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(54) Polyamides and anti-fouling compositions containing them.

(57) Novel liquid polyamides of formula $RCONH(CH_2CH_2NH)_n$-OCR where R is alkyl or alkenyl with 10 to 22 carbon atoms and n is an integer in the range 1 to 4 may be used in compositions to reduce fouling on heat exchange surfaces.

EP 0 087 277 A2

POLYAMIDES AND ANTI-FOULING COMPOSITIONS CONTAINING THEM

The present invention relates to novel polyamides, and to compositions containing said additives alone or in combination with other active ingredients for reducing the tendency of a petroleum material (either crude oil or petroleum fractions) to foul heat exchange surfaces (eg heat exchange tubes) when the heated petroleum material is in contact with heat exchange surface. The present invention further relates to an improved process for exchanging heat with a hot petroleum material through a heat exchange surface. The process is particularly applicable to heating petroleum materials by contact with a heat exchange material.

Heat transfer through heat exchangers is often reduced during operation due to the fouling of the tube walls by deposition from the process stream. Fouled exchangers then operate at lower efficiencies and this often results in throughput reductions and frequent shutdowns for cleaning.

The most serious heat exchanger fouling problem within oil refineries usually exists in the crude oil distillation unit (CDU) preheat train where the hottest exchanger, i.e. the one immediately prior to the furnace, is particularly susceptible to fouling by deposits which build up so quickly that frequent cleaning is required, sometimes as often as every four months.

In order that the distillation column inlet temperature is maintained so that fractionation efficiency and hence product quality is not lost, the heat input drop due to fouled exchangers has to be made up by increased firing of the furnace. With current fuel oil prices this can represent a significant increase in operating costs.

Analysis of deposits taken from these refinery exchangers indicates that both inorganic and organic deposition occurs, with the proportions of each varying from unit to unit. The inorganic deposits are predominantly salts of iron (corrosion products), sodium (salt in the water associated with crude oil and from caustic soda injection) and calcium and magnesium (hardness salts in desalter water). A high proportion of these salts originate from the desalter where salt is extracted from the crude oil by washing with water. The crude oil leaving the desalter can contain as much as 0.3% wt dissolved water. In addition to this dissolved water, carry-over of a separate water phase occurs from time to time and it is this aqueous phase which contains the iron corrosion products, the hardness salts and the alkali being injected to prevent corrosion of the column overheads condenser. At the temperatures in these hottest exchangers, particularly at the outlet end, some of the water can be vaporised so that even soluble salts can be deposited on the metal surfaces. Simultaneous lay-down of hydrocarbon polymers with their subsequent conversion to coke probably binds the inorganics into a hard deposit which is not readily flushed away by the flowing oil.

Frequent cleaning of heat exchangers is to be avoided for several reasons. Cleaning of the hottest CDU pre-heat exchangers usually requires the unit to be shut down or, if the exchangers are in parallel banks which can be isolated, the throughput to be reduced. Cleaning, particularly mechanical, requires a large maintenance effort and often lasts several days for each exchanger.

An alternative solution to the problem is the injection of an effective anti-foulant into the crude oil stream before it enters the heat exchanger. Anti-foulants are usually blends of additives in an organic solvent with injection levels in the range 5 - 30 ppm on crude. Because fouling is so complex and covers several different types and mechanisms, the active ingredients of anti-foulants can be very varied. Examples of anti-foulant types include dispersants, detergents, metal co-ordinators, anti-oxidants, film formers, corrosion inhibitors and anti-polymerants.

There is on the market a wide range of anti-foulants. The assessment of anti-foulants on a commercial unit is an expensive and time-consuming operation as a full trial would have to be run for several months. Some trials have even resulted in increased fouling. It is therefore desirable to carry out tests in the laboratory with the hydrocarbon stream and the anti-foulants before any refinery trials are planned.

