking place at elevated temperatures it is necessary to recover as much of the heat energy put into the reaction as possible. For this purpose it is customary to heat exchange the reactor effluent with the charge stock, with the recycle gas, if any, and with other heat transfer media. In the reforming of naphtha which takes place at temperatures above about 800° F. it is conventional to provide an indirect heat exchange relation between the reformer effluent and the charge stock.

The conventional tube and shell heat exchanger is used for indirect heat exchange between the reformer effluent and the charge naphtha. In a tube and shell heat exchanger used for this purpose the reformer effluent, i.e., hydrogen-containing recycle gas and reformed naphtha flows through the tubes while the charge naphtha flows around the outside of the tubes. Such tube and shell heat exchangers are constructed with the tubes connecting to an inlet manifold and an outlet manifold through tube sheets. Figure 1 of the drawings is a photolithographic reproduction of the tube sheet of the inlet manifold of one of four tube and shell heat exchangers installed in two parallel banks of two exchangers in series wherein the reformer effluent is heat exchanged with the charge naphtha as noted briefly hereinbefore. The photograph was taken about fourteen days after the heat exchanger initially was put on-stream. Inspection of Figure 1 reveals that the tube sheet is badly fouled. This condition resulted in an increase in pressure drop across the heat exchanger of about 23 p.s.i. The heat exchangers in series were designed for a pressure drop of 3.8 p.s.i. at the rate of 187,000 pounds per hour and had operated at the designed pressure drop for about four days after start up. When the pressure drop had increased to about 23 p.s.i. the heat exchanger was opened for inspection. The inspection revealed, as does Figure 1, a reproduction of a photograph taken at that time, that the tube sheets and tubes were badly fouled with a deposit. Difficulty was experienced in drilling the deposit from the tubes by use of the conventional hydraulically activated drill. Therefore, it was necessary to discover some means whereby the deposit could be removed more readily or find a means whereby the formation of the deposit could be eliminated or its deposition reduced and thus provide a longer period during which the heat exchanger could be kept on-stream without disabling increase in the pressure differential across the heat exchanger or excessive loss of temperature.

The present invention has as its object a method of reducing the rate of deposition of material fouling heat exchangers in service providing indirect heat exchange relation between a reformer effluent and another fluid in which the reformer effluent is at a temperature below about 500° to 600° F. at the entry to or during passage through the heat exchanger. The present invention has as another object the injection into the reformer effluent

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at a point in the system upstream of the point at which the temperature of the reformer effluent is about 450° F. or lower of a diluent or solvent for at least one component of the deposit on the tube side of the heat exchanger. It is a further object of the present invention to inject an aromatic hydrocarbon having a boiling point of at least 450° F. or a highly aromatic mixture of hydrocarbons having an initial boiling point of at least 400° F. and preferably of at least about 450° F. into the reformer effluent at a point upstream of the point in the system at which the temperature of the reactor effluent is below about 500° F. Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description taken in conjunction with the drawing Figure 2 which is a highly schematic flow sheet of a reforming unit showing several heat exchangers, fractionators, etc. and the point in the system upstream of the point at which the temperature of the reformer effluent drops to 450° F. or below at which it is preferred to introduce the preferred highly aromatic mixture of hydrocarbons having an initial boiling point of at least about 450° F.

Illustrative of the environment in which the problem for which the present invention is the solution arises is the highly schematic flow sheet of Figure 2. In the flow sheet a naphtha to be reformed flows, under a pressure in excess of reactor pressure, through pipe 1 to coil 2 in heater or furnace 3. In coil 2 the temperature of the naphtha is raised to a temperature within the range of about 850° F. to about 1080° F., preferably within the range of about 960° F. to about 1060° F.

