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LUBRICATING COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

A lubricating composition, particularly suitable for the lubrication of hypoid gears, which composition comprises a mineral lubricating oil and dissolved therein an additive combination which confers extreme pressure properties on the composition and which consists of

- (a) a chlorine-containing hydrocarbon having a boiling point or decomposition temperature of not less than 160° C.,
- (b) an oil-soluble polyvalent metal salt of a dithiophosphoric acid, and
- (c) a dialkyl phosphite,

the proportion of (a) being such as to provide from 0.42% to 6.0% by weight of chlorine in the composition, the proportion of (b) being such as to provide from 0.048% to 1.0% by weight of sulphur in the composition, and the proportion of (c) being such as to provide from 0.036% to 0.3% by weight of phosphorus in the composition.

This invention is for improvements in or relating to lubricating compositions and is particularly concerned with lubricating compositions having extreme pressure properties especially suitable for the lubrication of hypoid gears, which compositions will operate under conditions of low speed and high torque as well as under conditions of high speed and high load. The lubricating compositions of this invention may (however, be used for lubricating all kinds of industrial gears.

It is well known that under certain conditions, e.g. for the lubrication of hypoid gears, it is necessary to employ lubricants containing chemical compounds capable of reacting with metals at high temperatures and under high pressures to form films (e.g. of iron sulphide, iron chloride or iron oxide) which prevent seizure and welding of the metal surfaces. A variety of organic compounds have been suggested for this purpose, including sulphur compounds of various types and containing sulphur in varying degrees of activity. It has generally been found advantageous to use these sulphur compounds in conjunction with lead soaps or organic halogen compounds, or both. It is now recognised that many such lubricants, which behave perfectly satisfactorily under normal operating conditions and even under high loads at high speed, are not satisfactory under conditions of high torque and low speed, e.g. for lubricating rear axles of vehicles operating in mountainous terrain. Under these conditions, certain lubricants, e.g. those containing lead soaps or sulphur in "active" form, tend to cause high rates of wear or, in some cases, "rippling" or "ridging" of the gear teeth, and

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to promote the rusting of ferrous metal parts in the presence of condensed moisture.

On the other hand lubricants which perform well under conditions of high torque and low speed do not necessarily possess adequate load-carrying capacity under high-speed conditions and particularly under conditions of shock loading. In fact the two requirements have been for some time regarded as being conflicting and British Gear Oil Specification No. CS,3000A and the now obsolete U.S. Army Specification MIL-L-2102, to which most commonly used hypoid rear axle oils have conformed for some time, represent a compromise.

The practice among motor manufacturers for some time past has been to use lubricants having better E.P. properties under high-speed conditions than the conventional MIL-L-2105 oils for factory fills for passenger cars. After running-in the gears for a certain period on these oils, which generally contain "active" sulphur and sometimes also lead soaps, the rear-axle may be drained and filled with MIL-L-2105 oil. Some of these oils, particularly those containing lead soaps, while providing adequate protection of the gears against scuffing, have been found to give rise to an undesirable amount of wear in anti-friction bearings resulting in loss of pre-load with consequent deterioration of the gear and development of noise and other troubles. Furthermore, it is an obvious disadvantage to have different rear axle oils for factory fills for passenger cars and trucks, since confusion may occur and breakdown of heavily-loaded truck axles might take place under low-speed high-torque conditions if lubricated with an oil of the wrong type.

It is clearly desirable that hypoid gear oils used for factory fills should be compatible with hypoid gear oils used subsequently after the running-in process has been completed. It is, therefore, advantageous if the same additives are present in the oil used for factory fills as in the oil subsequently purchased from a garage and used either for topping-up or refilling the axle housing after draining. The additive combination of the present invention has the advantage that it may be used both for factory fill purposes and at a lower dosage level for general use in which case no problems due to incompatibility will be encountered.

