United States Patent [19]

Bryer et al.

[11] **3,915,871**

[45] **Oct. 28, 1975**

[54] **COMPOSITION COMPRISING NAPHTHENIC DISTILLATE, HYDRO-CRACKED LUBE AND AN ANTIOXIDANT**

[75] Inventors: **Robert P. Bryer,** Claymont, Del.; **Thomas D. Newingham,** Broomall, Pa.; **Ivor W. Mills,** Media, Pa.; **Glenn R. Dimeler,** West Chester, Pa.

[73] Assignee: **Sun Oil Company of Pennsylvania,** Philadelphia, Pa.

[22] Filed: **Oct. 16, 1972**

[21] Appl. No.: **298,126**

[52] **U.S. Cl.** ..... **252/33.6;** 208/19; 252/50; 252/52 R; 252/59; 252/74

[51] **Int. Cl.²..** **C10M 1/54;** C10M 3/48; C10M 5/28

[58] **Field of Search**..... 252/59, 50, 32.7 E, 74, 252/33.6; 208/18, 19

[56] **References Cited**

UNITED STATES PATENTS

3,236,770	2/1966	Matson	252/32.7
3,242,068	3/1966	Paterson	208/111
3,403,092	9/1968	Rausch	208/18 X
3,419,497	12/1968	Rocchini et al.	208/19 X
3,493,505	2/1970	Ries et al.	208/18 X
3,598,740	8/1971	Duling et al.	252/73
3,660,273	5/1972	Cummins	208/18

OTHER PUBLICATIONS

Jones "Oil & Gas Jour." 11/1/54, pp. 81–84.

Primary Examiner—Delbert E. Gantz
Assistant Examiner—I. Vaughn
Attorney, Agent, or Firm—George L. Church; Donald R. Johnson; Barry A. Bisson

[57] **ABSTRACT**

A lubricant composition comprises an unhydrorefined naphthenic distillate and a hydrocracked lube oil (preferably solvent extracted or hydrorefined to reduce or inhibit sludging on exposure to light) having a viscosity in the range of 80–3,000 SUS at 100°F and an oxidation inhibitor in amount effective to permit said composition to pass the ASTM D-943 oxidation test for a period of at least 300 hours, said amount being less than would be required to permit the same D-943 test performance for a similar composition wherein the hydrocracked lube oil is replaced by an unhydrocracked solvent refined lube of the same viscosity, viscosity-gravity constant, and viscosity index. The composition is useful in formulation of engine oils, refrigeration oils, transmission fluids, turbine oils, hydraulic oils, textile machinery lubricants, mist lubricants, etc.