Hydrogen-containing gas, such as recycle gas, flows under pressure greater than reactor pressure through conduit 4 to coil 5 in heater or furnace 6 where the hydrogen-containing gas is heated to a temperature within the range 1000° to 1400° F. such that when mixed with the heated charge naphtha in the ratio of about 1 to about 8 mols, preferably about 2 to about 5 mols of hydrogen per mol of charge naphtha to form a charge mixture, the charge mixture has a reaction temperature within the range of about 850° F. to about 1080° F., preferably about 960° F. to about 1060° F. The heated charge naphtha flows from heater 3 through pipe 7 to conduit 8. The heated hydrogen-containing gas flows from heater 6 through conduit 9. The heated naphtha and hydrogen-containing gas are mixed in conduit 8 in the proportions set forth hereinbefore.

In Figure 2 the reactor 10 in which the reforming reaction(s) takes place is illustrated as employing the moving bed technique for details of which those skilled in the art are referred to U.S. Patents Nos. 2,724,683, 2,726,994, 2,742,404 and others. Suitable catalysts are reforming catalysts, for example, comprising an oxide of one or more metals of group VI, left column, such as one comprising at least 70 weight percent alumina and the balance chromium oxide, usually designated chromia-alumina catalyst, or, for example, comprising a mixture of oxides of cobalt and molybdenum on a carrier such as alumina, or, for example, comprising about 0.1 to about 10 weight percent platinum group metal, balance alumina.

As illustrated, hot active reforming catalyst flows from a source not shown at at least reactor pressure through conduit 11 into reactor 10. The catalyst flows downwardly through reactor 10 as a substantially compact column of particle-form solid reforming catalyst. The at least partially deactivated catalyst flows from reactor 10 through conduit 12. While the flow sheet insofar as it relates to the reactor is illustrative of the moving bed technique, the reactor 10 can be operated in accordance with the fluidized technique or the static bed technique. It is to be noted that the type of reactor whether of the

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moving bed, the fluidized bed or the static bed type has little, if any, affect upon the deposition of heat exchange fouling material from the reactor effluent at temperatures below about 450° to about 500° F.

The charge mixture, i.e., charge naphtha and hydrogen-containing gas flows to reactor 10 through conduit 8. As illustrated, reactor 10 is piped to introduce the charge mixture into reactor 10 at a point intermediate the catalyst inlet and outlet. By means well known to those skilled in the art a portion of the charge mixture is caused to flow upwardly countercurrently to the downwardly flowing column of catalyst while the balance of the charge mixture is caused to flow downwardly concurrently with the downwardly flowing column of catalyst. The products of reaction flow from the upper reaction zone through conduit 13 while the products of reaction flow from the lower reaction zone through conduit 14. The reaction products from both zones mix in conduit 15 and flow to heat exchanger 16 where the total reactor effluent is in indirect heat exchange relationship with hydrogen-containing recycle gas flowing through conduit 24 from scrubber 25 on its way to the recycle gas heater 6. From heat exchanger 16 the total reactor effluent flows through conduit 17 to heat exchanger 18 where the total reactor effluent is in indirect heat exchange relationship with boiler feed water. From heat exchanger 18 the total reactor effluent flows through conduit 19 to heat exchanger 20 where the total reactor effluent is in indirect heat exchange relationship with the charge naphtha.

Between heat exchangers 18 and 20 the temperature of the reactor effluent falls to about 450° to about 500° F. As a consequence it is in heat exchanger 20 that the material is deposited which raises the pressure differential across the heat exchanger train. The photograph reproduced here as Figure 1 is of the tube sheet at the inlet of heat exchanger 20. In accordance with the principles of the present invention an aromatic hydrocarbon or a highly aromatic mixture of hydrocarbons boiling at least above about 450° F. is introduced into the stream of reactor effluent at a point upstream of heat exchanger 20. It is presently preferred to inject a stream of polymer obtained as hereinafter described into the stream of reactor effluent between heat exchanger 18 and heat exchanger 20 as, for example, into conduit 19.

