

⑫

EUROPEAN PATENT APPLICATION

⑰ Application number: **79301536.3**

⑸ Int. Cl.³: **C 10 M 1/32**

⑱ Date of filing: **01.08.79**

⑳ Priority: **01.08.78 GB 3188478**

⑦① Applicant: **The British Petroleum Company Limited,
Britannic House Moor Lane, London EC2Y 9BU (GB)**

④③ Date of publication of application: **20.02.80**
Bulletin 80/4

⑦② Inventor: **Neustadter, Ernst Ludwig, The British
Petroleum Company Ltd. Chertsey Road, Sunbury-on-
Thames Middlesex TW16 7LN (GB)**

⑧④ Designated Contracting States: **BE DE FR GB NL SE**

⑦④ Representative: **Eastman, Hugh Leonard, BP Trading
Limited Patents and Licensing Division Chertsey Road,
Sunbury-on-Thames Middlesex TW16 7LN (GB)**

⑤④ **Lubricating composition and method of lubricating a marine diesel engine.**

⑤⑦ A lubricating composition suitable for use in marine diesel engines comprises a lubricating base oil, a hydrocarbyl amine in microemulsified form and a dispersant for hydrocarbyl amine salts which may be formed during use.

The hydrocarbyl amine may be a polyalkalene polyamine, and the dispersant may be a polyisobutenyl succinimide or a known detergent additive, e.g. a barium, calcium or sodium phenate, sulphonate or carboxylate.

EP 0 008 193 A1

- 1 -

TITLE MODIFIED
see front pageLUBRICATING COMPOSITION

This invention relates to lubricating compositions suitable for use in marine diesel engines.

In the lubrication of some diesel engines running on high sulphur content fuel having a cylinder lubrication system, e.g. marine diesels, it is necessary to use a cylinder lubricant having a highly basic nature, i.e. having a high total base number. These lubricants usually contain an over-based metal salt such as an over-based calcium or barium phenate or sulphonate. However, metal-containing salts are ash forming, i.e. when they are burnt there is a metal containing residue. It would be desirable to reduce or eliminate the use of ash-forming additives for such applications by replacing at least a proportion of such additives with ashless additives.

Our UK Specification No. 1386620 does, in fact, disclose a lubricant containing an ashless basic additive viz a lubricating composition comprising a branched chain alkyl or alkenyl polyamine in which the alkyl or alkenyl group has a number average molecular weight of 350 to 500 and which has a total base number of at least 200. In this composition the polyamine component of the additive, (e.g. a polyalkylene polyamine) provides the required basicity and the branched chain alkyl or alkenyl group (e.g. a polyisobutenyl group) ensures that the additive is soluble in and compatible with the lubricating base oil.

However, the solubilising branched chain alkyl or alkenyl group in the additive is relatively bulky, and there would be advantages in being able to use a simple polyamine without the added solubilising group.

It has now been found that amines can form stable mixtures with lubricating oils if the mixture is in the form of a microemulsion.

- 1 -

- 2 -

Micro-emulsions in which the continuous phase is a liquid hydrocarbon medium (including hydrocarbon lubricating oils) are known from US Patent No. 3346494. The microemulsified phase may be a volatile medium such as water (which is preferred), methanol, or aqueous or methanolic solutions of inorganic salts and bases (oxides and hydroxides) or it may be a non-volatile medium such as ethylene glycol or glycerol.

As compared with the above prior art, it has been found that organic bases such as amines can also form the microemulsified phase in lubricating oils in the absence of water or methanol or other solvent. Since the amine is present to react with acidic products of combustion, e.g. sulphur oxides, it has also been found that the lubricating composition should contain a dispersant.

According to the present invention, a lubricating composition comprising a lubricating base oil as a continuous phase and a hydrocarbon insoluble compound as a microemulsified phase is characterised in that the microemulsified phase is a hydrocarbyl amine and the lubricating composition also contains a dispersant for hydrocarbyl amine salts which may be formed during use of the lubricating composition.

