FORM 8—REGULATION 12 (2)

COMMONWEALTH OF AUSTRALIA

PATENTS ACT, 1952-1973

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

(a) Here insert (in full) Name of Company.

In support of the Convention Application No. PCT/GB89/00530 made by (a) NATIONAL RESEARCH DEVELOPMENT CORPORATION

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here insert Title of Invention.

(b) METHOD OF AND COMPOSITIONS FOR REDUCING WEAR ON SURFACES SUBJECTED TO FRICTIONAL FORCES.

(c) and (d) Here insert Full Name and Address of Company Official authorised to make declaration.

I, (c) D.R. Chandler

of (d) National Research Development Corporation,
101, Newington Cuaseway, LONDON, SE1 6BU.

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was/were

(e) Here insert Basic Country or Countries followed by date or dates of Basic Application(s).

made in (e) GREAT BRITAIN on the 18th day of May 1988

on the ...... day of ...... 19......

(f) Here insert Full Name(s) of Applicant(s) in Basic Country.

by (f) FODOR, JOSEF and SCHOFIELD, JACK.

(g) Here insert (in full) Name and Address of actual Inventor or Inventors.

3. (g) JOSEF FODOR of Naphegy, Ter 5/B, H-1016 Budapest, and JACK SCHOFIELD of 12 The Paddock, Upton, Wirral, ~~UK~~ Merseyside, L49 6NP, United Kingdom

is/are the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

Applicant is the Assignee of the said Inventor(s).

JOSEF FODOR and JACK SCHOFIELD

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first Application(s) made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at LONDON

this 25th day of OCTOBER 1990

(h) Personal Signature of Declarant (c) (no seal, witness or legalisation).

For and on behalf of National Research Development Corporation

(h) [signature] D. R. CHANDLER

(Signature of Declarant)

Patent Agent

Authorised by the Corporation

To THE COMMISSIONER OF PATENTS.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-36977/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 622912

(54) Title
METHOD OF AND COMPOSITIONS FOR REDUCING WEAR ON SURFACES SUBJECTED TO FRICTIONAL FORCES

International Patent Classification(s)
(51)[4] C10M 133/38 C10L 001/22 C10M 133/40

(21) Application No. : 36977/89 (22) Application Date : 17.05.89

(87) PCT Publication Number : WO89/11518

(30) Priority Data

(31) Number (32) Date (33) Country
8811696 18.05.88 GB UNITED KINGDOM

(43) Publication Date : 12.12.89

(44) Publication Date of Accepted Application : 30.04.92

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(56) Prior Art Documents
US 3779920
US 3720616
US 2030033

(57) Claim

1. A composition having anti-surface wear properties comprising a carrier and dissolved and/or dispersed therein an effective amount of a compound capable of producing a multi-molecular lubricating layer having anti-surface wear properties characterised in that said compound is a heteropolar compound comprising at least one wholly unsaturated heterocyclic six-membered ring in which at least one unsubstituted heteroatom moiety acts as a hydrogen acceptor and in which said compound also comprises at least one hydrogen donor moiety and in which said heteropolar compound has no substituent which by itself or together with another substituent or substituents creates such steric hindrance and/or renders the molecule so basic or acidic or so alters

.../2

the steric geometry of the molecule as to prevent interaction of the hydrogen donor and acceptor moieties of one molecule of the heteropolar compound with the hydrogen donor and acceptor moieties of another molecule of the heteropolar compound nor any substituent which by itself or together with another substituent or substituents has the effect of solubilizing said heteropolar compound in the selected carrier to the extent that migration of the heteropolar compound to the interfaces of the carrier with the carrier environment is prevented.

21. A method of reducing wear on a surface which is subject to frictional forces which comprises forming and maintaining on said surface a protective layer by applying to said surface a composition comprising a carrier and a compound capable of producing a multimolecular lubricating layer characterised in that said compound capable of producing a multi-molecular lubricating layer is a heteropolar compound comprising at least one unsaturated heterocyclic six-membered ring in which at least one unsubstituted heteroatom moiety acts as a hydrogen acceptor and in which said compound also comprises at least one hydrogen donor moiety, and in which said heteropolar compound has no substituent which by itself or together with another substituent or substituents creates such steric hindrance and/or renders the molecule so basic or acidic or so alters the steric geometry of the molecule as to prevent interaction of the hydrogen donor and acceptor moieties of one molecule of the heteropolar compound with the hydrogen donor and acceptor moieties of another molecule of

.../3

(11) AU-B-36977/89
(10) 622912

said heteropolar compound nor any substituent which by itself or together with another substituent or substituents has the effect of solubilizing said heteropolar compound in the carrier to the extent that migration of the heteropolar compound to the interfaces of the carrier with the carrier environment is prevented.

