

[54] LUBRICANT FOR SPINDLES, NEEDLES OR TWISTER RINGS

[75] Inventors: **Walter J. Coppock**, Wallingford;  
**James R. Amaroso**, Newtown  
Square, both of Pa.; **John Q. Griffith, III**, Claymont, Del.

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

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### Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 35,231, May 6, 1970, and a continuation-in-part of Ser. No. 60,642, Aug. 3, 1970, abandoned, and a continuation-in-part of Ser. No. 178,193, Sept. 7, 1971, and a continuation-in-part of Ser. No. 178,479, Sept. 7, 1971.

[52] U.S. Cl. .... **252/32.5, 252/8.6, 252/49.8, 252/49.9, 252/56 R**

[51] Int. Cl. .... **C10m 1/46**

[58] Field of Search ..... **252/8.6, 49.9, 49.8, 32.5**

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| 2,285,855 | 6/1942 | Downing et al. .... | 252/49.8   |
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*Primary Examiner*—W. Cannon

*Assistant Examiner*—W. Cannon

*Attorney, Agent, or Firm*—G. L. Church, Esq.; J. E. Hess, Esq.; B. A. Bisson, Esq.

[57]

### ABSTRACT

A composition which does not cause pin hole damage to cotton, and which is useful as a spindle oil, or as a twister ring oil, or as a needle oil, said composition comprising an effective amount of a friction reducing additive and a hydrorefined naphthenic or paraffinic lube or a hydrocracked hydroisomerized paraffinic lube or a hydrogenated polyolefin oil, said additive containing at least one alkyl ester of a carboxylic acid (preferably a methyl ester of a triglyceride of a fatty acid) or an alkyl acid phosphate or alkyl ammonium alkyl acid phosphate (e.g., an alkyl amine-neutralized, alkyl acid phosphate having alkyl groups in the C<sub>8</sub>-C<sub>24</sub> range).

**4 Claims, No Drawings**

# LUBRICANT FOR SPINDLES, NEEDLES OR TWISTER RINGS

## CROSS REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part of U.S. Pat. application Ser. No. 35,231, filed May 6, 1970; U.S. Pat. Ser. No. 60,642, filed Aug. 3, 1970 (now abandoned); U.S. Pat. Ser. No. 178,193, filed Sept. 7, 1971; U.S. Pat. Ser. No. 178,479, filed Sept. 7, 1971; and U.S. Pat. Ser. No. 240,806, filed Apr. 4, 1972.

The following patents and applications are related to the disclosure of the present application in that they disclose additives which are useful in the present composition and/or methods of obtaining hydrotreated naphthenic oils (and other oils) which can be used to make the textile machinery lubricant oil composition of the present invention.

The disclosure of all of the following applications and patents is hereby incorporated in the present applications:

| Serial No. | Filing Date             | U.S. Pat. No. | Issue Date | Title                                                                                                                                            | 25 | 35,231  | 5-6-70                 | Hydraulic Oil Composition Containing a Blended Base Stock — John Q. Griffith III, Edward S. Williams, William H. Reiland, Jr., Ivor W. Mills & Glenn R. Dimeler                         |
|------------|-------------------------|---------------|------------|--------------------------------------------------------------------------------------------------------------------------------------------------|----|---------|------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 622,398    | 3-13-67                 | 3,642,358     | 8-19-69    | Clay Treatment of Hydrotreated Cable Oils — Ivor W. Mills & Glenn R. Dimeler                                                                     | 30 |         |                        |                                                                                                                                                                                         |
| 636,493    | 5-5-67                  | 3,681,279     | 8-1-72     | Process for Preparing an Aromatic Oil and Non-discoloring Rubber Composition — Ivor W. Mills, Glenn R. Dimeler & Merritt C. Kirk, Jr.            | 35 | 52,301  | 7-6-70                 | Polyisobutylene Oil Having a High Viscosity Index — Gary L. Driscoll, Irl N. Duling & David S. Gates                                                                                    |
| 652,026    | 7-10-67                 | 3,502,567     | 3-24-70    | Process for Producing Cable Oils by Sequential Refining Steps — Ivor W. Mills & Glenn R. Dimeler                                                 | 40 | 60,642  | 8-3-70 (now abandoned) | Textile Machinery Lubricant Composition — James R. Amaroso & John O. Griffith, III                                                                                                      |
| 730,999    | 5-22-68                 |               |            | Hydrotreated Transformer Oil and Process of Manufacture — Ivor W. Mills & Glenn R. Dimeler                                                       | 45 | 70,590  | 9-8-70                 | 3,732,154 5-8-73 Catalytic Hydrofinishing of Lube Oil Product of Solvent Extraction of Petroleum Distillate — Ivor W. Mills, Merritt C. Kirk, Jr. & Albert T. Olenzak                   |
| 812,516    | 2-19-69                 | 3,619,414     | 11-9-71    | Catalytic Hydrofinishing of Petroleum Distillates in the Lubricating Oil Boiling Range — Ivor W. Mills, Merritt C. Kirk, Jr. & Albert T. Olenzak | 50 | 140,398 | 5-5-71                 | Mist Lubricant Containing Polymeric Additive — James R. Amaroso, Walter J. Coppock, Thomas D. Newingham & Edward S. Williams                                                            |
| 828,746    | 5-28-69                 | 3,658,689     | 4-25-72    | Isomerization of Waxy Lube Streams and Waxes — Ib Steinmetz & David S. Barmby                                                                    | 55 | 178,193 | 9-7-71                 | Composition Comprising Stabilized Hydrocracked Lube and an Antioxidant — Robert B. Bryer, William W. Crouse, Jr., John Q. Griffith, III, Thomas D. Newingham, & William H. Reiland, Jr. |
| 850,716    | 8-18-69 (now abandoned) |               |            | Blended Hydrocarbon Oil and Process of Manufacture Ivor W. Mills & Glenn R. Dimeler                                                              | 60 |         |                        | Soap Thickened Hydraulic Oil Composition — John O. Griffith, III, Edward S. Williams & William H. Reiland, Jr.                                                                          |
| 850,717    | 8-18-69 (now abandoned) |               |            | Hydrotreated Lube Oil and Process of Manufacture — Ivor W. Mills & Glenn R. Dimeler                                                              | 65 | 178,479 | 9-7-71                 |                                                                                                                                                                                         |
| 850,778    | 8-18-69                 | 3,654,127     | 4-4-72     | Process for Preparing High Viscosity Hydrotreated Cable Oil — Ivor W. Mills, Glenn R.                                                            |    |         |                        |                                                                                                                                                                                         |