5 Claims, 3 Drawing Figures

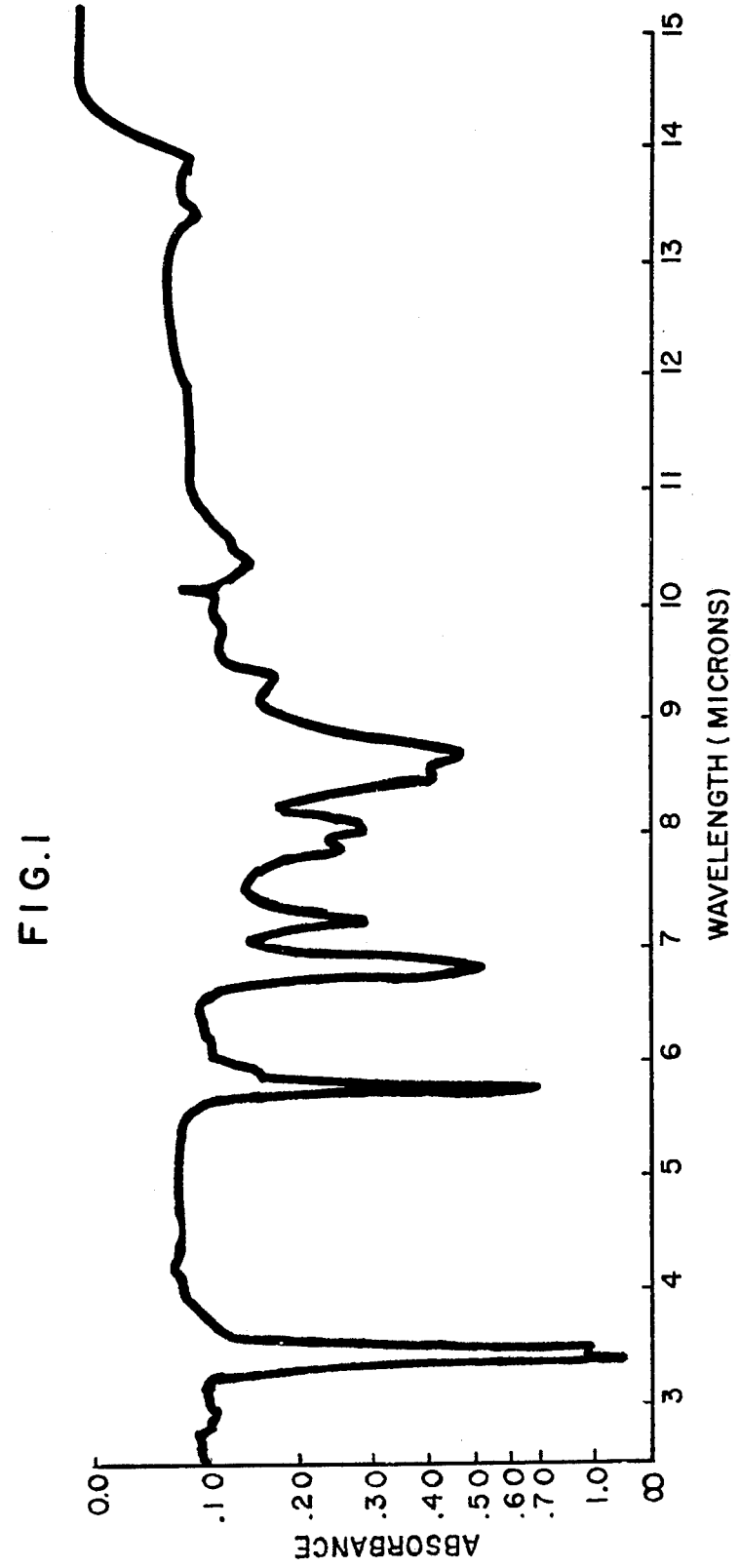
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

FIG. 1

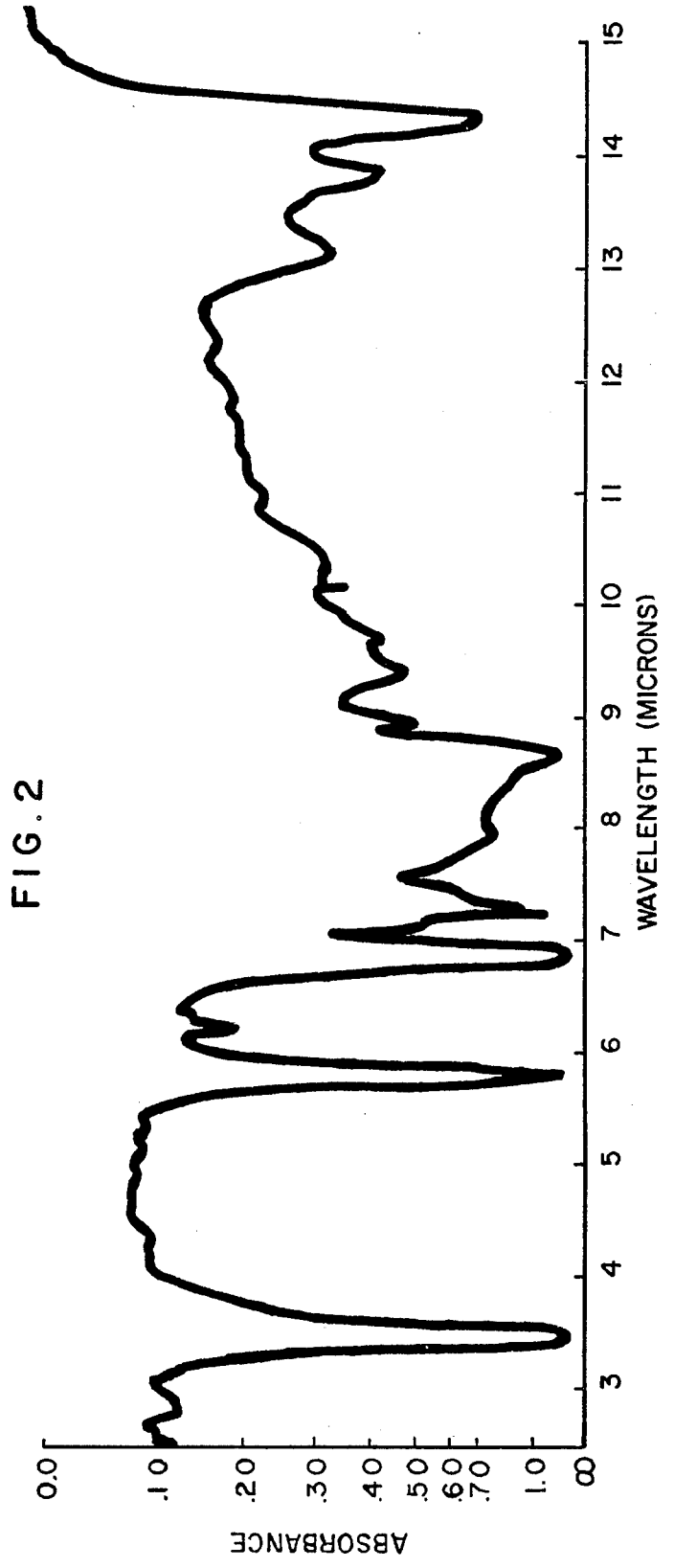
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

