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(54) **Lubrication and lubricants.**

(57) Compounds of formula $X[AR]_n$ in which X is a residue of an active hydrogen-containing amine, amide or ammonia, A is a random or block polyoxyalkylene residue comprising 6 to 170 alkylene oxide residues having 2 to 4 carbon atoms, R is a hydrogen or alkyl or aryl group and n is at least 1 are useful as heat resistant lubricants.

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LUBRICATION AND LUBRICANTS

THIS INVENTION relates to lubrication and lubricants

It is known to use polyoxyalkylated alcohols as lubricants as described for example in the sales brochure "Emkarox' Polyalkylene Glycols, Properties and Applications", published by Imperial Chemical Industries PLC, Chemical Products Business Centre. Typical applications include industrial gear oils and greases, compressor lubricants and rubber and textile lubricants. The compounds are normally used as compositions containing an antioxidant, a corrosion inhibitor, an anti-wear additive and an extreme pressure additive. However, even when formulated with an anti-oxidant these lubricants tend to degrade at temperatures above 250 °C. We have now found that polyoxyalkylated ammonia amines and amides are of improved thermal stability, and are good lubricants even at high temperatures.

The present invention comprises the use of compounds of formula

$X[AR]_n$

wherein

X is the residue of an active hydrogen-containing organic amine, amide or ammonia following active hydrogen removal;

A is a random or block polyoxylalkylene residue, comprising 6 to 170 alkylene oxide residues having 2 to 4 carbon atoms;

R is hydrogen or an alkyl or aryl group; and

n is an integer having a value of at least 1 wherein each AR segment may be the same or different as lubricants. In a specific form of the invention they are used as mould release agents.

The said compounds preferably have an average molecular weight of up to 40,000, for example from 300 to 10,000, more preferably from 600 to 8000, most preferably from 750 to 7000. Suitable compounds have a viscosity of from 10 to 1500 centistokes at 40 °C, more preferably from 100 to 1000 centistokes at 40 °C, most preferably from 100 to 460 centistokes at 40 °C. X may be a residue of a mono or polyhydric amine having primary and/or secondary amine groups or an amide. It is suitably the residue of an alkyl, cycloalkyl or aromatic amine or amide having 1 to 200 carbon atoms, for example 1 to 50 carbon atoms preferably 1 to 30 carbon atoms and more preferably 1 to 15 carbon atoms and preferably 1 to 100, for example 1 to 35 and more preferably 1 to 20 amine or amide groups, more preferably 1 to 10 amine or amide groups, most preferably 1 to 6 amine or amide groups. Suitable compounds for use in the present invention include those in which X is a residue of an alkylamine for example butylamine, an alkanolamine for example ethanolamine, diethanolamine, triethanolamine, or tripropanolamine, an alkylene diamine for example ethylenediamine, diethylenetriamine, triethylenetetramine, or piperazine. A preferably comprises 10 to 140 and more preferably 10 to 120 alkylene oxide residues having 2 to 4 carbon atoms. Preferred compounds are those in which A comprises 0 to 10, more preferably from 0 to 8 and most preferably from 0 to 4 ethylene oxide residues for every 10 propylene oxide residues.

Each R is individually hydrogen or an alkyl or aryl group containing 1 to 30 carbon atoms, preferably 1 to 15 carbon atoms and more preferably 1 to 6 carbon atoms for example a methyl, ethyl, propyl, isopropyl, or butyl group. n preferably has a value of 1 to 100 for example 1 to 20, more preferably 1 to 12, most preferably 1 to 8.

The compounds for use in the present invention may in general be prepared by reacting the corresponding amine, amide or ammonia with the desired alkylene oxide(s) successively or simultaneously, normally in the presence as catalyst of an acid or an alkali, for example sodium or potassium hydroxide. The reaction is suitably carried out at a temperature in the range 100 to 180 °C, preferably 150 to 160 °C for ethoxylation, 105 to 115 °C for propoxylation or butoxylation, or 120 to 130 °C for reaction with a mixture of alkylene oxides. Suitably the reaction is carried out at elevated pressure, preferably at 1.5 to 5 bars absolute.

The invention also comprises a lubricating fluid composition comprising a compound of formula $X[AR]_n$, an anti-oxidant, a corrosion inhibitor, an anti-wear additive and an extreme pressure additive. Suitable anti-oxidants include for example butylhydroxyanisole, phenothiazine, hydroquinone monomethyl ether, and/or butylhydroxytoluene. Corrosion inhibitors which may be used include half esters of alkenyl succinic acids, N-acyl sarcosine and benzotriazole. Suitable anti-wear and extreme pressure additives include tricresylphosphate and methylenebis(dibutyldithiocarbamate). Suitable compositions preferably contain 0.1 to 2% of anti-oxidant, 0.1 to 2% of corrosion inhibitor and 0.1 to 2% each of anti-wear and extreme pressure additives dissolved in the compound of formula $X[AR]_n$ which may suitably comprise the whole of the remainder of the composition. Optionally other lubricating and/or viscosity modifying substances may also be present if desired. The compositions are typically anhydrous but may be used with up to 5% water.