| Serial No. | Filing Date | U.S. Pat. No. | Issue Date | Title                                                                                                           |
|------------|-------------|---------------|------------|-----------------------------------------------------------------------------------------------------------------|
| 220,362    | 1-24-72     |               |            | Hydrogenated Ethylene-propylene Copolymer Oils — Richard S. Stearns, Irl N. Duling & David S. Gates             |
| 228,832    | 2-24-72     |               |            | Hydrotreated Lube Oil and Process of Manufacture — Ivor W. Mills & Glenn R. Dimeler                             |
| 240,806    | 4-4-72      |               |            | Improved Textile Machinery Lubricant Composition<br>Walter J. Coppock, James R. Amaroso & John O. Griffith, III |

### SUMMARY OF THE INVENTION

Novel compositions, which are useful as textile-machinery lubricants, are an improved needle oil, an improved twister ring oil, and an improved spindle oil. These oils have greater oxidation stability, cloth scourability and better antifriction properties than do prior art oils. These oils have little or no tendency to produce pinholes in cotton, which was a problem with prior art oils.

A composition which does not cause pin hole damage to cotton, and which is useful as a spindle oil, as a twister ring oil or as a needle oil, comprises a hydrogenated, hydrocracked or hydroisomerized oil, e.g., a hydrofined naphthenic or paraffinic lube, or a hydroisomerized or hydrocracked paraffinic lube or a hydrogenated polyolefin oil, and an effective amount of a friction reducing additive, said additive containing at least one alkoxy or alkyl phosphate or acid phosphate or at least one alkyl ester of a carboxylic acid, more preferred a triglyceride of a fatty acid. The fatty acid can contain in the range of C<sub>12</sub>-C<sub>24</sub> carbon atoms. The alkyl group is preferably methyl, but can be C<sub>2</sub> to C<sub>8</sub>. Preferably, the oil has an SUS viscosity at 100° F. in the range of 60-600 SUS (more preferred, 70-300 SUS) and contains in the range of 5-40 wt. percent aromatic hydrocarbons.

One such friction reducing additive is a surface-active organic phosphate ester, as of a linear aliphatic ethoxylated alcohol, (e.g., Ultrophos 11, Ortholeum 162, etc.) in an amount (e.g., 0.1-10 wt. percent) effective to reduce the static friction of the base oil as measured by the low velocity friction apparatus. Ortholeum 162 consists essentially of dilauryl phosphate and other similar mixed alkyl acid orthophosphates. Preferably, such acid phosphates are neutralized with an alkyl amine before use in the present lubricant. This test method and such phosphate esters are further described in U.S. Pat. Ser. No. 218,394, filed Jan. 17, 1972 of Haseltine, Jr., Gates and Hagstrom, said application being incorporated herein by reference.

Another useful additive is the synthetic sulfurized oil of U.S. Pat. application Ser. No. 135,466 of Recchuitte, filed Apr. 19, 1971 (now abandoned), which is made by heating sulfur and a blend of 30-95 percent lard oil and 70-5 percent of one or a mixture of C<sub>6</sub>-C<sub>24</sub> acyclic monoolefin.