ANNOUNCEMENT OF THE LATER PUBLICATION OF INTERNATIONAL SEARCH REPORTS

PCT

International Bureau

622912

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C10M 133/38, 133/40 C10L 1/22 — A3

(11) International Publication Number: WO 89/11518

(43) International Publication Date: 30 November 1989 (30.11.89)

(21) International Application Number: PCT/GB89/00530

(22) International Filing Date: 17 May 1989 (17.05.89)

(30) Priority data:
8811696.7 18 May 1988 (18.05.88) GB

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(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US.

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(88) Date of publication of the international search report: 8 February 1990 (08.02.90)

(54) Title: METHOD OF AND COMPOSITIONS FOR REDUCING WEAR ON SURFACES SUBJECTED TO FRICTIONAL FORCES

(57) Abstract

A method and composition for reducing wear on surfaces subjected to frictional forces. The lubricating compositions can be applied in a carrier which may be organic or inorganic in nature. They function by providing a regime in which multimolecular layers are adsorbed onto the surfaces to be protected, thus enabling comparatively thick protective films to be built up on the surfaces subjected to frictional wear. The molecules having this property are essentially single or condensed unsaturated ring systems which comprise at least one six-membered unsaturated heterocyclic ring comprising at least one heterocyclic moiety which acts as a hydrogen acceptor and a hydrogen donor moiety. If substituents are present they should not create steric hindrance and/or render the molecule so basic or acidic as to alter the steric geometry of the molecule as to prevent the interaction of the active groups.

DESCRIPTION

"METHOD OF AND COMPOSITIONS FOR REDUCING WEAR ON SURFACES SUBJECTED TO FRICTIONAL FORCES"

The present invention relates to a method of, and compositions for, reducing wear on surfaces subjected to frictional forces, particularly between moving surfaces.

The primary purpose of lubrication is separation of moving surfaces to minimise friction and wear. Several distinct regimes are commonly recognised in the field of lubrication. Thus in fluid film lubrication the load is supported entirely by pressures within the separating fluid film. This film pressure is frequently generated by relative motion of the surfaces involved, which pumps the lubricant into a converging, wedge-shaped zone. The hydro dynamic behaviour of such bearings is completely dependent on the viscous behaviour of the lubricant. Both the load-supporting oil film pressure and the power loss are functions of lubricant viscosity in combination with the geometry and shear rate imposed by the bearing operating conditions.

As the severity of operating conditions increases, a point is eventually reached where the load can no longer be carried completely by oil-film support. High spots, or asperities of the mating surfaces must then shear with the lubricant in load support and the lubrication regime shifts from full-film to mixed-film and then to complete boundary high load, low speed, low viscosity lubricant, misalignment, high surface roughness or an inadequate supply of lubricant. With boundary lubrication, chemical additives in the lubricating composition and chemical metallurgical, and mechanical factors involving the two rubbing surfaces will determine the extent of wear and the degree of friction.

Under boundary conditions of lubrication, metal contact through the oil film results in junctions of asperities and subsequent metal tearing on a microscopic scale. As loads increase these contacts become more frequent and result in more plastic deformation, higher temperatures and welding with seizure eventually occurring on a gross and devastating scale. Hypoid gears, since they impose severe sliding conditions in combination with high contact stress are particularly susceptible to this type of damage. The organic lubricant film normally present becomes ineffective under the intense heat which leads to very high surface temperatures.

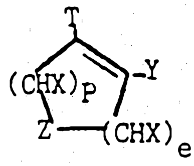
To combat welding under such extreme conditions, extreme pressure lubricants were developed. Such lubricants contain additives which react at the high contact temperatures to form high-melting inorganic lubricant films on the metal surfaces which prevent massive welding and breakdown. Generally, these additives consist of sulphur, chlorine, phosphorus and lead compounds which act either by providing layers of low shear strength to minimise metal tearing or by serving as fluxing agents to contaminate the metal surface and prevent welding. Since all extreme-pressure additives are affected by chemical action, i.e. the formation of covalent bonds, their use is generally avoided to eliminate possible corrosion difficulties.

Dry sliding, which involves solid-to-solid contact, not infrequently exists, even when adequate fluid film lubrication is provided. Dry sliding can occur for example, in starting up of a machine, with misalignment or inadequate clearance during run-in, during reversal of direction, and during any delays or interruptions in supply of the lubricating fluid. Where conventional oils and greases cannot be used because of extreme temperatures, high vacuum, radiation, or contamination, thin coatings of dry lubricants have been applied to reduce the higher friction and more extensive wear which otherwise obtain on rubbing the structural materials against each other.

