

Description

BACKGROUND OF THE INVENTION

This invention relates to a method of retarding or minimizing the effects of corrosion when N-methyl pyrrolidone is utilized in a petroleum processing operation.

N-methyl pyrrolidone (hereinafter referred to as NMP) has been known to be useful in various petroleum hydrocarbon compositions and processing operations. Such uses include that of a solvent for the separation of olefins, for the recovery of acetone from petroleum gas, for the extraction of naphthalenic hydrocarbons from various hydrocarbon mixtures, as a chemical reaction medium, as a polymer solvent, for use in industrial cleaning, for decolorizing petroleum oils and waxes, in paint removers, as a deicer for jet fuels and gasoline etc. Perhaps the most important and widest industrial use of NMP is as an aromatic extraction solvent in various petroleum refining processes. Illustrative processes are for the separation of benzene, toluene, and xylene or the well-known BTX process, the recovery and separation of relatively pure single-ring aromatics such as xylene, benzene and toluene from relatively light hydrocarbon mixtures known in the industry as the Arosolvan process, and in the extraction of aromatics from lube oil fractions in order to produce lube oils of relatively high VI and UV stability. Within the past ten years or so, a considerable amount of industrial research and development has been expended by the petroleum industry towards the utilization of NMP in lube oil deasphalting, extraction and dewaxing. See for example U.S. Patents 3,843,515; 4,013,549; 4,057,491; 4,125,458 and 4,168,226.

While the use of NMP in various petroleum processes has been growing and is for the most part quite successful, there has been one problem associated with its use, that is the corrosion which develops in various processing units.

A. I. Tsinman et al, Chemical abstracts Vol 82, 1975, pages 182, 183 No.89016y, refer to the corrosion of steels during the concentration of acetylene by DMF and NMP solutions. They report that the addition of ethanolamine an urotropine retards the corrosion.

Ethanolamine and alkyl — or alkylene amines are known as corrosion inhibitors.

The Applicants have found that, surprisingly, corrosion formed in petroleum processing units wherein NMP is utilized can be significantly reduced by using an ester of a polycarboxylic acid and a glycol/glycerol.

Such esters are known per se and US-A-3429817 discloses their use as lubricity additives in fuels and other middle distillates. It is further disclosed that the esters may be used in the fuels etc together with other additives, such as oxidation inhibitors, rust inhibitors, dyes, dispersants etc.

The present invention provides a petroleum — treatment or — processing method in which N-methyl pyrrolidone is used as a component in a hydrocarbon(s)-containing system or feed, characterised in that there is employed as a further component a corrosion-inhibiting amount of an ester, formed from at least one polycarboxylic acid and glycerol or at least one glycol, to retard corrosion.

The selected ester useful as a corrosion inhibitor in the petroleum process of this invention is generally an oil soluble hydroxy substituted ester of a polycarboxylic acid. More particularly, the ester component used in this invention is derived from the esterification of a polycarboxylic acid with a glycol or glycerol, preferably glycol.

Such an ester may be a partial, di- or polyester.

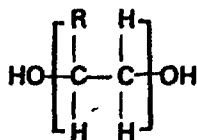
Typical formulae of the ester represented by the following general formulae when using a glycol:



wherein R'' is the hydrocarbon radical of said acid and each R and R' may be the same or different hydrocarbon radicals associated with a glycol or diol as hereinafter defined. It will, of course, be appreciated that esters of the type illustrated by the foregoing formulas can be obtained by esterifying a polycarboxylic acid, or a mixture of such acids, with a diol or mixture of such diols.

The polycarboxylic acid used in preparing the ester may be an aliphatic saturated or unsaturated acid. It will generally have a total of about 24 to about 90, preferably about 24 to about 60 carbon atoms. It generally has 2 to about 4, preferably about 2 to about 3 and more preferably about 2 carboxylic acid groups. The groups normally have 9 up to about 42 carbon atoms, preferably about 12 to about 42 and more preferably about 16 to about 22 carbon atoms between the carboxylic acid groups.