From heat exchanger 20 the total reactor effluent flows through conduit 21 to cooler 22 where the total reactor effluent is cooled to a temperature at the pressure existing of the order of 100 to 600 p.s.i.g., say about 140 p.s.i.g., at which the C₅ and C₅+ hydrocarbons in the total reactor effluent are condensed. From cooler 22 the condensed and uncondensed reactor effluent flow through conduit 23 to primary gas-liquid separator 26.

It is preferred to introduce a hydrocarbon quench stream comprising condensed reactor effluent into the total reactor effluent flowing through conduit 21 as hereinafter described. It is also preferred to introduce water into the effluent from cooler 22 as in conduit 23 as hereinafter described.

In primary separator 26 water and catalyst fines together with some of the heavier hydrocarbons form the liquid phase and are drawn off through pipe 27 to settler 28. In settler 28 a slurry of catalyst fines in water is drawn off through pipe 29 to fines settler 30. The water separates from the slurry in fines settler 30 and flows therefrom through pipe 31 back to conduit 23 for injection into the total reactor effluent stream. The catalyst fines are withdrawn from settler 30 to storage, waste or other disposal.

In slurry settler 28 an upper phase comprising heavier hydrocarbons, i.e., those hydrocarbons condensed at about the same temperature as water at the pressure existing in primary settler 26, forms and is withdrawn through pipe 32. The withdrawn hydrocarbons flow through pipe

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32 to pipe 33 where the withdrawn hydrocarbons are mixed with the uncondensed reactor effluent flowing from primary separator 26 through conduit 33. A portion of the hydrocarbons withdrawn from slurry settler 28 through pipe 32 is returned to pipe 21 through pipe 34 to serve as a quench for the reactor effluent. In general, about 0 to about 0.26 barrels of condensed hydrocarbons per barrel of charge naphtha are diverted from pipe 32 to pipe 34 as a quench stream.

The uncondensed reactor effluent flows from primary separator 26 through conduit 33, mixes with the condensed hydrocarbons withdrawn from settler 28 flowing through pipe 32 and the mixture is separated in recycle gas separator 35 into a gaseous phase comprising hydrogen, hydrogen sulfide and C₁ to C₄ hydrocarbons and a liquid phase comprising C₅ and heavier hydrocarbons. The gaseous, hydrogen-containing phase, hereinafter designated recycle gas, flows from separator 35 through conduit 36 to hydrogen sulfide absorber 37. As illustrated, the hydrogen sulfide absorber employs diethylaniline solution as the absorbent. The amine solution flows from a source not shown through pipe 38 to the scrubber 37, downwardly therethrough countercurrently to the upwardly flowing recycle gas from which the lean amine solution extracts the hydrogen sulfide to produce a fat amine solution. The fat amine solution flows from scrubber 37 through pipe 39 to an amine regenerator where the hydrogen sulfide is volatilized and the amine solution thus regenerated to provide a lean amine solution. The recycle gas stripped of hydrogen sulfide flows from recycle gas absorber 37 through conduit 40 to scrubber 25 where the recycle gas is scrubbed with water. The recycle gas flows from scrubber 25 through conduit 24 to heat exchanger 16.

In recycle gas separator 35 a liquid comprising C₅ and heavier hydrocarbons separates and is withdrawn through pipe 41. Any water carried into the separator is drawn off through pipe 42.

The C₅ and heavier hydrocarbons flow from separator 35 through pipe 41 to debutanizer 43. In debutanizer 43 a C₄ and lighter cut containing residual hydrogen sulfide and hydrogen is taken overhead through pipe 44 to accumulator 45. In accumulator 45, C₄ hydrocarbons form a liquid phase part of which is withdrawn through pipes 46 and 47 as reflux for debutanizer 43. The balance of the C₄ hydrocarbons is withdrawn from accumulator 45 through pipes 46 and 48 to butane-butylene storage not shown.