Recent improvements in engine designs have led to increased power output and this, combined with the tendency to increase the hypoid pinion offset, has brought about a very considerable increase in the severity of the operating conditions of the gears of passenger cars. The loading on truck axles has also increased and the high speeds at which many vehicles, particularly military vehicles, operate combined with the heavy loads carried have exposed the limitations of MIL-L-2105 oils both under high-speed conditions of operation and under low-speed high torque conditions.

In addition to having adequate extreme pressure properties, a universal hypoid axle lubricant must be relatively non-corrosive to cuprous metals at high operating temperatures and must provide adequate resistance to the corrosion of ferrous metals in the presence of water.

To obtain a satisfactory oil for first fill purposes, it is highly desirable that axle tests should be passed both under high speed/high load conditions and under low speed high torque conditions. It has generally been considered

that a compound containing a fair quantity of fairly active sulphur is necessary together with chlorine to pass the former type of test, whilst phosphorus compounds are required to pass the latter type of test.

A surprising feature of the present invention is that both requirements can be satisfied by using relatively small amounts of two readily available and inexpensive phosphorus compounds in conjunction with a chlorine compound. Furthermore, these compounds are freely oil soluble and without corrosive attack on copper at temperatures up to 135° C.

According to the present invention there is provided a lubricating composition comprising a mineral lubricating oil and dissolved therein an additive combination which confers extreme pressure properties on the composition and which consists of

- (a) a chlorine-containing hydrocarbon having a boiling point or decomposition temperature of not less than 160° C.,
- (b) an oil-soluble polyvalent metal salt of a dithiophosphoric acid, and
- (c) a dialkyl phosphite.

Where the lubricating compositions are for use specifically as hypoid gear lubricants, it is preferred that the total chlorine content is from 2.5% to 6.0% by weight, the proportion of (b) is such as to provide from 0.2% to 1.0% by weight of sulphur in the composition, and the proportion of (c) is such as to provide from 0.1% to 0.3% by weight of phosphorus in the composition. The proportion of (b) is preferably such as to provide from 0.3% to 0.7% by weight of sulphur in the composition.

Examples of additive (a) are:

Chlorinated paraffin wax,
Chlorinated kerosine,
Hexachlorethane,
Benzene hexachloride,
Chlorinated indenenes,
Dichlorodiphenyltrichlorethane (DDT) and
Chlorinated diphenyls.

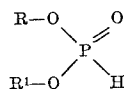
Examples of additive (b) are:

Zinc di-n-pentyl dithiophosphate
Zinc di(1,3 dimethyl butyl)dithiophosphate
Zinc isopropyl/1,3 dimethyl butyl dithiophosphate
Zinc isobutyl/amyl dithiophosphate
Zinc diamyl dithiophosphate derived from mixed amyl alcohols
Zinc dialkyl dithiophosphate derived from mixed straight chain C₆-C₁₀ alcohols
Zinc dialkyl dithiophosphate derived from mixed C₃-C₆ alcohols
Nickel di(2-ethyl hexyl)dithiophosphate
Barium di lauryl dithiophosphate
Chromium di(p-octylphenyl)dithiophosphate

Examples of additive (c) are:

Diethyl phosphite,
Di-isopropylphosphite
Di-n-butylphosphite,
Dioctyl phosphite,
Dilauryl phosphite.

These phosphites have the formula:



where R and R¹ are the same or different alkyl groups. Preferably R and R¹ together have a total of from 3 to 12 carbon atoms.

Additive (a) is preferably a paraffin wax containing from 40 to 70% of chlorine, additive (b) is preferably a zinc dialkyl-di thiophosphate wherein each alkyl group contains from 3 to 12 carbon atoms and additive (c) is preferably di-isopropyl phosphite.

It is to be understood that the composition may contain conventional lubricating oil additives, for example, anti-oxidants or corrosion inhibitors, dispersants, detergents, pour point depressants and V.I. Improvers.