Our British Patent Specification 1564757 discloses and claims a method for evaluating the fouling tendency of a heated liquid crude oil or petroleum fraction which method comprises heating the liquid, adding to it a solution or suspension containing one or more inorganic and/or organic foulants to give an enhanced concentration of foulant in the liquid, passing the resulting liquid through a heated tubular test section and measuring over a period of time the increase in pressure drop across the test section and/or the decrease in temperature of the liquid at the outlet of the test section.

The fouling produced in this method is similar to that produced in refinery heat exchangers, being a mixture of organic and inorganic deposits.

An alternative test for detecting fouling tendencies which is well known in the petroleum industry is the Jet Fuel Thermal Oxidation Test (JFTOT) - ASTM Test D-3241-74T. In this case, however, the deposits produced are wholly organic.

The selection of active ingredients for anti-foulant blends is a difficult and unpredictable exercise.

The present invention provides novel polyamides of the formula given below.

Thus, according to the present invention there is provided a liquid polyamide of general formula

$$R\ CONH\ (CH_2CH_2NH)_n\ OCR \qquad (I)$$

wherein R is an alkyl or alkenyl group containing 10 to 22 carbon atoms, and n is an integer in the range 1 to 4.

By liquid polyamide we mean a polyamide which is liquid at 25°C and atmospheric pressure.

Oil soluble compounds having the above formula are useful components of anti-fouling additives either alone as a solution in a solvent miscible with the petroleum material, or in admixture with other active materials. The oil soluble polyamides may have an anti-fouling action on their own in certain situations, which may be enhanced by the addition of other materials. In other situations the polyamides alone may increase fouling, but in combination with other additives will reduce fouling as explained below.

In a preferred polyamide R is alkenyl containing 17 carbon atoms. Preferably n is 2.

The novel polyamides may be prepared by reacting together a carboxylic acid of formula RCOOH and a polyamine of formula

$$NH_2(CH_2CH_2NH)_nH.$$

It is preferred to use carboxylic acids which are liquid at 25°C and atmospheric pressure.

Examples of suitable saturated carboxylic acids (ie R = alkyl) are dodecanoic acid (lauric acid), hexadecanoic acid (palmitic acid). An example of a suitable ethylenically unsaturated carboxylic acid (ie R = alkenyl) is octadec-9-enoic acid (oleic acid). Octadec-9-enoic acid is preferred.

Suitable polyamines include diethylene triamine, triethylene tetramine and tetraethylene pentamine.

The polyamide may be prepared by heating the acid and the polyamine together in solution eg in a light aromatic solvent in a molar ratio in the range 1:1 to 3:1, preferably 1.8:1 to 2.2:1.

Examples of suitable temperatures are those in the range 110° to 150°C. The reaction is preferably continued until the quantity of water released corresponds to that expected from the stoichiometry.

The polyamide is suitable for use as anti-fouling additive where fouling is chiefly due to organic contaminants, e.g. in heat exchangers associated with visbreaking units.

Where inorganic fouling is likely to be encountered in addition, e.g. in crude oil distillation duty, the polyamide is preferably employed in combination with an emulsifier. In fact when inorganic fouling is encountered, use of the polyamide alone may lead to an increase in fouling.

Thus, according to a further feature of the present invention, there is provided an anti-fouling additive composition comprising a polyamide as hereinbefore defined and an oil soluble emulsifier. The preferred emulsifiers are those of general formula:

$$R'COOCH_2\ (CHOH)_m\ CH_2OH$$

wherein R' is an alkyl or alkenyl group containing 10 - 22 carbon atoms and m is an integer in the range 1 to 4 inclusive.

The emulsifiers are partial esters of polyhydric alcohols and carboxylic acids.

Suitable polyhydric alcohols include mannitol, xylitol and erythritol and, preferably, sorbitol.

The preferred emulsifier is sorbitan monooleate. Any other emulsifier used is preferably as oil soluble as sorbitan monooleate.

The polyamide and the emulsifier are suitably present in a weight ratio in the range 20:1 to 1:1, preferably 7:1 to 11:1 for optimum properties.