Thus the goal of lubrication is elimination of this wear and minimising of friction which would otherwise be encountered in dry sliding. Whilst this can be accomplished by complete separation of the rubbing surfaces as by a full film of fluid lubricant, generally such complete separation is not possible under all working conditions and as a result, surface chemical effects have been brought into play in boundary lubrication to reduce friction and wear which does occur in boundary lubrication. Thus anti-wear agents have been added to liquid lubricants which produce a surface film on the sliding parts by either a chemical or physical adsorption mechanism, the film reducing friction and wear under boundary lubrication conditions.

A wide variety of compounds have been used for improving lubrication under boundary film conditions. Thus compounds containing oxygen such as fatty acids, esters and ketones, compounds containing sulphur or combinations of oxygen and sulphur, organic chlorine compounds such as chlorinated waxes, organic sulphur compounds such as sulphurised fats and sulphurised olefines, compounds containing both chlorine and sulphur, organic phosphorous compounds such as tricresyl phosphate, thiophosphates and phosphites and also organic lead compounds have been used.

When the conditions in boundary lubrication are mild, polar additives having a polar group at one end of the molecule and a solubilising group at the other - usually a long chain hydrocarbon to effect solubilisation in the lubricating oil, have been used to provide an adherent adsorped film over metallic surfaces. A class of heterocyclic compounds useful as additives which provide friction modification and improved fuel economy are disclosed in WO 87/0596 and have the general formula:



(I)

wherein Z is S, NR, $N\text{-}\overset{\overset{A}{\|}}{C}\text{-}AR$, $N\overset{\overset{A}{\|}}{C}\text{-}NHR$, $N\text{-}\overset{\overset{A}{\|}}{C}\text{-}R$, PR or PRA, wherein A is O or S and R is H, alkyl, alkenyl, hydrocarbyl acyl, hydrocarbyl phenolate or $-(CH_2)_mQ$, where m is 1 to about 12, and Q is O-alkyl or N-alkyl, X is independently H, COOH, NH_2, $CONH_2$, $NHNH_2$, OR, COR, NHR, OH, SH, or CN wherein R is the same as defined above; p is 0 to 2; e is 0 to 2 wherein e+p is 2 to about 4; T is NH_2, NHR wherein R is the same as defined above, SH, OH or their tautomers, hydrocarbyl acyl or hydrocarbyl phenolate; and Y is CN, $\overset{\overset{A}{\|}}{C}NH_2$, CO_2H

or CH_2NH_2 wherein A is the same as defined above. Such adsorped films of additive have hitherto only been successful under relatively mild boundary lubrication conditions, primarily because the thickness of such films is very low and usually of the order of one nanometer. Under more severe conditions of boundary lubrication, substances like tricresyl phosphate or zinc dialkyl dithiophosphates have been found necessary and in extreme rubbing conditions where severe metal-to-metal contact would otherwise be encountered, active sulphur, chlorine and lead compounds have been found essential. Such additives however react chemically to form low shear strength surface layers such as lead sulphide ion chloride or ion sulphide. This surface layer then prevents destructive welding, excessive metal transfer and severe surface breakdown. Such chemical reactivity with the surfaces of the sliding parts however is not in general desirable and is only undertaken when no other alternative is available.

As indicated, the polar type of compound which forms an adherent adsorped film over the moving surfaces is much to be preferred, but the thicknesses of such films which have been possible by the use of hitherto known additives in lubricating compositions have produced insufficient thicknesses of adsorped film to function under any conditions other than mild conditions.

It is an object of the present invention to provide a lubricating regime whereby adherent adsorbed films of polar material are provided up to 1,000 times thicker than have hitherto been possible.

The present invention concerns a radical advance in lubrication by providing a regime in which multimolecular layers are adsorbed onto the surfaces to be protected thus enabling comparatively thick protective films to be built up on sufaces subject to frictional wear. It has now been found that certain molecules have the property of forming such multimolecular layers when contacted with the surface as by incorporation in a carrier which is continuously or intermittently brought into contact with at least a portion of the surface to be protected. The molecules which have been found to have this property are essentially single or condensed unsaturated ring systems which comprise at least one six-membered unsaturated heterocyclic ring comprising at least one heterocyclic moiety which acts as a hydrogen acceptor, the molecule also comprising at least one hydrogen donor moiety. The molecules may comprise other five or six-membered unsaturated rings which together with the said six-membered unsaturated heterocyclic ring form a condensed ring system.

The multimolecular layers of the lubricating regime of the present invention are built up by initial adsorption of a layer of molecules onto the surface to be protected followed by adsorption of further molecules onto the initial layers to form a second layer and yet further adsorption to form more layers until films up to about 1 micrometer thick are formed. Without wishing to be bound by theory it is believed that presence of both hydrogen donor and hydrogen acceptor moieties in the heteropolar molecules enables this adsorption to take place.