The new, improved needle oil preferably comprises an effective amount of a friction reducing additive in a base oil consisting essentially of hydrotreated or hydro-

cracked paraffinic lube having a viscosity at 100° F. in the range of 70-150 SUS (typically 95-115), said hydrotreated or hydrocracked paraffinic lube containing in the range of 4-10 percent aromatics (e.g., 8 percent) and typically, having a 260 UVA in the range of 0.05-0.4 (e.g., 0.2) and having been obtained by hydrotreating of a 9-15 wt. percent (e.g., 12 percent) aromatic content, solvent refined paraffinic distillate to reduce the 260 UVA by at least 30 percent, or by hydrocracking a paraffinic distillate oil (which can be solvent extracted either before or after said hydrocracking). Although a hydrotreated naphthenic oil can be substituted in whole or in part for said hydrotreated paraffinic lube, the lubricant consisting essentially of the hydrotreated paraffinic lube or the hydrocracked paraffinic lube, or a blend of such lubes has better heat resistance. Butylacetate can be used instead of (or to replace part of) the methyl ester of a triglyceride of a fatty acid; however, butylacetate is less preferred because it has a low flash point.

A preferred formulation for such a needle oil (especially for high speed knitting needles for "double-knit" hosiery) having excellent stability, low drag and which produces little deposit build-up on the needle, is a 90-100 parts by weight (typically 94.5), hydrotreated or hydrocracked paraffinic lube of about 100 (e.g., 110) SUS viscosity at 100° F., 1-10 parts of a friction reducing additive (typically 5), one preferred additive being a mixture of methyl esters of mixed triglycerides of fatty acids in the C<sub>12</sub>-C<sub>20</sub> range. Further preferred is the product sold by Procter & Gamble Company under the trade designation TE-1618, which contains in the range of 2-6 percent C<sub>16</sub> monounsaturates, 17-24 percent C<sub>18</sub> saturates, 35-45 percent C<sub>18</sub> monounsaturates, has a saponification number in the range of 190-200, an iodine number in the range of 39-60, a refractive index of about 1.4472, a specific gravity at 88° F. of about 0.86, a melt point of about 15° C., a flash point (open cup) of about 340° F., a pH of about 7, a maximum acid number of 1 (more preferably less than 0.4), and a percent transmission at 460 mm of at least 80. This friction modifier is light in color and, with nylon or cotton, has good detergent scourability and is non-staining, non-abrasive and non-corrosive.

The needle oil can also contain other additives, such as 0.1-2 parts barium salts of alkylaryl or alkyl polyethylene oxyphosphorus ester acids (e.g., 0.5 parts of the 50 percent active material sold by General Aniline and Film Co. under the trade name "Antara LM-505") such a material is light colored and serves as a lubricant or antiwear agent, as an emulsifier or dispersant, inhibits rust, and also provides some detergency and scourability. Typically this additive contains 5-8 percent barium (e.g., 6.2 percent) and 1-2 percent phosphorous (e.g., 1.6 percent), has a viscosity at 100° F. of about 1,100 SUS and a flash point of about 350° F.

Also useful in the needle oil are an antioxidant, such as ditertiary butyl para cresol, known as DBPC, (e.g., 43 lbs. per 1,000 gallons of oil) and an ultraviolet stabilizer, such as the triazole types (e.g., 0.7 lb. per 1,000 gallon).

Another novel composition, useful in the textile field, is an improved spindle oil, containing 1-10 parts (e.g., 3.8) of a friction reducer, such as mixed methyl esters of glycerides of fatty acids, in the range of 85-99 parts hydrogenated oil having an SUS viscosity at 100° F. in

the range of 70–200 (and preferably hydrorefined naphthenic oil, e.g., 87.3 parts of 100 SUS and 5.2 parts of 2500 SUS). The spindle oil can also contain 0.2–1.0 parts of an antioxidant (e.g., 0.6 parts DBPC) and 0.5–5 parts of a rust preventative and detergent, such as 2.2 parts of the 80 percent active sodium salts of sulfonates of petroleum acids sold by the trade name “Shell 80–20 sulfonates” (barium salts can also be used).

The novel twister ring oil comprises hydrorefined or hydrocracked paraffinic lube, or a high VI hydrogenated polyolefin and a friction modifier, preferably an amine salt of an alkyl acid phosphate.

Tables 1, 2 and 3, attached hereto, present typical and a preferred range of properties for, respectively, such a needle oil, such a spindle oil and such a twister ring oil. However, operable products can be formulated which have properties outside these preferred ranges, for example, the viscosity at 100° F. of any of these products could be within the range of 70–300 SUS.

#### FURTHER DESCRIPTION

In general, improved lubricants of the present invention comprise a friction reducing additive and a base oil having an SUS viscosity in the range of 60–600 at 100° F. (more preferably 70–300), consisting essentially of one or more hydrorefined naphthenic oils, hydrogenated polyolefin oils, or hydrocracked or hydrorefined paraffinic oils (or blends of any of these oils) of the lubricating oil viscosity range (e.g., 45–12,000 SUS at 100° F.)

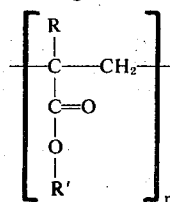
Preferably, the hydrorefined naphthenic oils have an aniline point in the range of 140°–190° F., more preferred 150°–170° F., a viscosity-gravity constant (VGC) in the range of 0.820–0.899, more preferred 0.850–0.899, and an ultraviolet absorptivity (i.e., UVA) at 260 millimicrons, (i.e., 260 UVA) which is at least 40 percent less than that of an unhydrorefined naphthenic lube of the same viscosity, viscosity-gravity constant, and boiling range.