In circumstances likely to give rise to the presence of free radicals, e.g. desulphurisation, the polyamide is preferably employed in combination with an anti-oxidant.

Thus, according to a further feature of the present invention, there is provided an anti-fouling additive composition comprising a polyamide and a hindered phenolic anti-oxidant.

Suitable hindered phenolic anti-oxidants include 2,6-di-tert. butyl phenol, 2,6-di-tert.butyl-4-methyl phenol and 4,4'-methylene bis (2,6-di-tert.butyl phenol).

The polyamide and the anti-oxidant are suitably present in a weight ratio in the range 4:1 to 1:4, preferably 0.5 to 1.5, eg 1:1.

In some situations, particularly where corrosion is an additional problem, it may be desirable to add a film-forming agent to the anti-foulant additive. The film-forming agent used in the present invention is a material which acts as a corrosion inhibitor by forming an impermeable film on a metal surface, thereby preventing corrosive substances from reacting the metal itself. Such film-forming agents are well-known materials.

Suitable film-forming agents include amines eg long chain amines and amine carboxylates. The preferred agent is morpholine.

The relative proportions may be the same as for polyamide/ antioxidant mixtures.

According to a further feature of the present invention there is provided a process for exchanging heat with a hot petroleum material containing an anti-fouling additive through a heat exchange surface characterised in that the anti-fouling additive comprises a polyamide of formula (I).

As explained above the antifouling additive may consist only of the polyamide in certain cases, while where inorganic fouling is present the addition of emulsifier may be necessary. Based on the disclosure of this specification however the skilled person will be easily able to produce a suitable anti-fouling additive containing polyamide.

The process is particularly applicable to heating petroleum materials.

The anti-fouling additive is preferably stored and used in the form of a solution in a hydrocarbon solvent eg an aromatic hydrocarbon solvent such as toluene or xylene. The concentration of the polyamide in the solution may for example be in the range 20-60% by weight. In order to improve the storage stability of the solution in particular under cold weather conditions it is desirable to introduce a minor proportion of methanol into the solution for example 0.1 to 0.4 parts by weight of methanol per part by weight of hydrocarbon solvent.

The optimum concentration will depend on the process to which the petroleum material is subjected. In crude oil distillation concentrations of additive solution of 20-30 ppm are usually used, typically corresponding to 8-12 ppm of polyamide. In visbreaking concentrations of additive solution of 50 ppm are more usual, typically corresponding to over 20 ppm of polyamide.

The invention is illustrated with reference to the following Examples.

Example 1

Preparation of polyamide

10g oleic acid (octadec-9-enoic acid) and 1.85g diethylene triamine (molar ratio of 2:1) were dissolved and heated in 18g toluene

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under reflux for 5 hours. Water produced in the reaction (0.65 ml) was removed using a Dean and Stark head.

The product was a yellowish brown liquid containing 40% by weight polyamide. The presence of

$$RCONH(CH_2CH_2NH)_2OCR$$

where R = $CH_3(CH_2)_7CH{=}CH(CH_2)_7$ was shown by the liberation of the amount of water corresponding to the production of this compound. Mass spectroscopy and nuclear magnetic resonance results were consistent with this formula.

Example 2

The polyamide made in Example 1 was tested for crude distillation unit duty in the Sunbury Fouling Rig (SFR) as described in GB 1564757 on a temperature basis and the JFTOT as described in ASTM Test D-3241-74T.

Feedstock: Kuwait Crude Oil
Oil Temperature: 290°C
Oil Pressure: 28.5 bar
Anti-foulant Concentration: 40 ppm

Example 3

Example 2 was repeated using as antifoulant a mixture of the polyamide made in Example 1 and sorbitan monooleate (an oil soluble emulsifier sold under the trade name Span 80) in the weight ratio (polyamide:emulsifier) of 4:1. The results are given in Table 1.

Comparative Tests A-E

Example 2 was repeated but using sorbitan monooleate alone as anti-foulant (Test A), or various commercially available anti-foulants (identified as AF1 to AF4 respectively (Tests B - E).