A corrosion inhibitor which is particularly useful in the compositions of the present invention is an oil-soluble basic alkaline earth metal sulphonate which may or may not be neutralized with a weak acid, e.g. carbon dioxide and is preferably employed in an amount of at least 0.05% and more preferably in an amount from 0.1 to 0.5% by weight of the total composition.

Examples of these additives are:

Basic barium petroleum sulphonate,
Basic calcium petroleum sulphonate,
Basic strontium petroleum sulphonate,
Basic barium dinonyl naphthalene sulphonate, and
Basic barium didodecyl or octadecyl benzene sulphonate.

Any of these compounds may be neutralized wholly or in part with CO₂ to give the corresponding carbonate complex.

Another additive which is particularly useful in this invention is the additive prepared by reacting a phosphosulphurised polyisobutylene with barium hydroxide in the presence of an alkyl phenol, carbonating and further reacting with a basic alkaline earth metal sulphonate.

The invention also includes an additive combination for conferring extreme pressure properties to a mineral oil lubricant, which combination comprises from 67% to 74% of a chlorinated paraffin wax containing from 40% to 70% by weight of chlorine, from 15% to 20% of a zinc dialkyl dithiophosphate having from 3 to 12 carbon atoms in each alkyl group, and from 4.8% to 5.5% of a dialkyl phosphite having a total of from 3 to 12 carbon atoms per molecule, the percentages being by weight on the total weight of addition. The dialkyl phosphite is preferably diisopropyl phosphite.

The combination may also with advantage contain from 6% to 8% of a phosphosulphurised polyisobutylene reacted with a barium alkyl phenate and over-based with a basic barium petroleum sulphonate as a detergent, and from 0.6% to 0.8% of a co-polymer of mixed fatty acid methacrylates as a pour point depressant. Reference is made to U.S. Patent No. 2,969,324 for further description of the phosphosulphurized detergents.

These additive combinations may be supplied either near or as oil concentrates for dilution to the extent required for the particular lubricating job for which they are to be used.

A representative lubricating composition of the invention consists essentially of a mineral lubricating oil having dissolved therein from 5% to 15% of a chlorinated paraffin wax containing from 40% to 70% by weight of chlorine, from 1.5% to 3.5% of a zinc dialkyl dithiophosphate having from 3 to 12 carbon atoms in each alkyl group, from 0.5% to 1.0% of a dialkyl phosphite having from 1 to 6 carbon atoms in each alkyl group, from 0.5% to 2% of a phosphosulphurized polyisobutylene reacted with a barium alkyl phenate and over-based with a basic barium petroleum sulphonate and from 0.05% to 0.2% of a co-polymer of mixed fatty acid methacrylates, all percentages being by weight on the weight of the composition.

Following is a description by way of example of typical compositions of the present invention.

EXAMPLE I

	Percent
Mineral oil A	44.0
Mineral oil B	41.65

	Percent
Chlorinated paraffin wax containing about 42% chlorine	10.0
Zinc isopropyl/1,3 dimethyl butyl dithiophosphate	2.5
Detergent D	1.0
Di-isopropyl phosphite	0.75
Pour Point Depressant A	0.1

Mineral oil A was a high viscosity, "Western" bright stock, having a viscosity of about 800 seconds Redwood I bright stock at 140° F.

Mineral oil B was a solvent refined mineral oil of viscosity about 150 seconds Redwood I at 140° F.

The zinc dithiophosphate was in the form of an approximately 80% concentrate in oil, the phosphorous content of the concentrate being approximately 8%. The detergent D was a phosphosulphurized polyisobutylene reacted with a barium alkyl phenate and overbased with a basic barium petroleum sulphonate. The pour point depressant A was a copolymer of mixed fatty acid methacrylates.

This composition possessed the following viscosity characteristics:

At 100° F.	cs.	263.9
At 210° F.	cs.	17.2
Viscosity index		70/71

The composition contained

	Percent
Sulphur	0.46
Chlorine	4.0
Zinc	0.23
Phosphorus	0.30

The composition gave good results when subjected to a relatively severe road test in the hypoid rear axle of a motor vehicle.