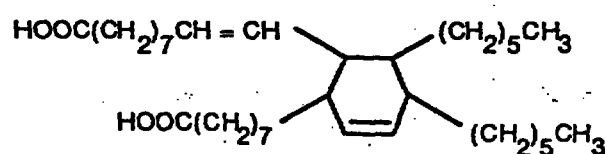
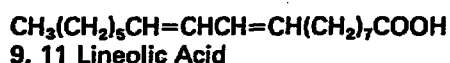
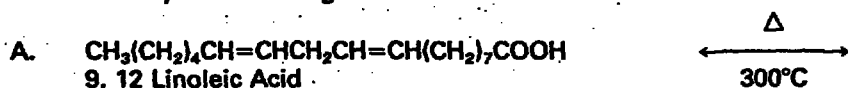
The oil insoluble glycol which is reacted with the polycarboxylic acid may be an alkane diol, i.e. alkylene glycol or an oxa-alkane diol, i.e. polyalkylene glycol, straight chain or branched. The alkane diol may have from about 2 to about 12 carbon atoms and preferably about 2 to about 5 carbon atoms in the molecule and the oxa-alkane diol will, generally, have from about 4 to about 200, preferably about 4 to about 100 carbon atoms. The oxa-alkane diol (polyalkylene glycol) will, of course, contain periodically repeating groups of the formula:



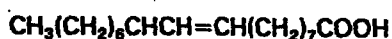
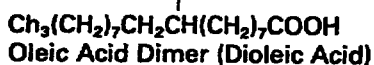
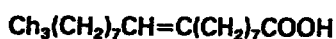
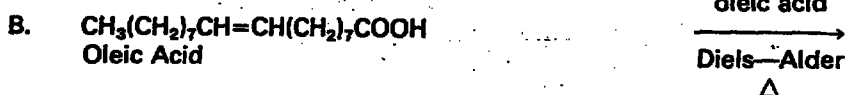
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wherein R is normally H, CH₃, C₂H₅ or C₃H₇, and x is normally 2 to 100, preferably 2 to 25. The preferred alkane diol or alkylene glycol is ethylene glycol and the preferred oxa-alkane diol or polyalkylene glycol is diethylene glycol. As indicated previously, glycerol may also be used in preparing the ester of polycarboxylic acid and it is contemplated that such component will also include its higher molecular weight analogues.

While any of the esters as set forth above can be effectively used, best results are obtained with such compounds wherein the carboxyl groups of the polycarboxylic acid are separated from each other by from about 16 to about 22 carbon atoms and wherein the hydroxy groups are separated from the closest carboxyl group by from about 2 to about 12 carbon atoms. Particular desirable results have been obtained with additives prepared by esterifying a dimer of a fatty acid, particularly those containing conjugated unsaturation with a polyhydroxy compound. Such dimers are, of course, clearly taught in U.S. Patent 3,180,832 which was granted on April 27, 1965 and U.S. Patent 3,429,817 which was granted on February 25, 1969, and as there indicated, the hydrocarbon portion of the dimer or dicarboxylic acid thus obtained may contain a six member ring. The formation of the dimer from linoleic acid, oleic acid and mixtures of these acids is illustrated by the following:



Linoleic Acid Dimer (dilinoleic acid)



It will, of course, be appreciated that while the reactions illustrated produce the dimers, commercial application of the reactions will, generally, lead to trimer formation and in some cases the product thus obtained will contain minor amounts of unreacted monomer or monomers. As a result, commercially available dimer acids may contain as much as 25% trimer and the use of such mixtures is within the scope of the present invention.

The preferred hydroxy-substituted ester additives useful in the present invention will be the reaction product of a dimerized fatty acid, such as those illustrated, and an oil insoluble glycol and may be produced by various techniques. As previously pointed out, the preferred acid dimers are the dimers of linoleic acid,

oleic acid or the mixed dimer of linoleic and oleic acids, which may also contain some monomer as well as trimer. Other specifically satisfactory glycols in addition to ethylene glycol and polyethylene glycol are, for example, propylene glycol, polypropylene glycol, butylene glycol, polybutylene glycol and the like.

The process of this invention will generally include any petroleum process operation wherein a hydrocarbon feed is being treated or processed and wherein NMP is used as one of the component ingredients. More particularly, this invention will involve a hydrocarbon feed which is contacted with N-methyl pyrrolidone as solvent, preferably in an extraction operation.