FIG. 2

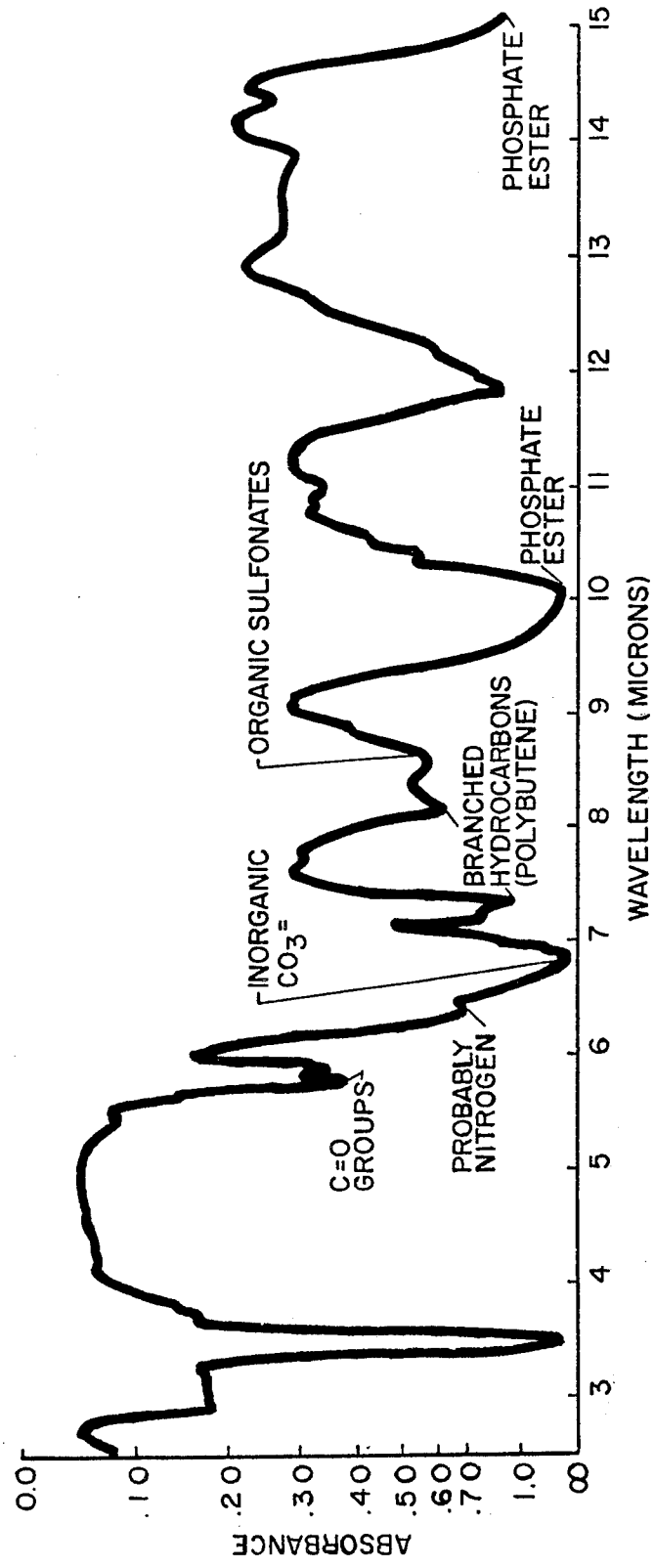
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)
PHOSPHATE ESTER
ORGANIC SULFONATES
PHOSPHATE ESTER
BRANCHED HYDROCARBONS (POLYBUTENE)
INORGANIC $CO_3^=$
C=O GROUPS
PROBABLY NITROGEN