Whilst unsubstituted heteropolar molecules are preferred substituents may be present on the heteropolar molecules provided they do not singly or collectively prevent interaction of the hydrogen donor and acceptor moieties as by steric hindrance. Thus, for example, hydrocarbon substituents such as alkyl groups should preferably not contain more than four carbon atoms, preferably not more than two carbon atoms. When the substituent is ortho to either the heteroatom or the hydroxyl group the steric hindrance effect is likely to be greater than when said substituent is in the meta or para position to either the heteroatom or a hydroxyl group. Alkene and alkyne substituents, carboxyl containing and amine containing substituents will all effect the activity of the heteropolar molecules and should be avoided.

In one embodiment of the invention therefore, a method of reducing wear on a surface which is subject to frictional forces which comprises forming and maintaining on said surface a protective layer characterised in that said protective layer is a multi-molecular layer of a heteropolar compound comprising at least one unsaturated heterocyclic six-membered ring in which at least one unsubstituted heteroatom moiety acts as a hydrogen acceptor and in which said compound also comprises at least one hydrogen donor moiety, and in which said heteropolar compound has no substituent which by itself or together with another substituent or substituents creates such steric hindrance and/or renders the molecule so basic or acidic or so alters the steric geometry of the molecule as to prevent interaction of the hydrogen donor and acceptor moieties of one molecule of the heteropolar compound with the hydrogen donor and acceptor moieties of another molecule of said heteropolar compound nor any substituent which by itself or together with another substituent or substituents has the effect of solubilizing said heteropolar compound in a selected carrier to the extent that migration of the heteropolar compound to the interfaces of the carrier with the carrier environment is prevented.

Formation of the multimolecular layer of heteropolar molecules may be effected by incorporating the heteropolar compound in a carrier which is brought into contact with the surface to be lubricated. It has been found that the heteropolar molecules migrate through the carrier onto the surface to be lubricated and build up on that surface to form multimolecular layers. The carrier may be a liquid such as an oil or grease or may even be aqueous. Solid carriers are also feasible such as polyamide plastics such as those used to build up worn machinery parts such as drive shafts and the like. Incorporation of a heteropolar compound in the plastic material enables a multimolecular layer of heteropolar molecules to form not only on the surface of the plastic by migration through the plastic material but also by transfer from the surface of the plastic to another surface which rubs against the surface of the plastic.

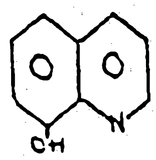
It has also been found that the heteropolar molecules migrate laterally over the surface on which they are adsorbed beyond the boundaries of contact of that surface with the carrier material. Contact of the carrier with the whole of the surface to be protected is not therefore necessary in order to form a lubricating layer of heteropolar molecules over all the surface to be protected. Nor is it necessary to have continuous contact between carrier and surface to be treated, but intermittent contact is also effective. The multimolecular layer is not of course formed instantaneously but builds up over a period of time. Relative movement of carrier and surface to be protected accelerate the formation and maintainance of the multimolecular layer of heteropolar molecules on the surface to be protected.

The heteropolar molecules migrate through the carrier to the interfaces of the carrier with the surrounding environment. Unsubstituted heteropolar heterocyclic unsaturated single or condensed ring systems having the aforementioned hydrogen donor and acceptor moieties have this property of migration. Any substituents in such heteropolar molecules should not exert such a solubilizing effect on the heteropolar molecules that they lose their ability to migrate through the carrier to the interfaces of the carrier's environment. Since a major application of the compounds of the invention is in oils and greases it is essential that the molecules should not exert such a solubilizing effect that they fail to migrate. Consequently, where they are to be added to oils and greases any substituted groupings should not "over solubilize" the molecule. Therefore hydrocarbon substituents should preferably not contain more than 4 carbon atoms, preferably not more than 2 carbon atoms.

According to another embodiment of the present invention there is provided a composition having anti-surface wear properties comprising a carrier and dissolved and/or dispersed therein an effective amount of a compound capable of producing a multi-molecular lubricating layer having anti-surface wear properties characterised in that said compound is a heteropolar compound comprising at least one wholly unsaturated heterocyclic six-membered ring in which at least one unsubstituted heteroatom moiety acts as a hydrogen acceptor and in which said compound also comprises at least one hydrogen donor moiety and in which said heteropolar compound has no substituent which by itself or together with another substituent or substituents creates such steric hindrance and/or renders the molecule so basic or acidic or so alters the steric geometry of the molecule as to prevent interaction of the hydrogen donor and acceptor moieties of one molecule of the heteropolar compound with the hydrogen donor and acceptor moieties of another molecule of the heteropolar compound nor any substituent which by itself or together with another substituent or substituents has the effect of solubilizing said heteropolar compound in the selected carrier to the extent that migration of the heteropolar compound to the interfaces of the carrier with the carrier environment is prevented.