The present invention also provides a process of lubrication for mechanical components in which mechanical parts to be lubricated are contacted with a compound of formula $X[AR]_n$. Such mechanical parts include gears especially worm gears, and parts of rolling mills, plastics callenders, paper making machines, compressors for example for use in refrigeration and air conditioning systems based on non chlorine containing hydro fluoro carbon refrigerants for example 1,1,1,2 tetrafluoroethane and vacuum pumps. The present invention further provides a process of lubrication for use in mould release applications in which a mould is coated with a compound of formula $X[AR]_n$ before moulding a polymer, especially a plastics or rubber material, and also a process for lubrication of textiles in which a textile yarn is contacted with a compound of formula $X[AR]_n$.

EXAMPLES

15 Production of Propoxylated Piperazine

5.5 kg of piperazine was mixed with a solution of potassium hydroxide (126g) in water (96g).

The mixture was heated to 110-120°, under a vacuum of 5-15 mm Hg for a period of 1 hour to dehydrate the mixture, and to mix the products fully in an autoclave.

The autoclave was charged with nitrogen to a pressure of 2 bar absolute, by bubbling N₂ through the mixture.

Propylene oxide (PO) was added in two stages.

1. 5.5kg PO was introduced to the reactor at 120-125° C over a period of 1 hour. The pressure in the reactor increased from 3 bars to 3.4 bars absolute.

After the propylene oxide had been added the reaction was allowed to continue for a further 2 hours to ensure completion.

The product was stripped for 1 hour at 110° C, with a vacuum of 5-15 mm Hg to remove unreacted propylene oxide.

2. 40kg of propylene oxide was added at 115° C to the first stage product over a period of 7.5 hours. The pressure increased from 2 bar to 8.6 bar absolute. After all the propylene oxide had been added, the reaction was allowed to progress for a further 3 hours at 115° C.

The product was stripped for 1 hour at 115° C, under a vacuum of 5-15 mm Hg, to remove unreacted propylene oxide.

16 kg of this product was mixed with 94.5 g of potassium hydroxide dissolved in water (60.5g).

The mixture was stirred at room temperature under at 5 mm-15 mm Hg vacuum for 1/2 hour before being heated to 120° C for 1 1/2 hours to remove water (second water removal). The reactor was then charged to a pressure of 2 bar absolute using N₂ bubbled through mixture, followed by the addition of 37.5 kg of propylene oxide over a period of 6.5 hours at 115° C. The pressure increased from 2 bar to 6.4 bar absolute.

After all the PO was introduced the reaction was allowed to continue for a further 3 hours at 115° C.

The product was stripped for 1 hour at 110° C under a 5-15 mm Hg vacuum to remove unreacted propylene oxide.

The final product was demineralised using 1.5 kg of "Ambosol" aluminium silicate and 0.3 kg of a filter aid sold under the trade name "Dicalite". The mixture was heated to 110° C for 1 hour then filtered using a Gauthier filter, at 110° C.

The viscosity of this product, coded as Piperazine 01-220, at 40° C was 262 cSt.

The following products were made similarly but with differing amounts of propylene oxide being added to give differing molecular weight.

1. Piperazine 01-150

Piperazine was propoxylated to give a product with a final viscosity of 150 cst at 40° C, and molecular weight of 1368.

2. Piperazine 01-460

Piperazine was propoxylated to give a product with a final viscosity of 460 cst at 40 °C, and molecular weight of 3909.

5 Production of Methyl End Capped Propoxylated Piperazine Derivative (PIP 01 240 Me).

Piperazine was propoxylated using similar techniques to those used for PIP 01 150, PIP 01 220, and PIP 01 460 to give a product with a final viscosity of cst 154 at 40 °C (ASTM 0445) and a molecular weight of 1950.

10 This product was then methyl end capped by the following process: 75 kg of the propoxylated piperazine (at ambient temperature) was mixed with 7.79 kg of sodium methoxide and stirred for $\frac{1}{2}$ hour. The mixture was then heated under vacuum for 4 hours (120 °C, 5-15 mm Hg). Methyl chloride (8 kg) was then slowly introduced to the reactor (120 °C-130 °C) over a period of 1 hour. Excess methyl chloride was then removed by vacuum stripping (5-15 mm Hg, $\frac{1}{2}$ hour, 120 °C). 4.5 Kg of 75% aqueous H₃PO₄ was then
15 added to adjust the pH to 6.8. The reactor was then cooled from 120 °C to 60 °C and washed twice with water. The first water wash used 11 kg of water and the second water wash used 8.8 kg of water.

The final product was essentially insoluble in water and slightly less dense, hence for both washes the water could be simply decanted from the bottom of the reactor. The washed product was vacuum stripped to remove excess water (1 Hr, 5-15 mm Hg, 120 °C) and filtered with a Gauthier filter using "Dicalite" filter
20 aid. This gave a final product of viscosity 240 cst at 40 °C and with approximately 95% methyl end capping (calculated from hydroxyl number analysis ASTM D1957).

Whilst the product as such showed good heat stability and acceptable properties as a base fluid for lubricants as shown in the following tables it is believed that its properties could be further improved by avoiding the use of phosphoric acid in the process of production. Phosphoric acid is only necessary to
25 protect vessels against corrosion and if omitted corrosion resistant vessels should be used, for example glass lined reactors.