The hydrocracked or hydrorefined paraffinic oils have a VGC in the range of 0.790–0.819 and an ASTM viscosity index of at least 90 (typically, at least 95).

Preferably, the UVA of the base oil at 335 millimicrons (i.e., 335 UVA) is in the range of 0.01 to 0.4 (typically 0.02–0.2) and the ASTM D1500 initial color is less than 4.0 (more preferably no greater than 2.5).

The additives comprise a friction reducing additive and can include viscosity index improvers, antirust, antifoam, antioxidant, etc. In some cases a tackiness agent is added. The preferred tackiness agents are olefin polymers (e.g., atactic polypropylene, or polyisobutylene rubber) and can partially or fully hydrogenated; however, any oil-compatible tackiness agent (e.g., polyacrylates, Al oleate, or natural rubber obtained from dehydrated latex) can be used. The preferred range for the polyisobutylene polymers as commercially available, as indilution with oil (about 50 percent) is about 0.3–6 percent, more preferably 1–3 percent. In any event, the amount used must be sufficient to cause the lubricant to be highly retentive on a bearing (or other part) and to reduce “splashing”; however, the amount must be less than that which will cause the lubricant to be “stringy.”

Preferred acrylates and methacrylates (e.g., the viscosity index improver types can be of the non-dispersant type and correspond to the structural formula:



where  $n$  is an integer such that the viscosity average molecular weight (VAMW) is in the range of 10,000 to 2,000,000, where R is H, for the acrylates and methyl for the methacrylates. In the copolymer type materials, R' is a single alkyl radical (branched or normal) having a carbon number in the range of six to about 30, preferably eight to 24 (usually an even number). In the terpolymer types of materials at least two different alkyl radicals (in the above carbon number ranges) are present in the polymer chain (e.g., normal octyl and normal decyl or each of the even numbered normal alcohols in the  $C_{10}$ – $C_{22}$  range). The dispersant type materials can also be used. In the dispersant type, the above noted copolymers or terpolymers have been grafted with vinyl pyrrolidone. Descriptions of such polymers can be found in U.S. Pat. Nos. 2,091,627; 2,489,671; 3,252,949; 3,417,021 and 3,510,425.

An especially preferred polymethacrylate is that sold by Rohm and Haas under the trade name “PL 10190” (which has a molecular weight of about 100,000 and is of the same chemical structure as the “700 Series”). Two operable polyisobutylenes are “Paratone N” (which has a molecular weight of about 20,000) and “Paratac 108” (which has a molecular weight less than 20,000). A mixture of 10 parts by weight of a 300,000 VAMW methacrylate terpolymer, wherein two or more of the alkyl groups are in the  $C_{12}$ – $C_{24}$  range and 1 to 4 parts by weight of a 150,000 VAMW polyisobutylene is also useful as a polymeric additive. Also useful is the dispersant type polymethacrylate terpolymer sold as “Acryloid 966S.” A useful acrylic is “Acryloid 162.”

In the twister ring oil and the needle oil the preferred lubricant base stocks are paraffinic lubes having a viscosity in the range of 70 to 300 SUS at 100° F. Such paraffinic lubes are generally solvent dewaxed and solvent refined and have an ASTM viscosity index in the range of 90–105. The preferred paraffinic lube is hydrorefined or hydrocracked or hydroisomerized. Blends of such paraffinic lubes with naphthenic lubes of about the same viscosity range or, more preferred, with hydrorefined naphthenic lubes can also be used. In general the naphthenic component is preferred in the spindle oils, and a high V.I. paraffinic oil is generally preferred in the twister ring oils.

Another preferred additive is an antiwear agent which will not harm textiles, most preferred is 0.3–10 percent of a chlorinated paraffin; however, 0.2–2 percent of tricresyl phosphate or a combination of these two additives can also be used. Optionally, the lubricant can also contain an antifoam (such as 0.5–20 ppm of “active” silicone antifoam). Generally such an antifoam is used as a dilute solution or suspension containing about 1 percent of the active ingredient.

To further safeguard against discoloration, an antioxidant such as 0.05–1 percent ditertiarybutyl paracresol (i.e., DBPC) can also be included.

In general, any additive used in the lubricants of the present invention should have an acid number less than 25 and the total, compounded lubricant should have an

acid number less than 0.5 and a "neutral" pH (preferably, 6.2-7.7, more preferred 6.8-7.2).

The base oil can consist essentially of a single narrow-boiling range, hydrorefined lube of the desired SUS viscosity or the desired viscosity base oil can be obtained from a wider boiling range blend of two or more narrow-boiling range oils (e.g., a 150 SUS base oil can be obtained directly by hydrogenation of a 160 SUS distillate or can be obtained by hydrogenating a blend of 100 and 2500 SUS distillate or, more preferred, the 150 SUS base oil can be obtained by blending a 100 SUS hydrorefined distillate with a 2500 SUS hydrorefined distillate, or with a "bright stock"). Processes for obtaining such distillates and such hydrogenated oils are disclosed, for example, in the previously referred to applications and patents. Such oils are available under the trade names "Sunthene," "Sundex," "Sunpar," "Sunpar H," etc.