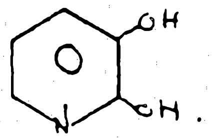
The carrier may be a liquid such as a lubricating oil or hydrocarbon fuel for an internal combustion engine or aqueous system, or the carrier may be a grease or semi-solid material (non-Newtonian fluid) such as a lubricating grease or grease-like lubricant. The carrier may also be a solid such as a plastics composite, e.g. a polyamide used in repairing or rebuilding beading surfaces. In the case of liquid the content of heteropolar compound may be from 0.5% to 4% by weight based on the total weight of carrier and additive and in the case of greases or non-Newtonian fluids may be from 3% to 10% by weight based on the total weight of carrier plus additive. Preferably, in the case of a liquid the content of heteropolar compound is greater than 1%, e.g. from 1.1% to 4% by weight based on the total weight of carrier and additive. The concentration necessary in a solid carrier will depend on the type of solid carrier involved. In the case of polyamides somewhat more additive is in general necessary than that required in a semi-solid for equivalent results. This is the case of a 'Polyamid' bearing 10% by weight based on the total weight of 'Polyamid" and additive was found satisfactory. However amounts of greater than 10% e.g. 10.1% to 20% are preferred.

The preferred hydrogen acceptor moiety is one involving nitrogen as the heteroatom in the form of an -N= moiety. The preferred hydrogen donor moiety is a hydroxyl group. Both such moieties occur in the preferred heteropolar compound of the invention which is 8-hydroxyquinoline:-

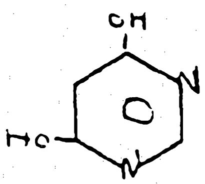


The condensed ring system in the heteropolar compounds useful in the invention may contain up to four -N= moieties, with preferably up to two such moieties being incorporated as ring forming atoms in any one ring. Other unsubstituted heteropolar compounds useful in the method and compositions of the present invention include:

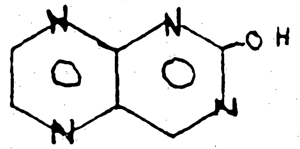
2,3 dihydroxypyridine



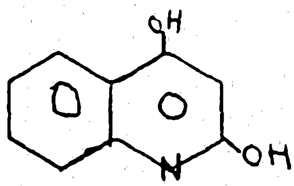
4,6 dihydroxypyrimidine



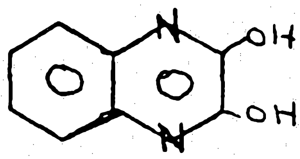
2 pteridinol



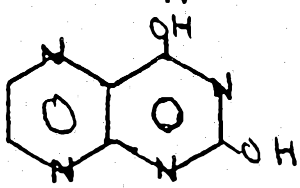
2,4 quinolindiol



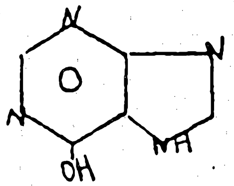
2,3 dihydroxyquinoxalin



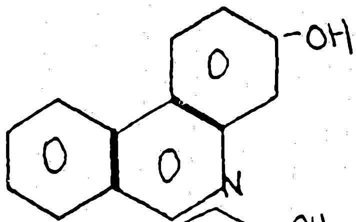
2.4 pteridinediol



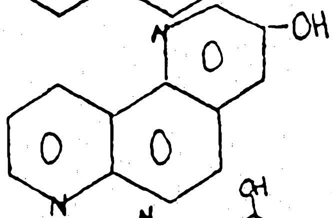
6 purinol



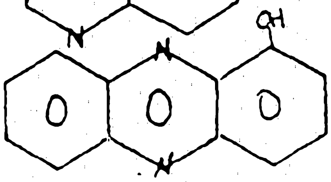
3 phenanthridinol



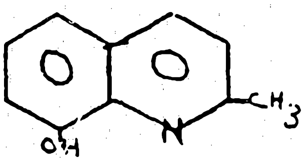
2 phenanthrolinol



2 phenazinilol



As previously indicated the preferred heteropolar compounds are unsubstitued materials. Substituents should not create steric hindrance which prevents interaction of the hydrogen donor and acceptor moieties. Thus the provision of a methyl group ortho to the -N= hydrogen acceptor moiety of 8-hydroxyquinoline to form the compound:-



2-methyl-8-hydroxy quninoline

does not materially affect the activity of this heteropolar molecule in forming adsorption film on metal surfaces. The number and size of the substituents which can be tolerated in the heteropolar molecule depends on the number and position of the hydrogen donor and acceptor moieties in the molecule. In general the substituents groups should not exceed four atoms in number (e.g. in the case of hydrocarbyl the butyl group), preferably no more than two atoms and more preferably still only one carbon atom.

A good indication of whether steric hindrance is likely to cause problems is given by measuring the adsorption-free energy of the compound in question. If the adsorption-free energy as measured on a copper surface is substantially in the range of 3 to 6 Kcal/mol then steric hindrance is unlikely to be a problem.