While any hydrocarbon feed may be used, preferable feedstocks are those common to the petroleum refinery industry, especially lube oil feedstocks. Lube oil feeds comprise petroleum fractions having an initial boiling point of above about 500°F (260°C). These fractions include deasphalted oils and/or distillate lube oil fractions boiling within the range of about 600°F (311°C) to 1050°F+ (566°C+) (at atmospheric pressure) and contain between about 5 to about 70% (by weight) of polar and aromatic compound such as substituted benzenes, naphthalenes, anthracenes and phenanthracenes, characterized by having a carbon content typically in the range of C₁₅—C₅₀. Nonlimiting examples of useful feedstocks include crude oil distillates and esasphalted resids; those fractions of catalytically cracked cycle oils, coker distillates and/or thermally cracked oils boiling above about 600°F (311°C) and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, and the like. These fractions may come from any source, such as the paraffinic crudes obtained from Aramco, Kuwait, The Panhandle, North Louisiana, etc naphthenic crudes such as Tia Juana and Coastal crudes, etc., as well as the relatively heavy feedstocks such as bright stocks having a boiling range of 1050°F+ (566°C+) and synthetic feedstocks derived from Athabasca Tar Sands, etc.

The amount of polycarboxylic acid glycol/glycerol ester used in this invention will be an effective corrosion inhibiting amount and can vary from about 0.001 to about 10% by weight, preferably from about 0.01 to about 5% by weight and more preferably from about 0.02 to about 3% by weight based on the total weight of the hydrocarbon composition or system being used in the process operation.

Other treating materials and additives conventionally used in petroleum process operations may of course be included in the composition being processed.

The following examples are further illustrative of this invention and are not intended to be construed as limitations thereof.

Example I

A sample comprising N-methyl pyrrolidone was contacted with an iron specimen and tested for iron corrosion at a temperature of 25°C using the Polarization Device for Petroleum Systems (PDPS) which is described in U.S. Patent 4,169,768 issued October 2, 1979. The iron corrosion rate was 405 µm/a (micrometers per annum).

Adding 0.05 wt% of an ester additive, formed by esterification of a dimer acid of linoleic acid and diethylene glycol, to the N-methyl pyrrolidone and again testing for iron corrosion using PDPS, the corrosion rate dropped to 16 µm/a.

Another test was made after adding 0.1 wt% of the same ester described above to the N-methyl pyrrolidone system. The iron corrosion rate was found to be 7.5 µm/a.

Example II

Another sample comprising 95% by weight N-methyl pyrrolidone and 5% by weight water was contacted with an iron specimen and tested for iron corrosion using PDPS as described in Example I. The iron corrosion rate was 487 µm/a.

Adding 0.05 wt% of an ester additive formed by esterification of a dimer acid of linoleic acid and diethylene glycol to the same NMP/water system and again testing for iron corrosion using PDPS, the corrosion rate was 22 µm/a.

Another test was made after adding 0.1 wt% of the same ester additive to the NMP/water system. The iron corrosion rate was found to be 10 µm/a.

Claims

1. A petroleum — treatment or — processing method in which N-methyl pyrrolidone is used as a component in a hydrocarbon(s)-containing system or feed, characterised in that there is employed as a further component a corrosion-inhibiting amount of an ester, formed from at least one polycarboxylic acid and glycerol or at least one glycol, to retard corrosion.

2. A method as claimed in claim 1, characterised in that the ester is formed from a dicarboxylic acid having from 9 to 42, preferably 16 to 22, carbon atoms between carboxylic acid groups.

3. A method as claimed in claim 1 or claim 2, characterised in that the ester is formed from a glycol selected from alkane diols having from 2 to 12 carbon atoms or oxa-alkane diols having from 4 to 200 carbon atoms.

4. A process as claimed in claim 1, wherein the ester is formed from a dimer acid of a conjugated fatty acid having from 16 to 22 carbon atoms between carboxylic acid groups.

5. A process as claimed in claim 1, where said ester is formed by esterification of a dimer acid of linoleic acid with diethylene glycol.

oleic acid or the mixed dimer of linoleic and oleic acids, which may also contain some monomer as well as trimer. Other specifically satisfactory glycols in addition to ethylene glycol and polyethylene glycol are, for example, propylene glycol, polypropylene glycol, butylene glycol, polybutylene glycol and the like.

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5. A process as claimed in claim 1, where said ester is formed by esterification of a dimer acid of linoleic acid with diethylene glycol.



6. A method as claimed in any preceding claim, characterised in that the additive is used in an amount of from 0.001 to 10% by weight based on the total weight of the hydrocarbon(s) content of the system or feed.