The hydrocarbyl amine may be an aryl, cycloalkyl or alkylamine. Alkylene polyamines are preferred, particularly polyalkylene polyamines and more particularly polyethylene polyamines. Since it is not necessary to have a large hydrocarbyl group to solubilise the amine, the hydrocarbyl amine may have a total of from 1 to 20 carbon atoms. Such a low content of hydrocarbyl groups means that the amine has a high total base number, e.g. a TBN of the order of 1000mgKOH/g. Examples of suitable amines are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine.

The lubricating base oil may be any known lubricating oil and may be synthetic or natural. Examples of synthetic oils may be the diesters or complex esters known as synthetic lubricants, or liquid polymers formed from low molecular weight olefins. Preferably, however, the oils are mineral oils derived from petroleum, e.g. petroleum fractions boiling above 300°C. These fractions may be distillate fractions boiling in the range 300 to 600°C or de-ashed residual fractions. The choice of base oil will be determined by the proposed use and, for the preferred lubricating compositions for use as cylinder lubricants for diesel engines, the oils may have a viscosity of from 8 to 23 centistokes at 100°C.

- 2 -

- 1 -

TITLE MODIFIED
see front pageLUBRICATING COMPOSITION

This invention relates to lubricating compositions suitable for use in marine diesel engines.

In the lubrication of some diesel engines running on high sulphur content fuel having a cylinder lubrication system, e.g. marine diesels, it is necessary to use a cylinder lubricant having a highly basic nature, i.e. having a high total base number. These lubricants usually contain an over-based metal salt such as an over-based calcium or barium phenate or sulphonate. However, metal-containing salts are ash forming, i.e. when they are burnt there is a metal containing residue. It would be desirable to reduce or eliminate the use of ash-forming additives for such applications by replacing at least a proportion of such additives with ashless additives.

Our UK Specification No. 1386620 does, in fact, disclose a lubricant containing an ashless basic additive viz a lubricating composition comprising a branched chain alkyl or alkenyl polyamine in which the alkyl or alkenyl group has a number average molecular weight of 350 to 500 and which has a total base number of at least 200. In this composition the polyamine component of the additive, (e.g. a polyalkylene polyamine) provides the required basicity and the branched chain alkyl or alkenyl group (e.g. a polyisobutenyl group) ensures that the additive is soluble in and compatible with the lubricating base oil.

However, the solubilising branched chain alkyl or alkenyl group in the additive is relatively bulky, and there would be advantages in being able to use a simple polyamine without the added solubilising group.

It has now been found that amines can form stable mixtures with lubricating oils if the mixture is in the form of a microemulsion.

- 1 -

- 2 -

Microemulsions in which the continuous phase is a liquid hydrocarbon medium (including hydrocarbon lubricating oils) are known from US Patent No. 3346494. The microemulsified phase may be a volatile medium such as water (which is preferred), methanol, or aqueous or methanolic solutions of inorganic salts and bases (oxides and hydroxides) or it may be a non-volatile medium such as ethylene glycol or glycerol.

As compared with the above prior art, it has been found that organic bases such as amines can also form the microemulsified phase in lubricating oils in the absence of water or methanol or other solvent. Since the amine is present to react with acidic products of combustion, e.g. sulphur oxides, it has also been found that the lubricating composition should contain a dispersant.

According to the present invention, a lubricating composition comprising a lubricating base oil as a continuous phase and a hydrocarbon insoluble compound as a microemulsified phase is characterised in that the microemulsified phase is a hydrocarbyl amine and the lubricating composition also contains a dispersant for hydrocarbyl amine salts which may be formed during use of the lubricating composition.

The hydrocarbyl amine may be an aryl, cycloalkyl or alkylamine. Alkylene polyamines are preferred, particularly polyalkylene polyamines and more particularly polyethylene polyamines. Since it is not necessary to have a large hydrocarbyl group to solubilise the amine, the hydrocarbyl amine may have a total of from 1 to 20 carbon atoms. Such a low content of hydrocarbyl groups means that the amine has a high total base number, e.g. a TBN of the order of 1000mgKOH/g. Examples of suitable amines are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine.