The invention will be further illustrated by reference to the following Examples which are purely illustrative. In each of the examples the heteropolar compound was 8-hydroxyquinoline.

EXAMPLE 1

0.5% by weight of heteropolar compound was incorporated in SAE 30 engine oil which was then used in a test-bed fully instrumented Whirlepeel system. The following results were obtained as shown in Tables 1 to 5.

Table 1

COMPRESSION

	WITHOUT HETEROPOLAR						WITH HETEROPOLAR					
CYLINDER	1	2	3	4	5	6	1	2	3	4	5	6
COMPRESSION, 10^5Pa	28	22	26	24	24	22	30	30	28	26	26	26

Table 2

FUEL CONSUMPTION (after 100 km of running)

(a) WITHOUT HETEROPOLAR (b) WITH HETEROPOLAR (c) WITH HETEROPOLAR AFTER 15,000 km RUNNING

	FUEL CONSUMPTION LITRES 100km AT A SPEED OF			
	40km/h	50km/h	60km/h	70km/h
(a)	22.83	27.39	33.55	42.73
(b)	20.96	25.97	31.25	39.84
(c)	20.32	23.47	28.49	35.59

Table 3

WEAR RATES

WITHOUT HETEROPOLAR	0.006g Fe/hour
WITH HETEROPOLAR	0.003g Fe/hour

Table 4

FRICTION

WITHOUT HETEROPOLAR	170.5 kPa FRICTION MIDDLE PRESSURE
WITH HETEROPOLAR	162.5 kPa " " "

Table 5

EMISSION (Bosch Units

(a) Ground Revs (Tick-over speed)

(b) Full Throttle (Revs)

1.5 MAX PERMISSIBLE VALUE

WITHOUT HETEROPOLAR		WITH HETEROPOLAR	
(a)	(b)	(a)	(b)
0.9	1.7	0.6	1.2

The following Examples show the EP effect of adding the heteropolar compound to different lubricants.

EXAMPLE 2

EXTREME PRESSURE (EP) EFFECT

Shell Four Ball Machine

Lubricating Medium: Lithium grease, with 3% by weight of heteropolar compound.

WITHOUT HETEROPOLAR welding at 2^7 - 2.2^7N

WITH HETEROPOLAR no welding at 3^7N

EXAMPLE 3

FALEX LUBRICANTS TESTER

To. L.P. Test 241/69 with 0.5% by weight of heteropolar compound.

	JAW LOAD	TIME TO FAILURE
SAE OIL WITHOUT HETEROPOLAR	3,000N	3 min 10 secs
SAE OIL WITH HETEROPOLAR	4,000N	5 min

Note: Jaw Load 1000N increments for a period of one minute.

EXAMPLE 4

COMPOSITE MATERIALS

'Polyamid' Bearing with 10% of M_oS_2 composite additive, compared with a similar bearing containing 10% of heteropolar compound. The bearing having the heteropolar compound in the 'Polyamid' lowered the friction by 30% as compound to the bearing containing the M_oS_2 additive.

EXAMPLE 5

NOISE REDUCTION

When the heteropolar compound was incorporated in the lubricant in a back axle differential gearing the noise reduced by 2dB. When the heteropolar compound was incorporated in the lubricant in a Vauxhall Astra engine the noise decreased by 86dB to 80dB.

....

CLAIMS

1. A composition having anti-surface wear properties comprising a carrier and dissolved and/or dispersed therein an effective amount of a compound capable of producing a multi-molecular lubricating layer having anti-surface wear properties characterised in that said compound is a heteropolar compound comprising at least one wholly unsaturated heterocyclic six-membered ring in which at least one unsubstituted heteroatom moiety acts as a hydrogen acceptor and in which said compound also comprises at least one hydrogen donor moiety and in which said heteropolar compound has no substituent which by itself or together with another substituent or substituents creates such steric hindrance and/or renders the molecule so basic or acidic or so alters the steric geometry of the molecule as to prevent interaction of the hydrogen donor and acceptor moieties of one molecule of the heteropolar compound with the hydrogen donor and acceptor moieties of another molecule of the heteropolar compound nor any substituent which by itself or together with another substituent or substituents has the effect of solubilizing said heteropolar compound in the selected carrier to the extent that migration of the heteropolar compound to the interfaces of the carrier with the carrier environment is prevented.

2. A composition as claimed in claim 1, in which the heteropolar compound comprises up to three condensed unsaturated rings, one of which rings is said wholly unsaturated heterocyclic six-membered ring.

3. A composition as claimed in claim 2, in which one of said condensed rings is a five-membered unsaturated heterocyclic ring.