EXAMPLE II

	Percent
Mineral oil A	39.5
Mineral oil B	46.15
Chlorinated paraffin wax containing 42% chlorine	10.0
Zinc isobutyl/amyl dithiophosphate	2.5
Di-isopropyl phosphite	0.75
Detergent D	1.0
Pour pont depressant	0.1

The zinc dithiophosphate was in the form of an approximately 80% concentrate in oil, the phosphorus content of the concentrate being about 8.0%.

In order to test the properties of these compositions that of Example I was run in the rear axle of a high performance 2 litre saloon car under high speed conditions, together with braking tests, these tests being carried out in the Alps over a total distance of approximately 5000 miles. Identical tests were carried out on an identical vehicle using a well-known prior art hypoid gear oil (Blend A) containing 5.5% of an Extreme pressure additive containing about 16% sulphur, 3% Zn, 3% P and 16.5% Cl, and 0.05% pour point depressant. This particular type of vehicle was chosen since the cooling air flow normally experienced by the rear axle had been greatly reduced due to the design of the axle unit, which was partly housed in a well in order to accommodate the suspension unit. Consequently the rear axle tended to run at higher temperatures than normal, these temperatures being greatly increased under heavy braking conditions by conduction from the disc brakes along the drive shafts to the axle casing.

The extreme pressure properties of both the prior art oil and the composition of the present invention (Example I) were examined before and after test by testing on the well-known Four-ball Machine, similar to that described by Boerlage in "Engineering" July 13, 1933, volume 136, page 46. This apparatus comprised four steel balls arranged in the form of a pyramid. The top ball was held in a chuck attached to a spindle rotating at approximately 1500 rev./min. and pressed against the three bottom balls clamped in a stationary ball-holder. The balls were immersed in the oil to be tested. Tests were normally run for one minute at a series of different loads. The results of these tests are given in Table I.

TABLE I.—FOUR-BALL MACHINE TESTS

Blend	Load (kg.) at Incipient Seizure	Weld pt. (kg.)	Sear diameter (mm.) at load in kg. of—					
			150	200	250	300	350	400
Example I:								
Before test..	160/165	390	0.5	1.8	2.1	2.5	3.0	---
After test..	185/190	480	---	0.8	1.7	2.1	2.1	2.1
Blend A:								
Before test..	105/110	380	0.8	1.0	1.5	1.6	1.8	---
After test..	90/95	390	0.76	1.7	1.8	2.0	2.2	---

The surprising effect was that the composition of the present invention was more efficient after test than before particularly with regard to the load at incipient seizure.

Although the above test showed that a typical composition of the present invention was efficient under rigorous conditions involving high speed operation with braking, it was felt that more controlled conditions could be obtained by carrying out tests on a test-track.

Accordingly another model of the same vehicle was fitted with a rear axle which had been previously run-in. Thermocouples were attached to the drain plug in order to measure the bulk oil temperature, to the bearing assembly in order to measure the temperature of the shaft and the gear in general, and to the inspection cover in order to measure the temperature of the oil jet leaving the teeth of the gear. The thermocouples were connected via a switch mechanism to a recording head fitted in the car. The cold junction was also located in the car and consequently all temperature readings had to be adjusted to the temperature ambient in the car. In order to prevent loss of heat from the forward end of the axle a fibreglass/asbestos lagging was wrapped around the housing at the nose end. The car towed a dynamometer by means of a draw bar. The load imposed was continuously adjustable from within the car by means of an electronic control, so enabling absolute control over the load to be maintained.

Four test sequences were devised in order to obtain a bulk oil temperature of about 150° C. These are given in Table II.