The lubricating base oil may be any known lubricating oil and may be synthetic or natural. Examples of synthetic oils may be the diesters or complex esters known as synthetic lubricants, or liquid polymers formed from low molecular weight olefins. Preferably, however, the oils are mineral oils derived from petroleum, e.g. petroleum fractions boiling above 300°C. These fractions may be distillate fractions boiling in the range 300 to 600°C or de-ashphalted residual fractions. The choice of base oil will be determined by the proposed use and, for the preferred lubricating compositions for use as cylinder lubricants for diesel engines, the oils may have a viscosity of from 8 to 23 centistokes at 100°C.

- 2 -

- 3 -

Microemulsions of a hydrocarbon insoluble component in a liquid hydrocarbon medium, particularly a mineral oil, can be formed by simple mixing provided the type and quantity of emulsifiers are correctly chosen. The disperse phase droplets are small, e.g. in the range 60 - 1000Å, and the microemulsions are stable at ambient temperature almost indefinitely.

The emulsifiers normally required for forming microemulsions are a fatty acid and an alkyl phenol with an amino alcohol as co-surfactant. The ratio is parts by weight of the three components may be:-

10	Fatty acid	1 to 2.5
	Alkyl phenol	1 to 2.5
	Amino alcohol	0 to 1

It has been found, however, that the amino alcohol co-surfactant can be an optional component in the present invention where the microemulsified phase is a hydrocarbyl amine.

The fatty acid may have from 12 to 25 carbon atoms and may be saturated or unsaturated. Examples of suitable acids are stearic, oleic, linoleic, lauric and palmitic acids. Mixtures of acids, e.g. tall oil fatty acids may also be used.

The alkyl phenol may be mono or polyhydroxy and the alkyl group is preferably a straight chain alkyl group and has preferably, from 6 to 15 carbon atoms. There may be additional C₁ - C₁₅ alkyl groups on the aromatic ring, although this is not necessary. Preferred alkyl phenols are octyl and nonyl phenols and octyl and nonyl cresols.

The amino alcohol, if present, is preferably an alkanolamine, which may be a primary, secondary or tertiary amine and the alkyl group or groups of which may have from 2 to 6 carbon atoms. Examples of suitable alkanolamines are mono-, di- and tri-isopropanolamines.

As compared with macroemulsions, microemulsions have a relatively high proportion of emulsifiers in relation to the microemulsified phase and the continuous phase. In the case of the present invention, where the microemulsified phase is a hydrocarbyl amine the total quantity of emulsifiers is preferably from 2 to 25% wt. by weight of the total composition.

The proportion of hydrocarbyl amine to lubricating base oil will

- 3 -

- 4 -

depend on the total base number of the amine and that required in the finished oil. The TBN of the finished oil may be from 5 to 500 mgKOH/g preferably 20 to 100, and the proportion of hydrocarbyl amine may be from 1 to 20% by weight of total composition.

5 As previously indicated, the microemulsions may be prepared by simple mixing at room temperature. Preferably the emulsifiers are added to the base oil and then the hydrocarbyl amine.

 As previously indicated, the primary function of the hydrocarbyl amine is to react with acidic products of combustion of the engine
10 being lubricated. With high sulphur content fuels these combustion products will be sulphur oxides or acids giving amine sulphates as the reaction products. Amine sulphates tend to be crystalline solids with a tendency to settle out on cooler parts of the engine. It is necessary, therefore, for the lubricating composition to have a dispersant
15 capable of holding the amine salts in suspension so that they are removed from the cylinder with the lubricant and other exhaust products.

 Dispersant additives capable of holding particulate solids, e.g. carbon, in suspension are well known in the lubricating oil art and suitable dispersants for use in the present invention may be selected
20 from the known dispersant additives by suitable experiments and/or engine tests.

 Preferred dispersants are the polyisobutenyl succinimides. They may be of the mono- or bis- type, preferably the latter. The polyisobutenyl group may have from 8 to 200 carbon atoms and the amine used
25 to form the compound may be a hydrocarbyl amine of the same type as that in the microemulsified phase, preferably an alkylene polyamine having a total of from 1 to 20 carbon atoms.