FIG. 3

COMPOSITION COMPRISING NAPHTHENIC DISTILLATE, HYDRO-CRACKED LUBE AND AN ANTIOXIDANT

BACKGROUND OF THE INVENTION

U.S. Pat. Nos. 3,617,484 (Nov. 12, 1971), 3,663,427 (Max 16, 1972) and 3,666,657 (May 30, 1972), for example, describe the production of high viscosity index, hydrocracked lube oils and a process of improving the stability of such oils, when exposed to ultraviolet light (especially in the presence of oxygen), by selective extraction of the hydrocracked oil with an aromatic selective solvent (e.g., furfural, phenol, etc.).

It has been discovered that certain "stabilized" hydrocracked oils can be characterized as having a shorter life (to an acid number end point) in the ASTM D-943 test (with an oxidation inhibitor) than do similar unstabilized hydrocracked oils. However, compositions containing such a stabilized oil and an oxidation inhibitor have a better D-943 life (as to an increased acid number of 2.0) than does a similar composition containing a conventional solvent refined oil instead of the stabilized hydrocracked oil.

SUMMARY OF THE INVENTION

Hydrocracked lub oils, especially those having as ASTM viscosity index greater than 85 (typically at least 100) and containing in the range of 3–30 wt. percent aromatics, are especially useful components of petroleum based lubricant compositions and/or functional fluids. Such hydrocracked lubes are especially useful in compositions which also contain an antioxidant, particularly the phenolic types, e.g., ditertiarybutyl paracresol or "DBPC," the amine types, the carbamate types (e.g., antimony or zinc dibutyl carbamate) and the organo thiophosphate types (e.g., zinc dialkyl dithiophosphate), or mixtures of such inhibitors. Such compositions are especially useful in engine oils, refrigeration oils, transmission fluids, turbine oils (especially with DBPC as the major inhibitor), hydraulic oils, textile machinery lubricants, mist lubricants, etc. It can also be useful to add to a hydrocracked paraffinic lube an unhydrorefined naphthenic distillate in amount effective to improve oxidation inhibitor response of the hydrocracked lube.

An especially useful lubricant composition comprises an unhydrorefined naphthenic distillate and a hydrocracked lube oil which has been solvent extracted or hydrorefined to reduce or inhibit sludging on exposure to light and having a viscosity in the range of 80–3,000 SUS at 100°F., and an oxidation inhibitor in amount effective to permit said composition to pass the ASTM D-943 oxidation test (to a total acid number increase of 2.0) for a period of at least 300 hours (more preferred, 500 hours), said amount being less than would be required to permit the same D-943 test performance for a similar composition wherein the hydrocracked lube oil is replaced by an unhydrocracked solvent refined lube of the same viscosity, VGC and viscosity index. In such a composition, where the hydrocracked oil is stabilized by extraction or hydrorefining, said D-943 life will be less than if an unstabilized hydrocracked lube were used. However, the formation of sludge in the D-943 test (which, for example is important in turbine oils) is less for compositions containing the stabilized hydrocracked oil.

BRIEF DESCRIPTION OF THE DRAWINGS

The novel composition, comprising a stabilized hydrocracked lube and an antioxidant, is especially useful in such lubricants as mist oils, textile machinery lubricants, engine oils and hydraulic oils, which contain a high molecular weight polymer of the viscosity index "builder" class, such as polyacrylates, polymethacrylates, dispersant polyacrylates and polymethylacrylates (typically grafted with N-vinyl-2-pyrrolidinone), polystyrenes (e.g., polymethyl styrenes), polyolefins (e.g., polybutenes), or mixtures of two or more of such polymers. The accompanying drawings FIGS. **1** and **2**, are typical infra-red absorption spectra (or "scana") of two such commercial polymers, which are especially useful in engine oils to improve the viscosity index thereof. FIG. **3** is an IR scan of a typical engine oil additive "package" of the "DI" or dispersant-inhibitor type.