TABLE II.—TEST SEQUENCES FOR DYNAMOMETER

Sequence	Load (lbs.) on Draw Bar	Car Gear	Car Speed, m.p.h.
1	700	2	40
2	800	2	35
3	100	3	35
4	200	3	40

Tests were carried out in the following order:

- (1) Fresh Blend A, sequence 1, 3 and 4. Allowed to cool to ambient (approximately 1½ hours), then run at normal road speed for 10 minutes.
- (2) Used Blend A, sequence 1, 3 and 4.
- (3) Fresh composition of Example II, sequence 1 and 2.
- (4) Used composition of Example II, sequence 1 and 2.

The results of these tests are given in Table III.

The results obtained on the two oils are given below.

TABLE III

	Rate of Inc. in temp. per minute (° C.)	Temperature (° C.) reached after—				
		25 min., seq. 1	No load, 5¼ min.	25 min., seq. 2	15 min., seq. 3	10 min., seq. 4
Blend A:						
Before test.....	4.2	178	162	-----	156	160
After test.....	3.6	162	142	-----	155	158
Example II:						
Before test.....	2.3	136	122	150	-----	-----
After test.....	2.5	130	115	141	-----	-----

All runs were conducted in similar climatic conditions of dry, warm weather with light winds.

These results showed clearly that the composition of the present invention allowed the rear-axle to run at a much lower temperature than the prior art hypoid gear oil. Furthermore, the load which had to be applied to cause the oil to reach a temperature of about 150° C., was very much higher than in the case of the prior art gear oil. This is shown by the fact that sequence 2 was much more severe than either sequence 3 or sequence 4, in fact so severe that undue strain was placed on the dynamometer, the engine of the car and on components not connected with the axle.

Four-ball tests were again carried out on Blend A before and after test and the composition of Example II as used in the above dynamometer tests and here again the improved extreme pressure properties of the composition according to the present invention after use were demonstrated, the results of these tests being given in Table IV.

TABLE IV

	Load kg. at incipient seizure	Weld pt. (kg.)	Scar diameter (mm.) at load in kg. of—						
			150	200	220	250	300	350	400
Blend A:									
Before test.....	120/130	400	1.20	1.56	-----	1.61	2.17	-----	-----
After test.....	120/135	310	1.34	1.64	1.71	1.78	2.13	-----	-----
Composition of Example II:									
Before test.....	160/165	350	0.58	1.73	-----	1.98	2.25	3.52	-----
After test.....	195/200	400	-----	0.89	1.02	1.62	2.02	2.34	2.69

In order to evaluate the oxidation stability of a typical composition in accordance with the invention, Example II was compared with a blend (Blend B) containing the same additive package as Blend A but in a higher concentration (9.5%). The test chosen was that laid down in U.S. Military Specification MI-L-2105B. In this test a small gear box is run for 50 hours at a controlled temperature, the gears being lubricated by the oil under test. At the end of the allotted time the oil is examined for viscosity increase and insolubles content.

The test is fully described in Federal Test Method Std.-191, method 2504-T, the conditions of test being as follows:

Temperature 325° F. ± 1° F. (157.2° C. ± 0.6° C.).

Load on gears provided by driving an electric generator to give an output of 128 watts.

Air flow through lubricant 1.11 litres per hour.

As well as the steel gears a copper catalyst was included in the system to determine the copper activity of the lubricant.

	Example II	Blend B	Spec. Required
Viscosity (cs.) at 210° F:			
Start.....	21.49	17.29	
Finish.....	28.61	30.19	
Percent Increase.....	33.1	74.6	100% max.
Acid No. of oil after test.....	3.06	7.2	None.
Pentane insolubles, percent.....	3.39	6.09	3% max.
Benzene insolubles, percent.....	2.07	2.72	2% max.
Catalyst weight loss (g.).....	0.44	2.21	Report.
Gear back lash (inches).....	0.0005	0.002	Do.
Bearing clearance (inches).....	0.0005	0.0005	Do.

The results indicated that the performance of Example II was a significant improvement over that of Blend B, a typical MIL-L-2105 lubricant.