TABLE 1

	SFR	JFTOT
Experiment	% Reduction in Inorganic Fouling	% Reduction in Organic Fouling
1	0	65
2	90	53
A	0	9
B	69	48
C	58	16
D	66	0
E	56	56

Example 4

The polyamide of Example 1 was mixed with an antioxidant (2,6-di-tert-butyl phenol) in a weight ratio of 1:1 and was tested in the JFTOT rig to determine its suitability for use with a desulphuriser feedstock and compared with several commercially available additives.

Feedstock:	Naphtha
Oil Temperature:	284°C
Oil Pressure:	32 bar
Anti-foulant Concentration:	30 ppm

The results are given in Table 2.

Example 5

Example 4 was repeated using a mixture of the polyamide of Example 1 and morpholine (a film forming agent) in the weight ratio 1:1.

The results are given in Table 2.

Comparative Tests F, G, H, I, J

Example 3 was repeated using various commercially available anti-fouling additives identified respectively as AF4, AF2, AF5, AF6 and AF1. The results are given in Table 2.

TABLE 2

	JFTOT
Experiment	% Reduction in Organic Fouling
4	50
5	83
F	45
G	40
H	40
I	40
J	25

The additive compositions according to the present invention are clearly superior.

Example 6

The polyamide of Example 1 was tested in a visbreaking pilot plant to determine its suitability in reducing visbreaking coking.

Feedstock: Qatar Vacuum Residue

Oil temperature: 500°C

Duration of test: 2 hours

Anti-foulant concentration: 50 ppm

The results are given in Table 3.

Comparative Tests K, L, M

Example 6 was repeated using commercially available antifouling additives identified as AF2, AF7 and AF4 respectively. The results are given in Table 3.

TABLE 3

	VISBREAKING PILOT PLANT
Experiment	% Reduction in Coking
6	27
K	11
L	0
M	0

The polyamide was the most effective.

Claims:

1. A liquid polyamide of formula:

$$RCONH(CH_2CH_2NH)_nOCR \qquad (I)$$

wherein R is an alkyl or alkenyl group containing 10 to 22 carbon atoms, and n is an integer in the range 1 to 4 inclusive.

2. A polyamide according to claim 1 wherein R is alkenyl containing 17 carbon atoms, and n = 2.

3. A process for producing a polyamide wherein a liquid carboxylic acid of formula RCO_2H and a polyamine of formula

$$NH_2(CH_2CH_2NH)_nH$$

are heated together in solution in a molar ratio of 1:1 to 3:1.

4. A process according to claim 3 wherein the molar ratio is 1:8.1 to 2.2:1.

5. An anti-fouling composition comprising a polyamide according to claims 1 or 2 and an oil soluble emulsifier.

6. An anti-fouling additive composition comprising a polyamide according to claims 5 and an emulsifier of formula

$$R'COOCH_2(CHOH)_mCH_2OH$$

wherein R' is an alkyl or alkenyl group containing 10 to 22 carbon atoms, and m is an integer in the range 1 to 4 inclusive.

7. An anti-fouling additive composition according to claim 6 wherein the emulsifier is sorbitan monooleate.

8. An anti-fouling additive according to any one of the claims 5 to 7 wherein the weight ratio of polyamide to emulsifier is 3.5:1 to 4.5:1.

9. An anti-fouling additive comprising a polyamide according to any one of claims 1 to 3 and a hindered phenolic antioxidant.

10. An anti-fouling additive according to claim 9 wherein the weight ratio of polyamide to anti-oxidant is 4:1 to 1:4.

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11. An anti-fouling additive comprising a polyamide according to any one of claims 1 to 3 and a film-forming agent.

12. A process for exchanging heat with a hot petroleum material, containing an anti-fouling additive, through a heat exchange surface characterised in that the anti-fouling additive comprises a polyamide according to any one of claims 1 to 3.