As articles of commerce, such polymers are well known and readily available but are generally trade secret compositions which require expensive analytical work to completely characterize and can require expensive laboratory work to duplicate. An important laboratory tool for identifying a particular commercial polymer is the infra-red (IR) scan. The scans of all of the FIGS. **1–3** are of commercially available additives and are provided in order to facilitate practice of the embodiment of the present invention wherein the commercial additives can be used.

FIG. **1** is an IR scan of a typical commercial dispersant type polymethacrylate viscosity index "builder," or "improver," marketed by Rohm and Haas as Acryloid 954. This VI builder and other typical builder polymers are described further in pending U.S. application Ser. No. 246,997 (filed Apr. 24, 1972) now U.S. Pat. No. 3,855,135, issued Dec. 17, 1974 [generally, the lower molecular weight materials are preferred in mist lubricants or in "shear stable" engine oils].

FIG. **2** is an IR scan of another commercial VI builder which is marketed by Lubrizol Corporation as "3702" and termed a dispersant type styrene copolymer (note, the IR scan shows a high carbonyl content).

FIG. **3** is an IR scan of Lubrizol 27563 and represents another class of commercial engine oil additive, the Dispersant-Inhibitor package or "DI package." Typically, a DI package can contain a magnesium petroleum sulfonate, an ashless dispersant, and an oxidation inhibitor (e.g., zinc dialkyldithiophosphate). Lubrizol 27563 analyzes 2.40 weight percent zinc, 1.9% magnesium, 2.15% phosphorous, 0.17% nitrogen and 5.0% sulfur.

FURTHER DESCRIPTION

The following Table I presents typical properties of stabilized hydrocracked oils which can be used in practice of the present invention.

TABLE I

Properties of Hydrocracked Oils*				
Viscosity (SUS. 100°F)	ASTM VI	Gravity API	Wt.% Aromatics	Aniline Point °F.
100	103	34.2	12	220
200	107	33.3	11	235
500	107	31.5	13	250

*All oils dewaxed to a 0°F. pour point by chilling in a solvent, and stabilizing by extraction with furfural.

In general, such hydrocracked and stabilized hydrocracked oils (of high VI and low pour point) can be substituted in whole or in part for the hydrorefined paraffinic oil or solvent refined paraffinic lube component in the compositions (or process where applicable) of U.S. pat. No. 3,502,567 of Ivor W. Mills and Glenn R. Dimeler, issued Mar. 24, 1970, for example. In such compositions the oxidation inhibitor concentration can be reduced when 85–100% of the solvent refined lube is replaced by the stabilized hydrocracked oil.

For example, in a mist lubricant formulation which contains a solvent refined paraffinic lube, the partial or whole substitution of a hydrocracked (preferably, a stabilized hydrocracked) lube permits the use of a lower concentration of the polymeric additive for a given degree of stray fog. This provides improved reclassification performance (for a given degree of stray fog) in the composition containing the hydrocracked lube. Alternatively, a lower molecular weight polymer can be used in the composition containing the hydrocracked lube.

In hydraulic oils, whether soap or polymer thickened, a preferred oil contains mainly DBPC (e.g., 0.5 weight percent) as the antioxidant and a minor amount (e.g., 0.01–0.1% Zn) of zinc dialkyl dithiophosphate to impart antiwear properties.

In turbine oils, the use of a stabilized hydrocracked oil in combination with an ashless or virtually ashless inhibitor improves the performance in test where sludging is measured (as in Mil-L-17672B). In engine oils, the composition containing an antioxidant (preferably zinc dialkyl dithiophosphate at levels imparting 0.1–3% Zn in the final composition) and a stabilized hydrocracked oil provides better performance in the Sequence IIIc test. Also, when tested in a natural gas burning engine, the composition containing the stabilized hydrocracked oil is superior.