Although the base oil can have a viscosity at 100° F. in the range of 60-600 SUS, the preferred viscosity range is 70-300 SUS and, more preferred, 100-200 SUS.

To improve such properties as color, flash point and oxidation stability, the base oil can also contain (in addition to a major amount of a hydrorefined, hydrocracked or hydroisomerized oil) in the range of 0.5-25 percent of solvent refined paraffinic oil, naphthenic distillate, naphthenic-acid free naphthenic distillate or polyolefin oils.

The base oils preferably contain less than 80 ppm of basic nitrogen, more preferably less than 30 ppm (in some cases 0-10 ppm), and can be those described in the previously cited U.S. Pat. application Ser. Nos. 622,398; 636,493; 812,516, and more preferably, are blends of two or more hydrorefined or hydrocracked oils (e.g., a 150 SUS blend of a 100 SUS at 100° F. hydrorefined naphthenic oil and a 2500 SUS at 100° F. hydrorefined naphthenic oil) or a blend of hydrorefined naphthenic oil and hydrocracked paraffinic oil.

In certain of the lubricants of the present invention, the base oil can have an aniline point in the range of 140-180, and in some cases the preferred aniline point of the base oil is in the range of 150°-170° F. to enable maintenance of good rubber seal condition, (or in the range of 195°-215° F. where silicone rubbers are used). Preferably, in such lubricants the oil or blend of oils is selected so as to obtain a base with the desired viscosity, an ultraviolet absorptivity at 335 millimicrons (i.e., 335 UVA) in the range of 0.01-0.4, more preferred 0.02-0.2, and an aniline point in the desired range. The hydrorefined naphthenic oil component of such a base stock will generally have an aniline point in the range of 140-190, more preferred 150°-170° F., and the hydrorefined or hydrocracked or hydroisomerized paraffinic oils will be above 190° F. (e.g., 200°-260° F.).

The phrases "severe hydrorefining" or "hydrogenation" refer to processes conducted in the presence of a hydrogenation catalyst at from about 500°-775° F., with hydrogen of 50-100 percent purity, and from 800-3,000 p.s.i. of hydrogen at the reactor inlet (at total pressures from 800-6,000 p.s.i.g.) at a fresh feed liquid hourly space velocity (LHSV) of from 0.1-8.0 (usually below 2.0), preferably conducted either in vapor phase or trickle phase. Such hydrogenation or severe hydrorefining is to be distinguished from hydrocracking in that the production of "overhead" (i.e., hydrocarbons boiling below 485° F.) is less than 25 per-

cent by volume per pass through the reactor (and, typically, less than 10 percent). Product recycle, for example, as in U. S. Pat. No. 2,900,433, can be used to increase severity. Recycle liquid hourly space velocity can vary from 0 to 20; however, it is preferred to operate at total liquid through-puts that obtain at greater than 25 percent of flooding velocity and more preferably at from 40-98 percent of flooding velocity.

Preferably, the temperature is below that at which substantial cracking occurs, that is, no more than 20 weight percent (preferably less than 10 percent) of the feed stock is converted to material boiling below 300° F. in a single pass through the reactor. Although the maximum hydrogenation temperature which will not produce substantial cracking is somewhat dependent upon the space velocity, the type of catalyst and the pressure, generally it is below 750° F. but can be as high as 785° F. To allow a margin of safety, it is preferred to operate below 700° F. (except when it is desired to obtain a hydrogenated oil containing more gel aromatics than are in the charge). At total pressures below about 2,000 p.s.i. the preferred temperature is below about 660° F., since above that temperature the degradation of oil viscosity can become large.

Typical of such severe hydrorefining methods, when conducted within the aforementioned processing conditions, are those of U.S. Pat. Nos. 2,968,614; 3,993,855; 3,012,963; 3,114,701; 3,144,404; 3,278,420 and 3,642 and those of the previously referred to copending U.S. Pat. applications, Ser. No. 622,398; 652,026; 636,493; 730,999 and 812,516. The terms "severely hydrorefined oil" or "hydrogenated oil" include the products, within the lubricating oil boiling range, of such severe hydrorefining or hydrogenation. One characteristic of a severely hydrorefined or hydrogenated oil is that the ratio of monocyclic aromatics to polycyclic aromatics is significantly greater than in hydrotreated oils or conventional distillate oils.

Where the desired hydrorefined oil is to be of the naphthenic class, a preferred charge to the hydrogenation reactor can be obtained by vacuum distillation of naphthenic or "mildly aromatic" crude oils (as in U. S. Pat. No. 3,184,396), especially those crude oils wherein the 1,500-3,000 SUS (at 100° F) distillate fractions have viscosity-gravity constants from 0.84 to 0.92. Preferably, such a charge stock should be substantially free of naphthenic acids prior to the hydrorefining (thus, in some cases distillation in the presence of caustic is advantageous). Usually materials boiling below about 600° F. (including residual H<sub>2</sub>S, NH<sub>3</sub>, etc.) are removed from the hydrorefined oils, as by atmospheric distillation (and the viscosity can also be adjusted by choice of distillation end point) prior to clay contacting (if the oils are to be clay finished). Such naphthenic distillate oils are available commercially under the trade name "Circosol."