 In another embodiment the dispersant may be a known detergent additive, e.g. a barium, calcium or sodium phenate, sulphonate or
30 carboxylate. Such additives, as previously explained, are known ash-forming detergent additives, so in this embodiment the lubricant will be a low-ash rather than a wholly ashless composition. However, the amount of ash-forming material can be significantly reduced and may be from 0.1 to 5% wt. of the total composition. The hydrocarbyl amine is
35 likely to have a relatively high TBN per unit of weight (particularly

- 4 -

- 5 -

the preferred hydrocarbyl amines with from 1 to 20 C atoms) and could make a significant contribution to the TBN of the composition even if present in relatively small amounts by weight. Preferred compositions may contain from 1 to 10% wt. of hydrocarbyl amine and from 1 to 15% wt. of ash-forming detergent.

The contribution of the ash-forming detergent additive to the overall dispersancy may, however, not be sufficient in itself and may be supplemented by another dispersant additive, e.g. a polyisobutenyl succinimide as described above or one or more of the dispersants described below.

Other dispersants for the hydrocarbyl amine sulphate reaction products may be alcohols and phenols having surfactant properties. These can be, for example, the type of organic compounds used to form the salts and overbased salts referred to above. Preferred compounds are alkyl and alkenyl alcohols or phenols having from 6 to 100 carbon atoms in the alkyl or alkenyl group. The group preferably has from 9 to 20 carbon atoms and is preferably a straight chain group. Examples of suitable compounds are nonyl phenol, dodecanol, lauryl alcohol and stearyl alcohol.

Although VI improvers are not normally required in marine diesel lubricants another type of dispersant may be a dispersant polymer used as a VI improver, e.g. a polyalkylmethacrylate.

The compositions of the present invention may contain other known additives suitable for use in diesel cylinder lubricants, e.g. corrosion inhibitors such as metal sulphonates.

The total amount of dispersant may be from 1 to 30% wt., preferably from 5 to 20% wt. by weight of the total composition. As indicated above, some of the compounds contributing to the dispersancy may be present partly for other reasons and for other functions. For example, a conventional ash-forming detergent may be present as indicated above and may contribute to the dispersancy. Also some of the dispersants listed above may be the same as the emulsifiers used to form the micro-emulsion (e.g. alkyl phenols). In such circumstances the quantity quoted above is the total quantity of dispersant in the composition irrespective of whether the dispersant has additional functions or not, it being

- 5 -

- 6 -

impractical to apportion the total amount in respect of differing functions. It has been found, however, that the total contribution to the overall dispersancy of the emulsifiers used to form the micro-emulsion or the conventional ash-forming detergent is relatively
5 small and that it is desirable to have an additional quantity or type of dispersant over and above that required for emulsification or detergency.

The effectiveness of any dispersant will be indicated by the cleanliness of the engine in which it is used and the type and quantity
10 of dispersant for any given use may be determined by established engine test procedures.

The invention is illustrated by the following examples.

Example 1

A microemulsion of tetraethylene pentamine in a lubricating base oil
15 was prepared using the following amounts of components by weight:-

	<u>%wt.</u>
Tetraethylene pentamine	4.1
Oleic acid	6.2
Nonyl phenol	4.5
20 Isopropanolamine	1.7
Polyisobutenyl mono-succinimide	5.0
Lubricating base oil	78.5

The polyisobutenyl mono-succinimide was an ashless dispersant sold by Orobis Limited under the Trade Name Oloa 1200. The lubricating base
25 oil was a petroleum lubricating oil having a viscosity of 10.09 cS at 100°C and a viscosity index of 73.

The microemulsion was prepared as follows.

The oleic acid and nonyl phenol were added to half the weight of the base oil and stirred at room temperature. The tetraethylene-pentamine
30 was then added and stirred until homogeneous and clear. The polyisobutylene mono-succinimide was next added followed by the isopropanolamine and the rest of the base oil.

The microemulsion was found to be stable for a period of at least 2 years. It had a total base number of 59.

35 The composition was tested for suitability as a cylinder lubricant

- 6 -

- 7 -

for a marine diesel engine using a 24 hour test in a Ruston engine. The wear rate obtained was comparable to that of a conventional non-ashless diesel cylinder lubricant.