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Propoxylated n-Butylamine (Code Butylamine 01-220)	
Starting Materials -	n- Butylamine Propylene Oxide
Weight of n Butylamine	4 kg
Catalyst	140g Sodium Hydroxide

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Alkoyxlation Stages	1	2
Weight of Propylene Oxide	8.5 kg	31.5 kg
PO Introduction Temperature	120-125 °C	115 °C
Duration of PO Introduction	1.66 hours	6 hours
Absolute Pressure (min/max)	5.2 bar-8.5 bar	2 bar-8.8 bar
Further Reaction		
Time and Temperature	2 Hours	2 Hours at 115 °C
Stripping	2 Hours at 90 °C	1 Hour at 110 °C
20 kg of this product was then reacted with further propylene oxide under the following conditions (a second water removal as previously described was carried out after the catalyst addition).		
Catalyst	99 g Potassium Hydroxide plus 6g water	

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<u>Alkoxylation Stages</u>		3	4	5
5	Weight of Propylene Oxide	30 kg	15 kg	13kg
	PO Introduction Temperature	115 ° C	115 ° C	115 ° C
5	Duration of PO Introduction	5 Hours	2.5 Hours	2.5 Hours
	Absolute Pressure (min/max)	2 bar-6.5 bar	2 bar-6.2 bar	3.4 bar-8 bar
Further Reaction				
10	Time and Temperature	2.5 Hours at 115 ° C	2 Hours at 115 ° C	2 Hours at 115 ° C
	Stripping	1 Hour at 110 ° C	1 Hour at 110 ° C	1 Hour at 110 ° C
	Viscosity at 40 ° C (ASTM D445)	134 cSt	185 cSt	223 cSt

<u>Demineralisation Stage</u>	
Filter	GAUTHIER
Materials	1 kg "AMBOSOL"
	0.3 kg "DICALITE"
Filtration Temperature	110 ° C
Stripping Conditions	1 Hour at 110 ° C

Propoxylated Triethanolamine Production (Code Tela 01-220)			
5	Starting Materials - Weight of triethanolamine Catalyst	TRIETHANOLAMINE	
		PROPYLENE OXIDE	
		21 kg	
		265 g POTASSIUM HYDROXIDE (90%)	
10	Alkoxylation Stage	1	2
15	Weight of Propylene Oxide (PO) PO Introduction Temperature Duration of PO Introduction Absolute Pressure (min/max)	24.4 kg	26 kg
		115 ° C-120 ° C	115 ° C-120 ° C
		3 Hours	approx 3 hours
		2 bar-3.6 bar	3.8 bar-5.9 bar
20	Further Reaction		
25	Time and Temperature Stripping	1.5 Hours at 115 ° C	1.5 Hours at 115 ° C
		1 Hour at 110 ° C	1 Hour at 110 ° C
8.5 kg of the product was added to 175 g of 90% KOH solution in water and a second water removal as previously described was carried out. The product was then propoxylated under the following conditions.			
25	Weight of Propylene Oxide (PO) PO Introduction Temperature Duration of PO Introduction Absolute Pressure (min/max)	44 kg	
		115 ° C	
		8.5 Hours	
		2 bar-6.4 bar	
30	Further Reaction		
35	Time and Temperature Stripping	2.5 Hours at 115 ° C	
		1 Hour at 115 ° C	
40	Demineralisation Stage		
35	Filter Materials Filtration Temperature Stripping Conditions	GAUTHIER	
		2.5 kg "AMBOSOL"	
		0.3 kg "DICALITE"	
		110 ° C	
		1 Hour at 110 ° C	

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PREPARATION OF PROPOXYLATED ALKYL DIETHANOLAMINE CODE 35 X 2 01-220

A commercial product of formula
 $R^*N - (CH_2 CH_2 OH)_2$
 in which R^* is a mixture of C_{13} and C_{15} alkyl chains in the approximate weight ratio of 70:30, 50% of these groups being linear, and the balance comprising mainly 2-methyl branched species (five kilogrammes) was mixed with 140 grammes of a 90% solution of potassium hydroxide in water (126 grammes KOH). The mixture was then heated to 110-120 ° C, under a vacuum of 5 mm Hg. The temperature and pressure was maintained for 1½ hours to dehydrate the mixture. N_2 was charged to the reaction to a pressure of 2 bars absolute. Following dehydration an alkoxylation stage was carried out as follows. 45 kilogrammes of propylene oxide was introduced into the reactor over an 11 hour period at 115 ° C, during which time the pressure in the reaction was increased from 2 bars to 8 bars absolute. The temperature was maintained for a further 2 ½ hours to ensure completion of reaction.

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The product was stripped for 1 hour at 115 ° C, under a vacuum of 5mm Hg.

A 700 gramme sample was taken and the viscosity of the product was measured according to ASTM D445. The viscosity was found to be 205 cSt at 40 ° C.