We claim:

1. A lubricating composition consisting essentially of a mineral lubricating oil having dissolved therein an additive combination which confers extreme pressure prop-

erties on the composition and which consists of

(a) a chlorine-containing aliphatic hydrocarbon having a boiling point or decomposition temperature of not less than 160° C. selected from the group consisting of chlorinated paraffin wax, chlorinated kerosine, hexachlorethane, benzene hexachloride, chlorinated indenenes, dichlorodiphenyltrichlorethane and chlorinated diphenyls;

(b) an oil-soluble polyvalent metal salt of a dialkyl dithiophosphoric acid wherein each alkyl group contains from 3 to 12 carbon atoms; and

(c) a dialkyl phosphite having a total of from 2 to 12 carbon atoms in the alkyl group, the proportion of (a) being such as to provide from about 2.5% to 6.0% by weight of chlorine in the composition, the proportion of (b) being such as to provide from about 0.2% to 1.0% by weight of sulphur in the composition, and the proportion of (c) being such as to provide from about 0.1% to 0.3% by weight of phosphorus in the composition.

2. A lubricating composition as claimed in claim 1 wherein the proportion of (b) is such as to provide from 0.3% to 0.7% by weight of sulphur in the composition.

3. A lubricating composition as claimed in claim 1 wherein (a) is a paraffin wax containing from 40% to 70% by weight of chlorine. 5

4. A lubricating composition as claimed in claim 1 wherein the polyvalent metal of (b) is zinc.

5. A lubricating composition as claimed in claim 1 wherein (c) is di-isopropyl phosphite.

6. A lubricating composition as claimed in claim 1 wherein there is also present at least 0.05% by weight of an oil-soluble basic alkaline earth metal sulphonate. 10

7. A lubricating composition as claimed in claim 6 wherein there is present from 0.1% to 0.5% by weight of the oil-soluble basic alkaline earth metal sulphonate. 15

8. A lubricating composition as claimed in claim 6 wherein the oil-soluble basic alkaline earth metal sulphonate is wholly or partially neutralised with carbon dioxide to give the corresponding carbonate complex.

9. A lubricating composition consisting essentially of a mineral lubricating oil having dissolved therein from 5% to 15% of a chlorinated paraffin wax containing from 40% to 70% by weight of chlorine, from 1.5% to 3.5% of a zinc dialkyl dithiophosphate having from 3 to 12 carbon atoms in each alkyl group, from 0.5% to 1.0% of a dialkyl phosphite having from 1 to 6 carbon atoms in each alkyl group, from 0.5% to 2% of a phosphosulphurised polyisobutylene reacted with a barium alkyl phenate and over-based with a basic barium petroleum sulphonate and from 0.05% to 0.2% of a co-polymer of mixed fatty acid methacrylates, all percentages being by weight on the weight of the composition. 25

10. An additive combination for conferring extreme pressure properties to a mineral oil lubricant, which combination consists essentially of

from 67% to 74% of a chlorinated paraffin wax containing from 40% to 70% by weight of chlorine from 15% to 20% of a zinc dialkyl dithiophosphate having from 3 to 12 carbon atoms in each alkyl group, and

from 4.8% to 5.5% of a dialkyl phosphite having a total of from 3 to 12 carbon atoms per molecule, the percentages being by weight on the total weight of the combination.

11. An additive combination as claimed in claim 10 wherein the dialkyl phosphite is di-isopropyl phosphite.

12. An additive combination as claimed in claim 10 containing from 6% to 8% of a phosphosulphurised polyisobutylene reacted with a barium alkyl phenate and over-based with a basic barium petroleum sulphonate as a detergent. 15

13. An additive combination as claimed in claim 10 containing from 0.6% to 0.8% of a co-polymer of mixed fatty acid methacrylates as a pour point depressant. 20

14. An additive combination as claimed in claim 10 in solution in a mineral lubricating oil.

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