The bottoms of the debutanizer, i.e., C₅ and heavier hydrocarbons, flows from debutanizer 43 through pipe 49. A minor portion of the bottoms is diverted through pipe 50, coil 51 in heater 52 and returned through pipe 53 to debutanizer 43 to maintain a temperature therein at which C₄ and lighter hydrocarbons are volatile. The major portion of the debutanizer bottoms flows through pipe 49 to primary rerun tower 54.

In primary rerun tower 54 a primary reformat having a high octane number is taken overhead through pipe 55 to accumulator 56. From accumulator 56 the primary reformat flows through pipe 57 to caustic treater 59 where the primary reformat is washed with aqueous caustic soda for the removal of traces of hydrogen sulfide and other sulfur compounds. From caustic treater 59 the primary reformat flows through pipe 60 to further finishing, distribution and/or storage. When desirable, one or more additives such as gum inhibitor can be added to the primary reformat in pipe 60 through pipe 61. A minor portion of the primary reformat is diverted from pipe 57 through pipe 58 to primary rerun tower 54 to serve as a reflux.

The bottoms of primary rerun tower 54 flow therefrom through pipe 62 to secondary rerun tower 63. In secondary rerun tower 63 a secondary reformat is taken as overhead through pipe 64 to accumulator 65. The

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secondary reformat flows from accumulator 65 through pipe 66 to caustic treater 67 where the secondary reformat is contacted with aqueous caustic soda to remove traces of hydrogen sulfide and other sulfur compounds. From caustic treater 67 the secondary reformat flows through pipe 68 to further finishing as the addition of additives, for example, gum inhibitor added from pipe 69, distribution or storage. A portion of the secondary reformat flowing from accumulator 65 is diverted through pipe 70 to secondary rerun tower 63 to serve as a reflux.

The bottoms of secondary rerun tower 63 have an initial boiling point of at least 450° F. and usually above 450° F. The bottoms flows from secondary rerun tower 63 through pipes 71 and 72 to coil 73 in heater 74 and back to secondary rerun tower 63 through pipe 75 whereby the temperature in secondary rerun tower is maintained high enough to volatilize constituents of the feed to tower 63 boiling below about 450° F. The balance of the bottoms of tower 63 flows through pipe 71 to heat exchanger 76 where the bottoms of tower 63 is in indirect heat exchange relationship with boiler feed water. From heat exchanger 76 the tower bottoms, designated "polymer," flows through pipe 77 to cooler 78 and thence through pipe 79 to polymer storage not shown.

As stated hereinbefore, fouling of piping and heat exchangers downstream of the point where the temperature of the total reactor effluent falls below 500° F. can be prevented or reduced by injecting sufficient aromatic hydrocarbons or highly aromatic mixture of hydrocarbons boiling at least at about 450° F. to dissolve or hold in suspension the material which is deposited from the reactor effluent in the piping and heat exchangers at temperatures below about 500° F. The "polymer" recovered as bottoms of secondary rerun tower 63 is such a suitable material as is evident from the following tabulation illustrative of the characteristics thereof.

Gravity, ° API	7
Distillation:	
Initial boiling point ° F	470
10 percent point ° F	486
50 percent point ° F	543
90 percent point ° F	728
End point ° F	760
Sulfur, weight percent	0.10
Aromatic hydrocarbons, volume percent	47
Viscosity, S.U.S. @ 100° F	46
Pour point, ° F	10

Another "polymer" material which has provided satisfactory heat exchanger operation has the composition and characteristics set forth hereinafter.