In order to increase the viscosity a further 10 kilogrammes of propylene oxide was added to remaining material in the reactor at 115 ° C over a period of 1½ hours, during which time the pressure rose from 2.2 bars to 5.5 bars absolute. The temperature was maintained for a further 2 hours to ensure completion of reaction.

The product was stripped for 1 hour at 115 ° C, under a vacuum of 5mm Hg.

An 800 gramme sample was taken, and its viscosity at 40 ° C was found to be 250 cSt.

The product was then treated in a demineralisation stage with an aluminium silicate sold under the trade mark "Ambosol" (2 kg) and, 1.5 to kilogrammes of "Dicalite" filter aid.

The mixture was maintained at 110 ° C for 1 hour and then filtered using a Gauthier filter.

The following products were made by the above procedure with the changes shown in the tables.

15	PROPOXYLATED ALKYL TRIETHANOL PROPYLENE DIAMINE (CODE 35N 3 X 3 01220)				
20	Alkyl triethanol Propylene Diamine,	R*			
		HOC ₂ H ₄	NC ₃ H ₆ N(C ₂ H ₄ OH) ₂		
25	Starting Materials -	Propylene Oxide			
	Weight of Compound (l)	14.5 kg			
	Catalyst	115 g Potassium Hydroxide (90%)			
30	ALKOXYLATION STAGE				
	Weight Of Propylene Oxide	34.5 kg	10 kg	15.5 kg	20 kg
	PO Introduction Temperature	115-120 ° C	115 ° C	115 ° C	115 ° C
35	Duration of PO Introduction	5.4 Hours	2 Hours	3 Hours	5.5 Hours
	Absolute Pressure (min/max)	2 bar-8.2 bar	2 bar-8.2 bar	2 bar-8.2 bar	2 bar-8.2 bar
40	Further Reaction				
	Time and Temperature Stripping	2 Hours at 115-120 ° C 1 Hour at 115-120 ° C	2 Hours at 115 ° C 1 Hour at 115 ° C	2 Hours at 115 ° C 1 Hour at 115 ° C	2 Hours at 115 ° C 1 Hour at 115 ° C
45	VISCOSITY AT 40 ° C (ASTM D445)	117 cSt	127 cSt	158 cSt	222 cSt
	DEMINERALISATION STAGE				
50	Filter	GAUTHIER			
	Materials	1 kg "AMBOSOL"			
		0.3 kg "DICALITE"			
55	Filtration Temperature				
	Stripping Conditions	1 Hour at 110 ° C			

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	PROPOXYLATED TRIISOPROPANOLAMINE (CODE TPLA 01 220)	
5	Starting Materials - Weight of Triisopropanolamine Catalyst	TRIISOPROPANOLAMINE PROPYLENE OXIDE 7 kg 334 g POTASSIUM HYDROXIDE (90%) plus 334g WATER
10	ALKOXYLATION STAGE	
	Weight of Propylene Oxide PO Introduction Temperature Duration of PO Introduction Absolute Pressure (min/max)	63.5 kg 115 ° C 11.75 Hours 2 bar-10.4 bar
15	Further Reaction	
	Time and Temperature Stripping VISCOSITY AT 40 ° C (ASTM D445)	3 Hours at 115 ° C 1 Hour at 115 ° C 248 cSt
20	DEMINERALISATION STAGE	
	Filter Materials	GAUTHIER 2 kg AMBOSOL 0.3 kg DICALITE
25	Filtration Temperature Stripping Conditions	120 ° C 1 Hour at 115 ° C

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PROPOXYLATED TRIETHYLENETETRAMINE PRODUCTION (CODE TETA 01-300)				
(H ₂ NC ₂ H ₄ NHC ₂ H ₄ NHC ₂ H ₄ NH ₂)				
Starting Materials -	TRIETHYLENETETRAMINE			
	PROPYLENE OXIDE			
Weight of Triethylene Tetramine	4kg			
Catalyst	SODIUM METHOXIDE - 190 g			
ALKOXYLATION STAGE				
Weight of Propylene Oxide	10 kg	41 kg	5 kg	12 kg
PO Introduction Temperature	120-125 ° C	115 ° C	115 ° C	115 ° C
Duration of PO Introduction	2.5 Hours	6 Hours	1 Hour	2.5 Hours
Absolute Pressure (min/max)	2.8 bar-4.2 bar	2 bar-7.3 bar	3.4 bar-4.6 bar	3.4 bar-6.8 bar
Further Reaction				
Time and Temperature Stripping	1.5 Hours at 115 ° C 1 Hour at 115 ° C	3 Hours at 115 ° C 1 Hour at 115 ° C	2 Hours at 115 ° C 1 Hour at 115 ° C	3 Hours at 115 ° C 1 Hour at 115 ° C
DEMINERALISATION STAGE				
Filter	GAUTHIER			
Materials	2 kg AMBOSOL			
	0.3 kg DICALITE			
Filtration Temperature	110 ° C			
Stripping Conditions	1 Hour at 115 ° C			