As an additional component (to hydrorefined oils and unhydrorefined oils) in textile oils or refrigeration oils, high viscosity index hydrocracked oils and/or hydrogenated polyolefin oils (e.g., polybutene in the C_{16}–C_{40} range) can be used. The polyolefin or hydrocracked oil can be partially or fully hydrogenated.

ILLUSTRATIVE EXAMPLES

The following automatic transmission fluid is prepared by blending each of the components with stirring at room temperature:

- 88.8 wt. % of a blend of "furfural stabilized" hydrocracked paraffinic oil having a 0°F. pour point, a viscosity of 140 SUS at 100°F. and 105 ASTM VI;
- 0.5 wt. % of dilauryl thiodipropionate (antioxidant);
- 0.2 wt. % of "Naugatuck 438," manufactured by Uniroyal, an amine antioxidant;
- 0.3 wt. % "Lubrizol 1097" (zinc dialkyl dithiophosphate) (an antioxidant and wear inhibitor);
- 0.5 wt. % "Amoco 121" (barium alkyldiphosphonate) (a detergent);
- 0.3 wt. % overbased magnesium petroleum sulfonate having a base number of 300;
- 0.1 wt. % tricresylphosphate;
- 3.0 wt. % a refined petroleum oil containing 95% aromatics as a seal swell agent;
- 10 p.p.m. dimethyl silicone defoamer having a viscosity of 60,000 cs at 68°F.;
- 3.0 wt. % of synthetic sulfurized sperm (see Canadian Ser. No. 134,156) and
- 3,75 wt. % dispersant polymethacrylate viscosity index improver which is a copolymer of laurylmethacrylate and methylmethacrylate having grafted thereon n-vinyl-2-pyrrolidinone.

This automatic transmission fluid provides superior performance (compared to a similar formulation containing solvent refined lube of the same viscosity) in the General Motors T-12 Powerglide Low Energy Transmission Cycling Test.

EXAMPLE II

A limited slip differential fluid is prepared by blending the following components at room temperature:

- 70.0 vol. % furfural stabilized hydrocracked oil having a viscosity of 500 SUS at 100°F. VI of;
- 21.6 vol. % unstabilized hydrocracked bright stock (2,500 SUS at 100°F.);
- 0.5 vol. % Friedel-Crafts condensation products of chlorinated paraffinic wax with phenol (pour depressant)
- 7.4 vol. % an chlorinated pressure additive comprising a mixture of zinc phosphorodithioate and cholorinated hydrocarbons containing 3% Zn, 3% P, 16.5% Cl and 16% S;
- 0.5 vol. % di-n-butyl tin dilaurate; and
- 10 p.p.m. dimethyl silicone defoamer having a viscosity of 60,000 cs at 68°F.

The high traction components of U.S. Pat. No. 3,608,385 of Irl N. Duling et al, issued Sept. 28, 1971, can be added to this fluid to increase the traction coefficient thereof.

EXAMPLE III

A turbine oil is prepared by blending each of the following components (in parts by weight) with stirring:

- 99.4 furfural stabilized hydrocracked oil having an SUS viscosity of 150 at 100°F.;
- 0.2 Enjay Paraflow 149 (pour depressant); and
- 0.4 ditertiary butyl paracresol.

Enjay Paraflow 149 is a Friedel-Crafts reaction product of chlorinated biphenyl.

This oil passes all turbine requirements for low sludge except for M-L-17642B. If 0.75 parts Vanderbuilt Vanalube 664 is used instead of the DBPC, the formulation can pass M-L-1762B.

This oil passes over 2000 hours of the D-943 test. A similar turbine oil containing a solvent refined paraffinic lube failed after 1500 hours of the D-943 test.

Vanalube 664 is a mixture of DBPC and amine type oxidation inhibitors and also includes a small amount of Butyl Zinate (zinc di-n-butyl carbamate).

EXAMPLE IV

An expecially high quality 10W-40 engine oil is made by blending the following (in parts by weight) with stirring:

- 42.2 solvent refined paraffinic oil viscosity of 110 SUS at 100°F., ASTM VI of 104;
- 42.2 solvent refined paraffinic oil of 210 SUS at 100°F., ASTM VI of 103;
- 9.0 Acryloid 954, VI builder; and
- 6.6 Lubrizol 4446. Lubrizol 4446 is the more common commercial designation of the product previously referred to as Lubrizol 27563 and further identified by the IR scan of FIG. 3 herein. Properties of this oil are shown in Table II below.