Gravity	7
Flash, ° F	230
Viscosity, S.U.S. @ 100° F	37
Distillation:	
IBP ° F	456
10 percent point ° F	472
50 percent point ° F	502
87 percent point ° F	650
Aromatics, volume percent	70
Olefins, volume percent	16
Bromine No	12.4
Ash, weight percent	0.06
Conradson carbon residue, weight percent	1.21
Pour point, ° F	Below 20
Sulfur, weight percent	0.23
Unulfonated residue, volume percent	14
Mercaptan	Nil

Although a material having an initial boiling point above 450° F. is preferred, a highly aromatic fraction having an initial boiling point of about 450° F. can be used. Thus, for example, a substantially sulfur dioxide free extract obtained by extracting gas oil with sulfur di-

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oxide can be used although the initial boiling point of the extract is only 450° F. Illustrative of such anti-fouling additives is a sulfur dioxide extract of the gas oil fraction from a catalytic cracking operation the characteristics of which are given in the following tabulation:

Gravity, ° API	14
Distillation:	
Initial boiling point, ° F	450
10 percent point, ° F	500
50 percent point, ° F	550
90 percent point, ° F	625
End point, ° F	665
Sulfur, weight percent	1.3
Aromatic hydrocarbons, volume percent	55
Pour point, ° F	<-20

Reference is made to Figure 2. In accordance with the principles of the present invention or anti-fouling additive comprising at least one aromatic hydrocarbon having a boiling point of at least 450° F. is mixed with the reforming reactor effluent before the temperature of the reforming reactor effluent has fallen below about 450° F. A suitable anti-fouling additive is the polymer bottoms of secondary rerun tower 63. Accordingly, it is preferred to use a portion of the polymer bottoms of secondary rerun tower 63 as an anti-fouling additive. In accordance with the principles of the present invention a portion of the polymer bottoms flowing through pipe 71 and preferably after the polymer bottoms has been cooled in cooler 76 is diverted from pipe 77 through pipe 80 to the suction side of pump 81. Pump 81 discharges into pipe 82 through which the polymer bottoms flows, preferably to pipe 19 intermediate heat exchangers 18 and 20. Since the anti-fouling effect of the additive is only obtained when it is added in amount sufficient to hold the fouling material in the liquid phase and at temperatures at which the anti-fouling additive is preponderantly in the liquid phase the point of introduction of the anti-fouling additive into the reactor effluent is dependent upon the boiling point of the additive at the pressure under which the reactor effluent exists and above 450° F. Accordingly, the anti-fouling additive is admixed with the reactor effluent at a point upstream of the point in the system at which the temperature of the reactor effluent falls below about 500° F., say upstream of the point where the temperature of the reactor effluent is about 450° F.

It has been found that for a unit reforming 19,000 barrels of naphtha per stream day the minimum requirement of anti-fouling additive such as the aforescribed polymer bottoms is about 500 barrels of polymer per stream day or about 26 barrels of polymer per 1000 barrels of naphtha. However, as much as 1500 barrels of polymer per 19,000 barrels of naphtha has been admixed with the total reactor effluent. The increased amount of polymer did not provide further improvement since the addition of 26 barrels of polymer per 1000 barrels of naphtha charged has kept the pressure differential across the heat exchanger within the design limit.

Illustrative of the affect of adding polymer to the total reactor effluent at a point up-stream of the point in the system where the temperature of the reactor effluent falls to 450° F. is the data set forth in the following table:

ΔT, hrs.	Exchanger Bank A*			Exchanger Bank B*		
	Inlet Pressure, p.s.i.g.	Outlet Pressure, p.s.i.g.	ΔP, p.s.i.	Inlet Pressure, p.s.i.g.	Outlet Pressure, p.s.i.g.	ΔP, p.s.i.
0	156	140	16	165	138	21
2.75	polymer added					
8	160	150	10	160	150	10
16	153	145	8	154	144	10
24	155	150	5	158	146	12
32	154	150	4	155	145	10
40	151	148	3	150	144	6

*Two heat exchangers in series.

Exchangers A and B operate in parallel.