PROPOXYLATED DIETHYLENE TRIAMINE (Code DETA 01-220)		
$\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$ (Diethylene triamine)		
Starting Materials - Catalyst	PROPYLENE OXIDE	
	DIETHYLENE TRIAMINE 20 KG	
	60 g Potassium Hydroxide as 90% w/w aqueous solution	
ALKOXYLATION STAGE		
Weight of Propylene Oxide	30 kg	9.5 kg
PO Introduction Temperature	115 °C	115 °C
Duration of PO Introduction	5.5 Hours	1.5 Hours
Absolute Pressure (min/max)	2 bar-8.2 bar	3.4 bar-6.8 bar
Further Reaction		
Time and Temperature	3 Hours at 115 °C	2 Hours at 115 °C
Stripping	1 Hour at 110 °C	1 Hour at 110 °C
VISCOSITY AT 40 °C (ASTM D445)	269.5 cSt	258.6 cSt
DEMINERALISATION STAGE		
Filter	GAUTHIER	
Materials	1.5 kg "AMBOSOL"	
	0.3 kg "DICALITE"	
Filtration Temperature	110 °C	
Stripping Conditions	1 Hour at 110 °C	

PREPARATION PROPOXYLATED OF DIETHANOLAMINE (CODE DELA 01-220)

4 kg of diethanolamine was heated in an autoclave to a temperature of 50 °C, under 5-15 mm Hg vacuum for 1/2 hour, then at 100 °C for 1 hour to dry it.

The autoclave was charged to a pressure of 2 bar absolute using N₂, bubbled through the mixture.

2.5 kg of propylene oxide was added over a period 1/2 hour at 125 °C. The pressure increased from 2 bar to 4.4 bar absolute. The reaction was allowed to progress for a further 1 hour at 125 °C to ensure completion.

The product was then stripped for 1 hour at 100 °C under a vacuum of 5-15 mm Hg to remove unreacted propylene oxide.

4 kg of this product was mixed with 4 kg of diethanolamine and 205g of 90% Potassium Hydroxide in water solution (184.5g KOH)

The mixture was heated to 50 °C for 1/2 hour then 110-120 °C for 1 1/2 hours under a vacuum of 5-15 mm Hg to dehydrate.

The reactor was charged to 2 bar absolute using N₂ bubbled through the mixture.

69 kg of propylene oxide was added over a period of 14 1/2 hours at a temperature of 115 °C. The pressure increased from 2 bar to 10.5 bar absolute.

Reaction was allowed to continue for a further 2 hours at 115 °C to complete reaction. The product was then stripped for 1 hour at 100 °C under a vacuum of 5-15 mm Hg.

In order to increase the viscosity of the product a further 4.5 kg of propylene oxide was added over a period of 1 hour. The pressure increased from 2 bar to 3.8 bar absolute. Reaction was continued for a further 2 hours at 115 °C, before stripping at 100 °C for 1 hour with vacuum of 5-15 mm Hg.

To increase the viscosity still further 3.5 kg of propylene oxide was added at 115 °C over 1/2 hour. The pressure increased from 2 bar to 3.4 bar absolute. Reaction continued for a further 1 1/2 hours at 115 °C. The product was stripped for 1 hour at 100 °C under 5-15 mm Hg vacuum.

To the product was added 2 kg "Ambosol" aluminium silicate and 0.5 kg "Dicalite" filter aid. The mixture was heated to 110 °C for 1 hour before being filtered using a Gauthier filter at 110 °C.

The viscosity of the product, code DELA 01-220 at 40 °C was 213 cSt.

The following product was then made by a similar process using the following materials and conditions

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	PROPOXYLATED MONOETHANOLAMINE PRODUCTION (CODE MELA 01-220)			
10	Starting Materials -	MONOETHANOLAMINE		
		PROPYLENE OXIDE		
	Weight of Monoethanolamine	4 kg		
	ALKOXYLATION STAGE			
15	Weight of Propylene Oxide	8 kg	64kg	9kg
	PO Introduction Temperature	115-120 ° C	115-120 ° C	115-120 ° C
	Duration of PO Introduction	3-4 Hours	8 Hours	1.5 Hours
	Absolute Pressure (min/max)	2 bar-3.6 bar	2 bar-10.8 bar	2 bar-5 bar
	Further Reaction			
20	Time and Temperature Stripping	3.5 Hours at 115-120 ° C 0.5 Hours at 110 ° C	1 Hour at 115 ° C 1 Hour at 110 ° C	2 Hours at 115 ° C 1 Hour at 110 ° C
	DEMINERALISATION STAGE			
25	Filter	GAUTHIER		
	Materials	2 kg "AMBOSOL"		
		0.3 KG "DICALITE"		
	Filtration Temperature	110 ° C		
30	Stripping Conditions	1 Hour at 115 ° C		

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ALKOXYLATION OF ETHYLENE DIAMINE DIAMINE ADDUCT

The adduct is a condensation product formed by the reaction of ethylene diamine and four moles of propylene oxide and is available commercially from Arco. It is sold under the trade name 'Arcol 3400'.