TABLE II

Characteristics	ASTM Method	Test Results
No. Viscosity, cP/0°F.	D2602	2100
Viscosity, SUS/100°F.	D2161	447
No. Viscosity, SUS/210°F.	D2161	83.5
Viscosity Index	D2270	105
Viscosity, cSt/210°F.	D445	16.40
Gravity, °API	D287	30.0
Flash COC°F.	D92	410
Pour, °F.	D97	−45
Color	D1500	14.5
pH		7.8
Total Acid No., mgKOH/g	D664	3.6
Total Base No., mgKOH/g	D664	6.9
Sulfur, %	D129	0.44
Conradson Carbon %	D189	1.2
Foam, Tend/Stab	D892	
Sequence I, ml		5/0
Sequence II, ml		20/0
Sequence III, ml		5/0
No. Appearance	Visual	Bright
Magnesium, %		0.146
No. Zinc, %		0.185
Phosphorous, %	D1091	0.165
Sulfated Ash, %	D874	1.0

SAE 10W-40
API Service Classification SE, CB

When 110 and 210 SUS stabilized hydrocracked oils are substituted for 90–100% of the solvent refined oils, the zinc dialkyl dithiophosphate content of the oil can be reduced by 20% (e.g., 0.18% Zn to 0.14% Zn in final oil) and the oil will perform at least as well in the Sequence IIIc test. Furthermore, the Acryloid 954 can be reduced to 8.5% and the oil will still perform at least as well as is indicated in Table II.

Preferably, with the stabilized hydrocracked oil, engine oils can contain 0.07–0.18% Zn (as zinc dithiophosphate), depending on desired performance.

The VI builder of FIG. **2** can be substituted in whole or in part for the Acryloid 942.

EXAMPLE V

The oxidation stability of hydrocracked paraffinic lube oils is improved by the addition of small amounts (up to 15%) of unhydrorefined naphthenic distillate. Such improvement is observed in the rotary bomb oxidation test (RBOT)**as follows

Vol. % of 100 SUS (at 100°F.) naphthenic distillate*	0	10	15
RBOT, 300°F. minutes hydrocracked lube oil	205	264	257
Solvent refined lube oil	190	160	—

*Naphthenic acid-free (i.e., total acid number or "neutralization number" less than 0.2 mg. KOH/g).
** ASTM D2272.

The test oils also contain 1.25% Vanlube 664, antioxidant and rust inhibitor package. The data indicate that the naphthenic distillate improves the oxidation inhibitor response of hydrocracked lubes, while reducing the oxidation inhibitor response of the conventional solvent refined lubes. However, the addition of hydrorefined naphthenic oils to conventional solvent refined lubes does improve inhibitor response.

As used herein, the term "hydrocracked paraffinic lube" refers to a hydrocracked oil having a viscosity-gravity constant no greater than 0.819. Naphthenic (including relatively naphthenic oils) have a VGC in the range of 0.820 to 0.899, the more preferred naphthenic oils being in the range of 0.840–0.899. The hydrocracked paraffinic oils can be obtained by hydrocracking a naphthenic charge stock since hydrocracking can cause reduction of the VGC.

EXAMPLE VI

Motor lubricants containing hydrocracked lubes (compared to conventional solvent refined lubes) can also provide decreased consumption and, thus, greater oil economy. For example, a 5W-40 motor oil having excellent oil economy in both suburban and turnpike service in passenger automobiles was made according to the following formulation:

Component	Volume %
Hydrocracked 110 SUS (at 100°F.) lube	81.8
Zinc dialkyl dithiophosphate in carrier (Amoco 5959 containing 9.0% Zn)	0.6
VI improver (Acryloid 954)	11.5
Motor oil package, Lubrizol 4441, containing a detergent, antioxidant and dispersant and analyzing S, Mg, Zn, P and N	6.1

Table III herein presents typical data of commercially available naphthenic distillate oils which can be blended with a hydrocracked lube to provide improved oxidation stability (including improved response to additives which are oxidation inhibitors).