Example 2

5 A microemulsion of tetraethylene pentamine in a lubricating base oil was prepared using the following components:-

	<u>%wt.</u>
Tetraethylenepentamine	5.4
Nonyl phenol	5.4
10 Oleic acid	6.8
Lubricating base oil	82.4

The base oil was a petroleum lubricating oil having a viscosity of 17.6 cS at 100°C.

The microemulsion was prepared as follows:-

15 The oleic acid and nonyl phenol were added to half the weight of the base oil and stirred. The tetraethylenepentamine was then added together with the rest of the base oil and stirred. The whole operation was carried out at room temperature and the finished microemulsion had a TBN of 71.

20 A solution containing an overbased calcium phenate in lubricating base oil was blended using the following components:-

	<u>%wt.</u>
Overbased calcium phenate	27
Lubricating base oil	73

25 The overbased calcium phenate was an ash-forming alkaline marine cylinder lubricant additive sold by Orobis Limited under the Trade Name Oloa 219. The lubricating base oil was the same as that used for the microemulsion. The finished oil had a TBN of 70.

30 Both oils were then 90% neutralised with concentrated sulphuric acid, the amount of acid being based on the respective TBN values.

The neutralisations were carried out by adding sulphuric acid dropwise to the stirred oils which were then stirred at 90°C for 10 minutes.

35 Equal weights of the two neutralised oils were mixed with stirring giving, as the final product, a 90% neutralised half-ash microemulsion.

- 7 -

- 8 -

The corrosivity of this product was tested at 300°C using a mild steel Magna corrosometer probe.

The corrosion rates obtained were comparable to those obtained from similar testing of a 90% neutralised conventional ash-forming
5 marine cylinder lubricant.

	90% Neutralised Oil	Corrosion Rate at 300°C (mls per year)
	Half-Ash Microemulsion	140
10	Conventional Lubricant	122

Example 3

A half-ash microemulsion of tetraethylenepentamine in a lubricating
15 base oil was prepared using the following components:-

		<u>%wt.</u>
	Tetraethylenepentamine	2.7
	Nonyl phenol	2.7
	Oleic acid	3.4
20	Overbased calcium phenate(Oloa 219)	13.5
	Polyisobutenyl mono-succinimide (Oloa 1200)	5.0
	Polyisobutenyl bis-succinimide (Oloa 373)	5.0
	Lubricating base oil	67.7

The overbased calcium phenate was the same as in Example 2. The
25 polyisobutenyl succinimides were also supplied by Orobis Limited under the Trade Names indicated above.

The lubricating base oil was a blend of distillate and bright stock oil chosen so that the finished composition was of SAE 50 grade viscosity (16.7 to 17.2 cS at 100°C).

30 The microemulsion was prepared as follows.

The oleic acid and nonyl phenol were added to half the weight of the base oil and stirred. The tetraethylene pentamine was then added and stirred until homogeneous and clear. The overbased calcium phenate, the polyisobutenyl succinimides and the rest of the base oil were then
35 added and stirred at 50°C for 15 minutes. The finished microemulsion had a TBN of 69.5

- 8 -

- 9 -

This composition (which had a sulphated ash content of 2.73%wt.) was tested for suitability as a cylinder lubricant for marine diesel engines using a 125 hour test in a Ruston engine.

The results of the test were as follows:-

5 Demerit Ratings

	Ring sticking	0
	Ring land deposit	2.23
	Piston skirt deposit	0.05
	Ring groove deposit	5.695
10	Cylinder liner deposit	0.16
	Total cleanliness demerit	8.135
	Cylinder oil consumption (kg)	7.06
	Cylinder liner wear (0.001 inch/1000 hr)	2.72
	Top ring weight loss (g/1000 hr)	13.84

15 Example 4

A low-ash microemulsion of tetraethylenepentamine in a lubricating base oil was prepared using the following components:-

	<u>%wt.</u>	
	Tetraethylenepentamine	4.2
20	Nonyl phenol	4.2
	Oleic acid	5.3
	Dispersant/detergent package (Oloa 855)	10.0
	Polyisobutenyl mono-succinimide (Oloa 1200)	2.5
	Lubricating base oil	73.8

25 The polyisobutenyl mono-succinimide was the same as in Example 3.

The dispersant/detergent package was also supplied by Orobis Limited under the Trade Name indicated above. The package was a blend of overbased calcium phenate, polyisobutenyl bis-succinimide and metal sulphonate.