The viscosity of the base oil, or of the final hydrorefined oil, can be adjusted by the addition of other oils of higher or lower viscosity and which are within the lube oil boiling range. Where desired, the basic nitrogen content can be lowered by contacting the charge or hydrogenated oil or the blend of hydrogenated oils with sufficient acidic adsorbent or mineral acid to reduce the basic nitrogen content of the oil, as to below 10 p.p.m.

By naphthenic distillate, we refer to a distillate fraction (or a mildly acid treated distillate fraction, or a solvent raffinate fraction or an acid-treated raffinate) usually from vacuum distillation, of a crude which is classified as naphthenic (including "relatively naphthenic") by the viscosity-gravity constant (VGC) classification method, (see p. 79-80, *Plasticizer Technology*, Vol. 1, p. 5 Bruins, Reinhold Publishing Corp., N. Y., 1965). Preferably, such crudes are "Grade A" (wax-free), typically Gulf Coastal, and include, for example, Refugio, Mirando, and Black Bayou. The lower VGC oils can be obtained from mid-continental crudes; and can be dewaxed if desired (as by extraction or isomerization). Such naphthenic fractions will have a VGC in the range of 0.820 to 0.899 and, typically, a viscosity in the range of 150-12,000 SUS at 100° F. (for example, 500-6,000). In some cases the crude (and distillate) can have a VGC as high as 0.94 (such crudes are characterized as "mildly aromatic," or higher (e.g., 0.96+). Deep furfural extraction (e.g., about 50 percent yield) of a high VGC Grade A crude can be used to produce a wax-free, lower VGC fraction (e.g., 0.83 VGC).

Typically, paraffinic oils are those having a viscosity-gravity constant (VGC) in the range of 0.790 to 0.819 (preferably above 0.799). Typical of solvent refined paraffinic lubes are those available commercially under the trade name "Sunpar." Typical hydrorefined paraffinic lubes are those available commercially under the trade name "Sunpar," H series (e.g., "Sunpar 110H").

Naphthenic oils have a VGC in the range of 0.820 to 0.899 and the preferred hydrorefined naphthenic oils have a VGC in the range of 0.850 to 0.899. Hydrorefined, relatively aromatic oils, having a VGC in the range of 0.900 to 0.920, can sometimes be used as a whole or partial substitute for the hydrorefined naphthenic lube. Aromatic oils (including hydrorefined or hydroaromatized oils) having a VGC in the range of 0.921 to 1.050 and greater, can be useful in minor proportions (e.g., 1-20 percent) for adjusting the aniline point of the base oil, particularly when the base oil contains a high proportion (e.g., 20 percent) of a high VI hydrocracked paraffinic oil.

As an additional component to the hydrorefined naphthenic oils previously described, the lubricant can contain a hydrogenated polyolefin oil (e.g., see U.S. Pat. Ser. No. 220,362 of Stearns et al.; U.S. Pat. Ser. No. 52,301 of Driscoll et al.; Canadian U.S. Pat. No. 842,290; and U.S. Pat. No. 3,598,740) or a high viscosity index, hydrocracked oil or a mixture of such components, (such oils can be dewaxed, if desired). In such blends an aromatic oil or concentrate rich in aromatic hydrocarbons (e.g., cycle oil) may have to be added to obtain the proper aniline point for seal swelling.

The preferred polyolefin oils are polymers or copolymers of C<sub>2</sub>-C<sub>8</sub> olefin which have a pour point no greater than -35° F., and preferably below -50° F. The hydrogenation can be from 50 to 100 percent of saturation, and, preferably, is to a bromine number no greater than 10, more preferably less than 5. Preferred polyolefins include ethylene-propylene copolymer, polypropylene, polybutene (especially polyisobutylene), and poly(1-octene).

The high VI hydrocracked paraffinic oil component can be obtained by hydrocracking a high viscosity distillate or dewaxed distillate from a paraffinic crude (such as Lago-medio) and typically has a VI in the

range of 90-105 and contains in the range of 3-30 percent of aromatics by clay-gel analysis. The hydrocracked lubes are preferably stabilized (against UV light degradation and sludging) by extraction of the hydrocracked oil with aromatic selective solvents, such as furfural or phenol or by hydrorefining to reduce the 260 UVA at least 30 percent (preferably 40 percent). For examples of such oils see U.S. Pat. Ser. No. 178,193 of Bryer et al. and U. S. Pat. No. 3,579,435 to Olenzak et al.

The preferred "stabilized" hydrocracked oils (whether extracted or hydrorefined) are characterized by having a D-943 test life (to an increase in acid number of 2.0) which is at least 20 percent lower than the D-943 life of an unstabilized hydrocracked oil but which is at least 20 percent greater than the D-943 life (with the usual amount of inhibitor, e.g., 0.5 percent DBPC) of an unhydrocracked solvent refined paraffinic lube of the same viscosity. Also useful is an "isomerized" paraffinic oil, as in U. S. Pat. No. 3,658,689.