7. A method as claimed in claim 6, characterised in that the ester is used in an amount of from 0.01 to 5%, preferably 0.02 to 3%, by weight based on the total weight of the hydrocarbon(s) content of the system or feed.

8. A petroleum extraction method employing N-methyl pyrrolidone, which method is characterised as defined in any preceding claim.

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Patentansprüche

1. Erdölbehandlungs- oder -verarbeitungsverfahren, bei dem N-Methylpyrrolidon als Komponente in einem Kohlenwasserstoff(e) enthaltenden System oder Einsatzmaterial verwendet wird, dadurch gekennzeichnet, daß zwecks Korrosionshemmung als eine weitere Komponente eine korrosionsinhibierende Menge eines Esters verwendet wird, der aus mindestens einer Polycarbonsäure und Glycerin oder mindestens einem Glykol gebildet ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Ester aus einer Dicarbonsäure mit 9 bis 42 und vorzugsweise 16 bis 22 Kohlenstoffatomen zwischen den Carbonsäuregruppen gebildet ist.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Ester aus einem Glykol ausgewählt aus Alkandiolen mit 2 bis 12 Kohlenstoffatomen oder Oxaalkandiolen mit 4 bis 200 Kohlenstoffatomen gebildet ist.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Ester gebildet ist aus einer Dimersäure einer konjugierten Fettsäure mit 16 bis 22 Kohlenstoffatomen zwischen den Carbonsäuregruppen.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Ester durch Veresterung einer Dimersäure von Linolsäure mit Diethylenglykol gebildet ist.

6. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das Additiv in einer Menge von 0,001 bis 10 Gew.%, bezogen auf das Gesamtgewicht des Gehalts an Kohlenwasserstoff(en) des Systems oder Einsatzmaterials, verwendet wird.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß der Ester in einer Menge von 0,01 bis 5 Gew.% und vorzugsweise 0,02 bis 3 Gew.%, bezogen auf das Gesamtgewicht des Gehaltes an Kohlenwasserstoff(en) des Systems oder des Einsatzmaterials, verwendet wird.

8. Erdölextraktionsverfahren unter Verwendung von N-Methylpyrrolidon, das wie in einem der vorangehenden Ansprüche angegeben gekennzeichnet ist.

Revendications

1. Procédé de traitement ou de transformation de pétrole, dans lequel on utilise la N-méthyl pyrrolidone à titre de constituant dans un système ou une alimentation contenant un ou des hydrocarbure(s), procédé caractérisé en ce qu'on utilise, à titre de constituant supplémentaire, une quantité, capable d'inhiber la corrosion, d'un ester formé à partir d'au moins un acide polycarboxylique et de glycérol ou d'au moins un glycol, pour retarder la corrosion.

2. Procédé selon la revendication 1, caractérisé en ce que l'ester est formé à partir d'un acide dicarboxylique ayant de 9 à 42, de préférence 16 à 22, atomes de carbone entre les groupes acide carboxylique.

3. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que l'ester est formé à partir d'un glycol choisi parmi les alcane diols ayant 2 à 12 atomes de carbone ou les oxa-alcane diols ayant 4 à 200 atomes de carbone.

4. Procédé selon la revendication 1, dans lequel l'ester est formé à partir d'un acid dimère d'un acide gras conjugué ayant de 16 à 22 atomes de carbone entre les groupes acide carboxylique.

5. Procédé selon la revendication 1, dans lequel ledit ester est formé par estérification d'un acide dimère de l'acide linoléique par le diéthylène glycol.

6. procédé selon l'une quelconque des revendications précédente, caractérisé en ce qu'on utilise l'additif en une quantité de 0,001 à 10% en poids, par rapport au poids total du ou des hydrocarbure(s) contenu(s) dans le système ou l'alimentation.

7. Procédé selon la revendication 6, caractérisé en ce qu'on utilise l'ester en une quantité de 0,01 à 5%, de préférence 0,02 à 3% en poids par rapport au poids total du ou des hydrocarbure(s) contenu(s) dans le système ou l'alimentation.

8. Procédé d'extraction de pétrole, utilisant la N-méthyl pyrrolidone, ce procédé étant caractérisé en ce qu'il est tel ue défini dans l'une quelconque des revendications précédentes.