30 The lubricating base oil was a blend of distillate and bright stock oil chosen so that the finished composition was of SAE 50 grade viscosity (16.7 to 17.2 cSt at 100°C).

The microemulsion was prepared as follows.

35 The oleic acid and nonyl phenol were added to half the weight of the base oil and stirred. The tetraethylenepentamine was then added and

- 10 -

stirred until homogeneous and clear. The dispersant/detergent package (Oloa 853), polyisobutenyl mono-succinimide (Oloa 1200) and the rest of the base oil were added and stirred at 50°C for 15 minutes. The finished microemulsion had a TBN of 70.

- 5 This composition (which had an ash content of 1.85%wt.) was tested for suitability as a cylinder lubricant for marine diesel engines using a 125 hour test in a Ruston engine.

 The results of the test were as follows:

Demerit Ratings

10	Ring sticking	0
	Ring land deposit	3.05
	Piston skirt deposit	1.05
	Ring groove deposit	3.35
	Cylinder liner deposit	0.2
15	Total cleanliness demerit	7.65
	Cylinder oil consumption (kg)	8.17
	Cylinder liner wear (0.001 inch/1000 hr)	3.2
	Top ring weight loss (g/1000 hr)	23.12

20

25

30

35

- 10 -

- 11 -

Claims:

1. A lubricating composition comprising a lubricating base oil as a continuous phase and a hydrocarbon insoluble compound as a microemulsified phase, characterised in that the microemulsified phase is a hydrocarbyl amine and the lubricating composition also contains a dispersant for hydrocarbyl amine salts which may be formed during use of the lubricating composition.
2. A lubricating composition as claimed in claim 1 characterised in that the hydrocarbyl amine is a polyalkylene polyamine having from 1 to 20 carbon atoms.
3. A lubricating composition as claimed in claim 1 or 2 characterised in that the microemulsion is formed using emulsifiers in the ratios of parts by weight:-

Fatty acid	1 to 2.5
Alkyl phenol	1 to 2.5
Amino alcohol	0 to 1
4. A lubricating composition as claimed in claims 1, 2 or 3 characterised in that it contains from 1 to 20% wt. of hydrocarbyl amine and from 2 to 25% wt. of emulsifiers by weight of total composition.
5. A lubricating composition as claimed in any of claims 1 to 4 characterised in that the dispersant is a polyisobutenyl succinimide.
6. A lubricating composition as claimed in any of claims 1 to 5 characterised in that the dispersant is a barium, calcium or sodium phenate, sulphonate or carboxylate.
7. A lubricating composition as claimed in any of claims 1 to 6 characterised in that it contains from 1 to 30% wt. of dispersant by weight of total composition.
8. A lubricating composition as claimed in claim 1 substantially as described in the Examples.

- 11 -

- 12 -

9. A method of lubricating a marine diesel engine having a cylinder lubricating system characterised in that the lubricant used is a lubricating composition as claimed in any of claims 1 to 8.

- 12 -



EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ¹⁾)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>FR - A - 2 311 839</u> (ETHYL COOPER LTD.) * Claims 1-6; 14; page 6, lines 5-7; page 8, line 31 - page 9, line 2 * -- <u>US - A - 3 451 931</u> (D.J. KAHN et al.) * Claim 1; column 7, line 73 - column 10, line 58 * -- <u>GB - A - 1 386 620</u> (BP) <u>US - A - 3 346 494</u> (M.L. ROBBINS et al.) ----	1,2,5 1-3,5-9	C 10 M 1/32
			TECHNICAL FIELDS SEARCHED (Int.Cl. ³⁾) C 10 M 1/32 B 01 F 17/40 17/00
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search	Date of completion of the search	Examiner	
The Hague	09-11-1979	RO TSAERT	