The data given in the table show that approximately 5 hours (8-2.75) after polymer was added to the total reactor effluent the pressure drop across exchanger bank A had decreased from 16 p.s.i. to 10 p.s.i. and reached a minimum after about 37 hours (40-2.75) of 3 p.s.i. It will also be observed that the initial pressure drop across exchanger bank B was much greater than the initial pressure drop across exchanger bank A. This difference is accounted for by the fact that exchanger bank B had been in service for a longer period of time and exhibited a greater degree of fouling than exchanger bank A. Since the exchangers are operated in parallel and the flow rates are not individually controlled by instrumentation, it is possible that one exchanger bank received a disproportionate amount of reactor effluent resulting in the difference in pressure drops. However, it will also be observed that, although the pressure drop across exchanger bank B originally was 27 p.s.i.g. compared with 16 p.s.i.g. pressure differential across exchanger bank A, nevertheless, the pressure drop across exchanger bank B was reduced to 6 p.s.i. as compared with 3 p.s.i. for exchanger bank A after addition of polymer for about 37 hours. While total process rates were maintained substantially constant during the 40-hour period the amount of polymer added to the total reactor effluent was reduced from an initial rate of 750 barrels per stream day to each exchanger bank to 500 barrels after about 24 hours and further reduced to about 400 barrels at the end of 40 hours. More recently, the amount of polymer has been reduced to 250 barrels per stream day to each exchanger bank and found to substantially eliminate fouling of the heat exchangers.

The total reactor effluent enters conduit 19 at a temperature of about 450 to 600° F. The polymer is introduced into conduit 19 at a temperature of about 250° F. Prior to introduction of polymer into the system upstream of exchanger 20 the exchanger(s) were fouled sufficiently at the end of fourteen days to require a shutdown for cleaning. Since addition of polymer upstream of exchanger 20 it has been unnecessary to shut the exchanger(s) down to remove any fouling deposits. Thus, during a period of at least several months the addition of polymer upstream of the point at which the temperature of the total reactor effluent has fallen below 500° F. has maintained clean exchangers substantially free from deposits of the nature which caused the increase in pressure drop discussed hereinbefore. While greater amounts of polymer than 26 barrels per 1000 barrels of charge can be injected there are economic disadvantages which result from the injection of more than a minimal amount of anti-fouling additive. Larger amounts of injected poly-

mer increase the power costs for additional pumping, the expense of heating and the expense of cooling the surplus polymer or anti-fouling additive. Accordingly, it is preferred to inject not more than about 26 barrels of aromatic hydrocarbon per 1000 barrels of charge into the total reactor effluent at a point upstream of the point in the system at which the temperature of the total reactor effluent reaches about 450° to about 500° F.

I claim:

1. In the reforming of naphtha wherein a charge naphtha is contacted with particle-form solid reforming catalyst in the presence of hydrogen at reforming temperature to produce a reactor effluent having a temperature of at least 700° F., and wherein the aforesaid reactor effluent is in indirect heat exchange with another fluid at temperatures below about 500° F. in an indirect heat exchanger, the improvement which comprises injecting at least one aromatic hydrocarbon having a boiling point of at least 400° F. into said reactor effluent before the temperature thereof is lowered below about 500° F. thereby maintaining the pressure drop across said indirect heat exchanger substantially constant.

2. The improvement set forth in claim 1 wherein a hydrocarbon mixture containing at least about 47 volume percent of aromatic hydrocarbons and having a 10 percent point of at least 450° F. is injected into said effluent before the temperature of said effluent is lowered below about 500° F.

3. The improvement set forth in claim 1 wherein polymer containing at least about 47 volume percent aromatic hydrocarbons and having a 10 percent point of at least 450° F. is injected into said effluent before the temperature of said effluent is lowered below about 500° F.

4. The improvement set forth in claim 1 wherein a portion of liquid reformat having an initial boiling point of at least 450° F. is injected into the reactor effluent.

5. The improvement set forth in claim 1 wherein at least 26 barrels of polymer per 1,000 barrels of charge naphtha are injected into said reactor effluent, and wherein said polymer has a 10 percent point of at least 450° F.

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