The adduct (17 Kilogrammes) was charged to a reactor and mixed with 190 grammes of a 90% solution of potassium hydroxide. The mixture was dehydrated by stirring for $\frac{1}{2}$ hour at ambient temperature under a vacuum of 5 mm Hg, and raising the temperature to 120 °C for a further period of $1\frac{1}{2}$ hours. N₂ was charged to the reactor to a pressure of 2 bars absolute. Then 57 kilogrammes of a mixture of propylene oxide and ethylene oxide (1:1 weight ratio, pre-mixed) was introduced into the reactor over a period of 8 hours, at 115-120 °C, during which time the pressure in the reactor increased from 2 bars to 6.1 bars absolute. The temperature was maintained for a further 1 hour to ensure completion of reaction.

A 1.1 kilogramme sample was taken and the viscosity of the product was determined according to ASTM D445 to be 176 cst at 40 °C.

In order to increase the viscosity a further 5 kilogrammes of the propylene oxide and ethylene oxide mixture was added to the remaining material in the reactor at 115-120 °C over a period of 1 hour, during which time the pressure increased from 3.4 bars to 4.6 bars absolute. The temperature was maintained for a further 1 hour to ensure completion.

A 1.3 kilogram sample was taken and its viscosity determined according to ASTM D445 to be 175 cst at 40 °C.

The product was then treated in a demineralisation stage with an aluminium silicate sold under the trade mark 'Ambosol' (2kg) and 0.4 kg at a filter aid sold under the trade mark of 'Dicalite'.

The mixture was maintained at a temperature of 110 °C for 1 hour and then filtered using a Gauthier filter. The product was given the code Ethylene diamine adduct 11-175.

PROPOXYLATION OF ETHYLENE DIAMINE ADDUCT

The ethylene diamine adduct Arcol 3400 was reacted with propylene oxide in a similar manner to that previously described. The previous preparation was repeated except that propylene oxide only was used instead of the 1:1 mixture of ethylene oxide and propylene oxide until a product with a final viscosity of 210 cst at 40 °C, and molecular weight 2137 was produced. This was given the code Ethylene diamine adduct 01-210.

10 ALKOXYLATION OF ETHYLENE DIAMINE ADDUCT

The previous example was repeated using a 4:1 ratio of propylene oxide to ethylene oxide in appropriate quantities instead of pure propylene oxide.

1. Ethylene Diamine Adduct 14-220 (A)
15 A product having a final viscosity of 201 cst at 40 °C, and a molecular weight of 1049.
2. Ethylene Diamine Adduct 14-220 (B)
A product having a final viscosity of 214 cst at 40 °C, and a molecular weight of 2416.

20 PROPOXYLATION OF AZIRIDINE POLYMER

Product Code: Aziridine Polymer 01-1200

An aziridine Polymer (thought to contain 35 N-H units) available from BASF and sold under the trade mark 'Polymine G35' was propoxylated, using techniques previously described, to give a product with a final viscosity of 1268 cst at 40 °C, and molecular weight of approximately 30,000.

PHYSICAL AND THERMAL PROPERTIES

30 The above materials were tested as follows, and the results are given in the following table.

1. Viscosity and Viscosity Index

35 Kinematic viscosity of a lubricating fluid was determined according ASTM (American Society of Testing Materials) D445-79. By measuring the viscosity of the fluid at 40 °C and at 100 °C the Viscosity Index of the fluid was determined according to ASTM D2270-79.

40 2. Pour Point

Pour points were determined according to ASTM 97-66 (Reapproved 1978).

45 3. Flash Point

Flash points were determined using the Cleveland Open Cup technique, according to Institute of Petroleum Test Method IP36/ASTM D92

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4. Heat Stabilities

Heat stability of the lubricating fluid was determined by placing triplicate samples in a forced draught oven at 180 °C for a period of up to 180 hours. The weight loss, determined as a percentage of the original weight is recorded as a function of time.

5. Lubrication Testing

The lubricating properties of the lubricating fluid were determined using the Shell 4-ball technique, according to ASTM 4172.

The lubricating fluid was tested at 75 °C and 220 °C.

A 40 kg load is applied and the test was run for 1 hour at 1450 rpm, and the diameter of the scar produced was determined.

6. Corrosion Test

Corrosion was tested in two ways. Test A is carried out by immersing a freshly cleaned steel cylindrical test piece, according to ASTM D665-82, in the fluid for 1/2 hour. The test piece was drained and placed in 200 cm³ of demineralised water in an oven at 60 °C. The test was complete when the water became discoloured and/or the test piece showed signs of rusting. Test B was according to ASTM D665-82. 0.5% of an anticorrosion additive known as Atmot 9013, and commercially available from ICI Speciality Chemicals, was added to the alkoxyated products shown, prior to the test being carried out. The anticorrosion properties were determined in distilled water and synthetic sea water.