## ILLUSTRATIVE EXAMPLES

### EXAMPLE 1

A twister ring oil was made by blending the following:

|                                                     | Wt. % |
|-----------------------------------------------------|-------|
| Hydrorefined naphthenic oil<br>(100 SUS at 100°F.)  | 72.3  |
| Hydrorefined naphthenic oil<br>(2400 SUS at 100°F.) | 21.5  |
| NaSul. BSN (Rust Inhibitor)                         | 0.2   |
| TE 1618 (Friction modifier)                         | 5.0   |
| Oletac 100 ("tacky" polypropylene)                  | 1.0   |

The blend had a viscosity of 207.0 SUS at 100° F. and 46.0 SUS at 210° F., an ASTM-VI of 85, and API gravity of 22.9 and an IFT (interfacial tension) of 11.0 dynes/cm. The IFT of the base oil was in the range of 35-40.

When the TE 1618 is replaced by 1.5 wt. percent butyl acetate, the IFT is about 8.

### EXAMPLE 2

A twister ring oil (having a viscosity at 100° F. of about 200 SUS) was made by blending the following:

| Component                                             | Vol. % |
|-------------------------------------------------------|--------|
| Solvent Refined Paraffinic Oil<br>(110 SUS at 100°F.) | 65.0   |
| Solvent Refined Paraffinic Oil<br>(510 SUS at 100°F.) | 32.3   |
| Antioxidant (DBPC)                                    | 0.6    |
| *Acrylic Polymer additive                             | 1.6    |
| **Ortholeum RP-2<br>(friction reducer and antirust)   | 0.5    |
| Silicone Antifoam (1% soln.)                          | 0.02   |

\* The acrylic polymer additive is a viscosity-index improver and is commercially available as "Acryloid 772" from Rohm and Haas Co. and has a viscosity at 210° F. in the range of 4300-4800 SUS.

\*\* Ortholeum RP-2 is a commercial additive package marketed by DuPont Company and contains 80 percent alkylamino fatty acid phosphates and 20 percent kerosine. The SUS viscosity at 210° F. is in the range of 65-75, the pH 6.5-7.5 and the wt. percent phosphorus is in the range of 5.7-6.9 percent. This twister ring oil provided low power consumption and was especially useful in automotive tire manufacture with rayon, nylon or polyester cords.

Even better performance can be obtained when hydrocracked paraffinic oil is used instead of the solvent refined paraffinic oil.

Another useful fatty acid phosphate, useful as a friction modifier, is marketed as Ortholeum 162. When Ortholeum 162 is neutralized with an amine (e.g., trimethylamine), it becomes similar to Ortholeum RP-2.

It is important that a twister ring oil have a high viscosity index; therefore, with the usual paraffinic lubes, a viscosity index improving additive is generally necessary. However, the VI improver can be reduced or eliminated if a high VI oil (such as the ethylene-propylene copolymer of U.S. Pat. Ser. No. 220,362) is substituted for the paraffinic lube.

#### EXAMPLE 3

A needle oil was made by blending the following:

|                                                     | Wt. % |
|-----------------------------------------------------|-------|
| Hydrotreated naphthenic oil<br>(100 SUS at 100°F.)  | 89.9  |
| Hydrotreated naphthenic oil<br>(2400 SUS at 100°F.) | 5.0   |
| NaSul BSN                                           | 0.1   |
| TE-1618 (Friction modifier)                         | 5.0   |

The resulting needle oil had a viscosity of 102 SUS at 100° F. and 38.0 SUS at 210° F., an ASTM-VI of 20, an API gravity of 24.1 and an interfacial tension (IFT) of 11.0 dynes/cm (whereas the base oil IFT was in the range of 35–40 dynes/cm.)

The heat stability of this needle oil is greatly improved by replacing the hydrotreated naphthenic oil with a hydrotreated or hydrocracked paraffinic oil (preferable with a pour point of 0 or below) of about the same 100° F. viscosity.

#### EXAMPLE 4

A spindle oil was made by blending the following:

|                                                    | Wt. % |
|----------------------------------------------------|-------|
| Hydrotreated naphthenic oil<br>(100 SUS at 100°F.) | 94.9  |
| NaSul BSN                                          | 0.1   |
| TE-1618 (Friction modifier)                        | 5.0   |

The blend had a viscosity at 100° F. of 95.0 SUS and 37.5 SUS at 210° F., an ASTM-VI of 18, API gravity 24.4 and IFT of 11.0 dynes/cm.

NaSul BSN is a neutral barium sulfonate marketed by R. T. Vanderbilt and Co.