4. A composition as claimed in claim 2, in which all the condensed rings are six-membered unsaturated rings.

5. A composition as claimed in any of claims 1 to 4, in which the carrier is a liquid.

6. A composition as claimed in claim 5, in which the liquid is a lubricating oil.

7. A composition as claimed in claim 6, in which the lubricating oil comprises at least one unsaturated hydrocarbon.

8. A composition as claimed in claim 7, wherein the heteropolar compound is present in the range 1.1% to 4% by weight based on the total weight of carrier and additive.

9. A composition as claimed in claim 5, in which the carrier is an aqueous liquid.

10. A composition as claimed in claim 5, in which the carrier is a liquid hydrocarbon fuel for an internal combustion engine.

11. A composition as claimed in any of claims 1 to 4, in which the carrier is a lubricating grease or grease-like material.

12. A composition as claimed in claim 11, wherein the heteropolar compound is present in the range 3% to 10% by weight based on the total weight of carrier and additive.

13. A composition as claimed in any of claims 1 to 4. in which the carrier is a solid plastics material.

14. A composition as claimed in claim 13, in which the solid plastics material is a polyamide.

15. A composition as claimed in claim 14, wherein the heteropolar compound is present in the range 10.1% to 20% based on the total weight of carrier and additive.

16. A composition as claimed in any of the preceding claims, in which the heterocyclic moiety which acts as a hydrogen acceptor is an -N= moiety.

17. A composition as claimed in claim 16, in which the heteropolar compound contains up to four -N= moieties.

18. A composition as claimed in any of the preceding claims, in which the hydrogen donor moiety is an -OH group.

19. A composition as claimed in any of the preceding claims, in which the heteropolar compound is 8-hydroxyquinoline.

20. A composition as claimed in any of claims 1 to 18, in which the heteropolar compound is selected from 2,3-dihydroxypyridine, 4,6-dihydroxypyrimidine, 2-pteridinol, 2-methyl 8-quinolinol, 2,4-quinolindiol, 2,3-dihydroxyquinoxalin, 2,4-pteridinediol, 6-purinol, 3-phenanthridinol, 2-phenanthrolinol and 2-phenazinol.

21. A method of reducing wear on a surface which is subject to frictional forces which comprises forming and maintaining on said surface a protective layer by applying to said surface a composition comprising a carrier and a compound capable of producing a multimolecular lubricating layer characterised in that said compound capable of producing a multi-molecular lubricating layer is a heteropolar compound comprising at least one unsaturated heterocyclic six-membered ring in which at least one unsubstituted heteroatom moiety acts as a hydrogen acceptor and in which said compound also comprises at least one hydrogen donor moiety, and in which said heteropolar compound has no substituent which by itself or together with another substituent or substituents creates such steric hindrance and/or renders the molecule so basic or acidic or so alters the steric geometry of the molecule as to prevent interaction of the hydrogen donor and acceptor moieties of one molecule of the heteropolar compound with the hydrogen donor and acceptor moieties of another molecule of

said heteropolar compound nor any substituent which by itself or together with another substituent or substituents has the effect of solubilizing said heteropolar compound in the carrier to the extent that migration of the heteropolar compound to the interfaces of the carrier with the carrier environment is prevented.

22. A method as claimed in claim 21, in which the protective layer is formed on the surface to be protected by contacting at least a portion of the said surface with a composition as claimed in any of claims 1 to 20.

23. A method as claimed in claim 22, in which at least a portion of the surface to be protected is continuously contacted with said composition.

24. A method as claimed in claim 22, in which at least a portion of the surface to be protected is intermittently contacted with said composition.

DATED this 14th day of February, 1992.

NATIONAL RESEARCH DEVELOPMENT CORPORATION
Patent Attorneys for the Applicant:
PETER MAXWELL & ASSOCIATES.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 89/00530

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [8]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 10 M 133/38, C 10 M 133/40, C 10 L 1/22

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 10 M, C 10 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7,20-25,39-60; column 2, lines 1-3,18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4,8,20-24,29 --	1,2,4-6, 16-19,21-23
X	FR, A, 1577581 (J.R. GEIGY S.A.) 8 August 1969 see page 1, lines 5-21; page 4, lines 1-4; examples 4-6; claims 1-3 --	1-3,5,6,16-18
A	WO, A, 87/05926 (THE LUBRIZOL CORP.) 8 October 1987 cited in the application --	
X	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract: column 1, lines 3-7,20-25,39-60; column 2, lines 1-3,18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4,8,20-24,29 --	7,8
Y	EP, A, 0098717 (NIPPON MINING CO. LTD) 18 January 1984, see abstract; page 21, line 23 - page 22, line 11; claims 1,8,11 --	7,8

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10th August 1989	15.01.90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	T.K. WILLIS