Code or Name of Product	Molecular Weight	Moles PO/EO per mole product	Viscosity cSt		VI*	Flash Pt °C	Pour Pt °C	Wear Scar (mm)
			40 °C	100 °C				
Propoxylated n-Butanol	2100	34	222	38	215	225	-36	0.51
Propoxylated Glycerol	2000	32	214	31	188	222	-33	0.56
35X2 01-210	3178	50	245	38	208	240	-30	0.55
Butylamine 01-220	2847	48	225	33	182	190	-31	0.53
Piperazine 01-220	2730	46	261	36	188	270	-25	0.54
35N3X3 01-210	3889	60	222	31	183	235	-33	0.56
MELA 01-220	3082	52	233	32	182	244	-30	0.59
DELA 01-220	2942	49	213	30	182	224	-33	0.57
TELA 01-220	3585	60	260	37	193	220	-30	0.54
TPLA 01-220	3197	52	251	34	182	215	-36	0.59
DETA 01-220	2295	38	258	25	126	230	-25	0.52
TETA 01-220	2900	48	295	29	133	270	-23	0.51
Ethylene Diamine Adduct 01-210	2137	31	107	23	136	225	-27	0.47
Piperazine 01-150	1368	22	142	19	152	246	-21	0.40
Piperazine 01-460	3909	65	445	70	236	227	-23	0.47
Aziridine Polymer 01-1200	30,000	550	1383	203	278	286	-13	0.50
Ethylene Diamine Adduct 14-220(A)	1049	11/3	201	17	92	260	-34	0.50
Ethylene Diamine Adduct 14-220(B)	2416	30/8	214	27	163	250	-34	0.46
Ethylene Diamine Adduct 11-175	1268	9/9	176	25	176	270	-22	0.42
Piperazine 01-240 Me	1300	21	240	28	152	258	-34	1.26

* Viscosity Index

Name of Product	Corrosion Test A Properties (Time to Failure).	Temperature Stability at 180 °C (Weight Loss)													Test B Corrosion Properties				
		0	10	20	30	40	50	60	70	80	90	100	120	140	160	Distilled Water	Synthetic Sea Water		
Propoxylated n-Butanol Propoxylated Glycerol 35X2 01-210 Butylamine 01-220 Piperazine 01-220 35N3X3 01-210 MELA 01-220 DELA 01-220 TELA 01-220 TPLA 01-220 DETA 01-220 TETA 01-220 Ethylene Diamine Adduct 01-210 Piperazine 01-150 Piperazine 01-460 Aziridine Polymer 01-1200 Ethylene Diamine Adduct 14-220A Ethylene Diamine Adduct 14-220B Ethylene Diamine Adduct 11-175 Piperazine 01-240 Me	<1 Hour 16 Hours	0	15	28	40	51.5	62	59	62	65	67	68	71	75		PASS	FAIL		
		0	25	37	45	50	55	57	6.5	7.3	8	8.8	9.6				PASS	PASS	
		0	1.8	3.2	4.1	4.9	5.7	6.5	7.3	4	4.6	5.2	6	8.5	12.3	17.5		PASS	PASS
		0	0.7	1.2	2.1	2.4	2.9	3.5	4	4.6	2.25	2.5	2.75	3.25	3.75		PASS	PASS	
		0	0.5	0.75	1	1	1.25	1.5	1.7	2	2.25	2.5	2.75	3.25	3.75		PASS	PASS	
		0	1.1	1.9	2.5	3.1	3.7	4.3	4.9	5.4	6.1	6.6	9.4	13.2	18.6		PASS	PASS	
		0	0.8	1.3	1.5	1.8	2.1	2.7	3.4	4.3	5.2	6.4	9.4	13.2	18.6		PASS	PASS	
		0	0.4	0.6	1	1.3	1.6	2	2.4	2.9	3.3	3.6	4.4	5.4	6.7		PASS	PASS	
		0	0.2	0.4	0.6	0.9	1.2	1.5	2	2.4	3	3.7	5.6	7.9	11.1		PASS	PASS	
		0	0.6	1.2	2	2.4	4.2	6.4	8.2	10.2	12.2	14	18	22	26				
		0	5	9	13	17	21	25	29	32	35	37	42	46	49				
		0	0.8	1.8	2.8	3.7	4.6	5.6	6.5	7.5	8.5	9.6	11.8	12.2	16.4				
		0	1.5	2.7	3.9	5.1	6.3	7.4	8.5	9.7	10.8	12.0	14.0	16.2	18.0				
		0	0.8	1.8	2.5	3.2	3.5	4.0	4.6	5.2	5.9	6.5							
		0	3.5	7.2	15	24	34	42	50	55	59	63							
		0	0.2	0.6	1.1	1.5	2.2	3.0	3.8	4.8	6.0	7.5	10.6	14.5	18.5				
		0	1.5	2.5	5.0	7.0	8.5	10.5	12.0	14.0	15.5	17.5	20.5	23.5	26.5				
		0	0.5	1.5	2.5	3.5	4.0	5.0	6.0	7.0	8.5	9.0	10.0	11.5	13.0				
		0	0.1	2.5	3.5	5.0	6.0	7.5	8.5	10.0	11.0	12.0	14.5	16.5	19.0				
		0	2.8	4.7	6.1	7.4	8.6												

Lubricating Properties of Aged Lubricating Fluids

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The products shown in the following table were heated in an oven through which a forced draught of air was passed at 180 °C so as to 'age' the products. At various intervals samples were taken and their lubricating properties determined by the Shell 4-ball technique according to ASTM D4172 as previously described.