TABLE III

TYPICAL DATA
COMMERCIALLY AVAILABLE NAPHTHENIC DISTILLATE OILS

Property	ASTM Designation	Oil A	ASTM Oil No. 3	Oil B	Oil C	Oil D	Oil E	Oil F	Oil G	Oil H
Viscosity, SUS at 100°F	D-2161-66	108	156	208	310	515	780	1276	2525	5945
Viscosity, SUS at 210°F	D-2161-66	38.2	41	43.2	46.8	52.4	58.8	68	87.2	135
API Gravity at 60°F	D- 287-67	22.2	22.1	21.0	20.1	19.6	19.1	18.4	17.6	17.3
Specific Gravity at 60°F	D-1250-56	.9206	.9194	.9279	.9334	.9365	.9396	.9440	.9490	.9509
Flash Point, COC, F	D- 92-66	320	330	345	355	380	390	405	430	495
Volatility 22 hrs. at 225 Wt. %	D- 972-56	7.58	5.96	5.40	4.35	3.08	2.11	1.67	0.16	0.02
Pour Point, F	D- 97-66	−45	−35	−30	−15	−10	−5	0	+10	+20
Color, ASTM D-1500	D-1500-64	1.25	1.75	1.75	2.0	2.0	2.5	3.0	3.5	5.75
Molecular Weight	D-2502-67	295	325	325	345	355	370	380	395	450
Viscosity-Gravity Constant	D-2501-67	0.884	0.878	0.884	0.887	0.885	0.885	0.885	0.889	0.884
Refractive Index n_D^{20}	D-1747-62	1.5081	1.5079	1.5121	1.5160	1.5167	1.5190	1.5210	1.5222	1.5250
Refractivity Intercept	D-2159-64	1.0502	1.0479	1.0500	1.0511	1.0503	1.0510	1.0508	1.0495	1.0495
Carbon Type Analysis	D-2140-62									
Aromatic Carbon Atoms, C_A%	—	21	20	21	22	21	22	22	21	20
Naphthenic Carbon Atoms C_N%	—	37	36	37	36	37	36	36	39	38
Paraffinic Carbon Atoms C_P%	—	42	44	42	42	42	42	46	40	42
Molecular Type Analysis (Clay										

TABLE III-continued

TYPICAL DATA
COMMERCIALLY AVAILABLE NAPHTHENIC DISTILLATE OILS

Property	ASTM Designation	Oil A	ASTM Oil No. 3	Oil B	Oil C	Oil D	Oil E	Oil F	Oil G	Oil H
Gel)	D-2007-56T									
Asphaltenes, Wt. %	—	0	0	0	0	0	0	0	0	0
Polar Compounds, Wt.%	—	1.1	1.2	1.8	2.0	2.5	2.7	3.0	2.7	4.2
Aromatics, Wt.%	—	43.0	41.7	44.0	44.0	43.8	43.6	44.0	44.8	44.7
Total Aromatics %	—	44.1	42.9	45.8	46.0	46.3	46.3	47.0	47.5	48.9
Saturates, Wt. %	—	55.9	57.1	54.2	54.0	53.7	53.7	53.0	52.5	51.1
Analine Point, F	D- 611-64	145	156	152	153	156	162	166	172	183
ASTM Type	D-2226-69	103	103	103	103	103	103	103	103	103

Oils, B, C, E and F are blends of oils A and G

The invention claimed is:

1. A composition, useful as a lubricant, comprising an unhydrorefined naphthenic distillate of lubricating viscosity in amount sufficient to provide improved oxidation stability and a major amount of a hydrocracked lube oil which has been solvent extracted or hydrorefined to reduce or inhibit sludging of the oil on exposure to ultraviolet light and having a viscosity in the range of 80–3,000 SUS at 100°F., and a minor amount of an oxidation inhibitor consisting essentially of a mixture of phenolics, amines, and zinc carbamate, said amount being effective to permit said composition to pass the ASTM D-943 oxidation test for a period of at least 300 hours, said amount being less than would be required to permit the same D-943 test performance for said composition wherein the hydrocracked lube oil is replaced by an unhydrocracked solvent refined lube of the same viscosity, viscosity-gravity constant and viscosity index.

2. The composition of claim **1** wherein said naphthenic distillate is substantially free of naphthenic acids.

3. The composition of claim **2** wherein the amount of said naphthenic distillate is in the range of 0.5–20 volume %.

4. The composition of claim **1** wherein said hydrocracked lube oil has been solvent extracted.

5. The composition of claim **3** wherein said hydrocracked lube oil has been solvent extracted.

* * * * *