International Application No. PCT/GB 89/00530

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	EP, A, 0168534 (EXXON RESEARCH AND ENGINEERING CO.) 22 January 1986 --	7
A	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7,20-25,29-60; column 2, lines 1-3,18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4,8,20-24,29	9
A	EP, A, 0103737 (BASF AG) 28 March 1984 see abstract; page 1, line 5 - page 2, line 20; tables 1,2 --	9
Y	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7, 20-25,39-60; column 2, lines 1-3, 18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4, 8,20-24,29 --	10
Y	US, A, 4295861 (L.D. BURNS) 20 October 1981 see abstract --	10
Y	FR, A, 1577581 (J.R. GEIGY S.A.) 8 August 1969 see page 1, lines 5-21; page 4, lines 1-4; examples 4-6; claims 1-3 cited in the application --	10
X	US, A, 2030033 (E.B. McCONNELL) 4 February 1936 see the whole document --	10
X	EP, A, 0069507 (EXXON RESEARCH AND ENGINEERING CO.) 12 January 1983 see abstract; claims 1-3 --	10
X	Chemical Abstracts, volume 110, no. 6, 1989, (Columbus, Ohio, US), D. Wei: "Lubricity of fuels. II. Wear studies using model compounds", see page 160, abstract 41666e, & Shiyou Xuebao, Shiyou Jiagong 1988, 4(1), 90-9 --	10
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International Application No. PCT/GB 89/00530

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	DE, A, 3131950 (NIPPON OIL CO.) 25 March 1982 see abstract, claims 1,4-6; page 4, lines 4-14; tables 4-6; page 18, lines 1-5	10
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Y	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7, 20-25,39-60; column 2, lines 1-3, 18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 36 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4,8,20-24,29	11
A		12
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Y	US, A, 3078228 (R.K. SMITH et al.) 19 February 1963 see column 1, line 11 - column 3, line 33; column 6, lines 14-60; example XIII	11
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X	Chemical Abstracts, volume 97, no. 18, 1982, (Columbus, Ohio, US), see page 165, abstract 147467u, & SU, A, 939527 (SPECIAL CONSTRUCTION-TECHNOLOGICAL BUREAU OF SPECIAL MATERIAL MANAGEMENT, NOVOCHERKASSK et al.) 30 June 1982	11
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A	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7, 20-25,39-60; column 2, lines 1-3, 18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4, 8,20-24,29	13
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A	US, A, 4075111 (N. BILOW et al.) 21 February 1978 see abstract; column 1, lines 10-52	13,14
	--	
X	US, A, 3939084 (J.D. SULLIVAN) 17 February 1976 see abstract; column 2, line 63 - ./...	20

International Application No. PCT/GB 89/00530

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	column 3, line 21, lines 51-55; tables I,II	
A	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7, 20-25,39-60; column 2, lines 1-3, 18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4, 8,20-24,29	20
A	FR, A, 2249879 (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) 30 May 1975	20
Y	Chemical Abstracts, volume 95, no. 19, 1981, (Columbus, Ohio, US), A.S. Kuzharov et al.: "Formation of coordination compounds under model friction contact conditions", see page 128, abstract 83302k, & Zh. Fiz. Khim. 1980, 54(12), 3118-22	24
Y	US, A, 3779920 (D.L. DEVRIES) 18 December 1973 see abstract; column 1, lines 3-7, 20-25,39-60; column 2, lines 1-3, 18-53, line 68 - column 3, line 6; column 3, lines 14-18, line 66 - column 4, line 2; column 4, lines 7-47; column 7, line 43 - column 8, line 4; examples 5,6,10,12,13; column 11, lines 36-43; claims 1-4, 8,20-24,29	24

International Application No. PCT/GB 89/C0530

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.[ ] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.[ ] Claim numbers ...., because they relate to subject matter not required to be searched by this Authority, namely:

2.[ ] Claim numbers ...., because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful International search can be carried out, specifically:

3.[ ] Claim numbers ...., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.[X] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. claims 1 - 6, 16 - 19, 21 - 23
2. claims 7, 8
3. claims 9
4. claims 10
5. claims 11, 12
6. claims 13 - 15
7. claims 20
8. claims 24

1.[X] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.[ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.[ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.[ ] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

[X] The additional search fees were accompanied by applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 8900530
SA 28790

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 19/12/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3779920	18-12-73	CA-A- 974225	09-09-75
		GB-A- 1375242	27-11-74
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US-A- 2030033		None	
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DE-A- 3131950	25-03-82	None	
US-A- 3078228		None	
US-A- 4075111	21-02-78	None	
US-A- 3939084	17-02-76	BE-A- 696664	05-10-67
		DE-A- 1644909	19-05-71

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 8900530 SA 28790

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The members are as contained in the European Patent Office EDP file on 19/12/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		GB-A- 1188813	22-04-70
		GB-A- 1192910	28-05-70
		NL-A- 6704601	09-10-67
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		US-A- 3759829	18-09-73
		US-A- 3788992	29-01-74
FR-A- 2249879	30-05-75	None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82