10 The viscosity at 40 °C, of the same samples was measured according to ASTM D445, as previously described.

Results as follows: (see table)

	HEATING TIME							
	BEFORE AGEING		17 HOURS		41 HOURS		203 HOURS	
	Viscosity at 40 °C	Wear Scar Diameter	Viscosity at 40 °C	Wear Scar Diameter	Viscosity at 40 °C	Wear Scar Diameter	Viscosity at 40 °C	Wear Scar Diameter
15								
20	Propoxylated Glycerol MW* 2000	208 cSt	0.51 mm	87 cSt	0.71 mm	149 cSt	0.83 mm	- -
25	Propoxylated n-Butanol MW* 2100	224 cSt	0.56 mm	115 cSt	0.65 mm	96 cSt	0.87 mm	- -
	PIPERAZINE 01-220	262 cSt	0.54 mm	252 cSt	0.53 mm	251 cSt	0.56 mm	246 cSt 0.57 mm
30	DELA 01-220	213 cSt	0.57 mm	202 cSt	0.57 mm	194 cSt	0.51 mm	187 cSt 0.65 mm

* MW = Molecular Weight

35 The above data shows in the case of propoxylated glycerol that there is a severe fall in viscosity indicative of decomposition and a severe decline in lubricating efficiency as shown by the wear scar test after 17 hours of heating; a further decline in lubricating efficiency after 41 hours of heating was found as shown by the wear scar test accompanied by further degradation which produced an increase in viscosity.

40 In the case of propoxylated n-butanol a continuing decline in both viscosity and lubricating efficiency was found. The products of the invention showed substantially maintained lubricating efficiency and satisfactory resistance to viscosity changes even after 203 hours of heating.

Claims

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1. The use as lubricants of compounds of formula

$X[AR]_n$

wherein

50 X is the residue of an active hydrogen-containing amine, amide or ammonia following active hydrogen removal;

A is a random or block polyoxyalkylene residue, comprising 6 to 170 alkylene oxide residues having 2 to 4 carbon atoms;

R is hydrogen or an alkyl or aryl group; and

55 n is an integer having a value of at least 1 wherein each AR segment may be the same or different.

2. A lubricating fluid composition which comprises a compound of formula

$X[AR]_n$

wherein

X is the residue of an active hydrogen-containing amine, amide or ammonia following active hydrogen

removal;

A is a random or block polyoxyalkylene residue, comprising 6 to 170 alkylene oxide residues having 2 to 4 carbon atoms;

R is hydrogen or an alkyl or aryl group; and

- 5 n is an integer having a value of at least 1 wherein each AR segment may be the same or different and at least one additive selected from a corrosion inhibitor, and anti-oxidant, an anti-wear additive and an extreme pressure additive.

3. A lubricating fluid composition comprising a compound of formula $X[AR]_n$, an anti-oxidant, a corrosion inhibitor and an anti-wear additive.

- 10 4. A lubricating fluid according to claim 3 which comprises an extreme pressure additive.

5. A process of lubrication in which mechanical parts, textile yarns or moulds for forming plastics components are contacted before use with a compound of formula

$X[AR]_n$

wherein

- 15 X is the residue of an active hydrogen-containing amine, amide or ammonia following active hydrogen removal;

A is a random or block polyoxyalkylene residue, comprising 6 to 170 alkylene oxide residues having 2 to 4 carbon atoms;

R is hydrogen or an alkyl or aryl group; and

- 20 n is an integer having a value of at least 1 wherein each AR segment may be the same or different.

6. A process of lubrication of machinery in which the surfaces of relatively movable components are contacted with a composition according to claim 2, 3 or 4.

7. A process, use or fluid according to any preceding claim in which the compound of formula $X[AR]_n$ has an average molecular weight of 300 to 10,000.

- 25 8. A process, use or fluid according to any preceding claim in which the compound of formula $X[AR]_n$ has a viscosity of 10 to 1500 centistokes at 40° C.

9. A process, use or fluid according to any preceding claim in which X is a residue of a primary or secondary amine or an amide and in which n is at most 100.

- 30 10. A process, use or fluid according to any preceding claim in which A comprises 0 to 10 ethylene oxide residues per 10 propylene oxide residues.

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EUROPEAN SEARCH REPORT

EP 90 30 9132

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 851 144 (P.W. McGRAW) * Column 2, lines 9-27,51-60; column 3, lines 19-39; claim 2 * - - -	1-10	C 10 M 105/62 C 10 M 105/68 C 10 M 107/40
X	EP-A-0 109 515 (UNION CARBIDE CORP.) * Page 3, line 5 - page 4, line 26; page 5, lines 13-19 * - - -	1-10	C 10 M 169/04 // (C 10 M 169/04 C 10 M 105:62 C 10 M 107:40)
P,X	EP-A-0 379 175 (THE DOW CHEMICAL CO.) * Page 2, line 45 - page 3, line 33; claim 2 * - - -	5	C 10 N 40:00 C 10 N 40:30
A	EP-A-0 017 072 (THE DOW CHEMICAL CO.) * Page 2, line 19 - page 3, line 19; page 5, lines 10-13 * - - - - -	5	C 10 N 40:36
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 10 M
Place of search The Hague		Date of completion of search 27 November 90	Examiner HILGENGA K.J.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document			