#### EXAMPLE 5

A needle oil was made by blending the following:

|                                                     | Wt. % |
|-----------------------------------------------------|-------|
| Hydrotreated naphthenic oil<br>(100 SUS at 100°F.)  | 84.0  |
| Hydrotreated naphthenic oil<br>(2400 SUS at 100°F.) | 14.1  |
| Butyl acetate (Friction modifier)                   | 1.5   |
| NaSul BSN                                           | 0.4   |
| Silicone antifoam (1% solution)                     | 0.05  |

The needle oil had a viscosity at 100° F. of 132 SUS and 40 SUS at 210° F., a flash point (D92) of 295° F., a pour point (D97) of less than -50° F., an API gravity (D287) of 23.3, a total acid No. (ASTM D664) of 0.16, an IFT (ASTM D971) of 7.8 dynes/cm, a saponification number (D94) of 3.29 and rated 38–39–3 (20) in the ASTM D1401 demulsibility test.

#### EXAMPLE 6

A spindle oil was made by blending the following:

|                                               | Parts by Wt. |
|-----------------------------------------------|--------------|
| Solvent refined paraffinic oil<br>(Sunvis 11) | 98.3         |
| Ultraphos 11 (Friction modifier)              | 1.5          |
| NaSul BSN                                     | 0.2          |
| DBPC (antioxidant)                            | 0.6          |
| Silicone antifoam (1% soln.)                  | 0.05         |

The spindle oil had a viscosity at 100° F. of 107 SUS and 40 SUS at 210° F., ASTM-VI (D567) of 99, flash point of 390° F., 0° F. pour point, API gravity 33.1, IFT of 0.0 dynes/cm, and a surface tension (ASTM D94) of 33.3.

TABLE 1  
PROPERTIES OF IMPROVED NEEDLE OIL

| Test                                                | Method* | Typical        | Preferred Range |
|-----------------------------------------------------|---------|----------------|-----------------|
| Viscosity, SUS/100°F.                               | D2161   | 92.0           | 80–110          |
| Viscosity, SUS/210°F.                               | D2161   | 38.7           | —               |
| Viscosity Index                                     | D2270   | 100            | 90 min          |
| Viscosity, cSt/100°F.                               | D445    | 18.72          | 18.1–20.5       |
| Viscosity, cSt/210°F.                               | D445    | 3.76           | —               |
| Flash, COC, °F.                                     | D92     | 380            | 340 min         |
| Fire, COC, °F.                                      | D92     | 430            | —               |
| Color                                               | D1500   | 0.25           | 0.5 max         |
| Gravity, °API                                       | D287    | 33.5           | 32.5–34.5       |
| Appearance                                          | visual  | clear & bright | —               |
| Total Acid No., mgKOH/g                             | D664    | nil            | —               |
| Saponification No., mgKOH/g                         | D94     | 9.3            | 8.5–10/5        |
| Copper Strip, Class., 3 hrs/212°F.                  | D130    | LA             | 1 max           |
| Aniline Point, °F.                                  | D611    | 207            | —               |
| Sulfated Ash, %                                     | D874    | 0.02           | —               |
| Rusting, Syn. Sea Water                             | D665B   | pass           | Pass            |
| 4-Ball Wear Scar, mm 20 Kg, 1800 RPM, 130°F., 1 hr. |         | 0.40           | —               |
| Barium, %                                           |         | 0.036**        | 0.02–0.06       |
| Phosphorous, %                                      | D1091   | 0.008          | —               |
| DBPC, %                                             | D2668   | 0.6            | 0.1–1.0         |

\*ASTM Test Method Numbers

\*\*Greater or lesser amounts may be present, depending on the amount of Barium-containing additive needed to pass the ASTM D665B rusting test.

TABLE 2  
PROPERTIES OF IMPROVED SPINDLE OIL

| Test                                                | Method* | Typical | Preferred Range |
|-----------------------------------------------------|---------|---------|-----------------|
| Viscosity, SUS/100°F.                               | D2161   | 108     | 90–120          |
| Viscosity, SUS/210°F.                               | D2161   | 38.6    | —               |
| Viscosity Index                                     | D2270   | 20      | 0–80**          |
| Viscosity, cSt/100°F.                               | D445    | 20.4    | 20.5–24.0       |
| Viscosity, cSt/210°F.                               | D445    | 3.73    | —               |
| Flash, COC, °F.                                     | D92     | 330     | 310 min         |
| Fire, COC, °F.                                      | D92     | 360     | —               |
| Color                                               | D1500   | 1.0     | 2.0 max         |
| Gravity, °API                                       | D287    | 23.8    | 23–25           |
| Total Acid No., mgKOH/g                             | D664    | Nil     | —               |
| Saponification No.                                  | D94     | 9.3     | 8.5–10.5        |
| Copper Strip, Class., 3 hrs/212°F.                  | D130    | 1A      | 1 max           |
| Aniline Point, °F.                                  | D611    | 150     | **              |
| Sulfated Ash, %                                     | D874    | 0.20    | 0.18–0.22       |
| Rusting, Syn. Sea Water                             | D665B   | Pass    | —               |
| 4-Ball Wear Scar, mm 20 Kg, 1800 RPM, 130°F., 1 hr. |         | 0.40    | —               |
| Total Sulfur, %                                     | D129    | 0.11    | —               |
| DBPC, %                                             | D2668   | 0.6     | —               |

\*ASTM Test Method Numbers

\*\*Hydrogenated naphthenic or paraffinic lubes or blends of oils of these two types can be used to obtain a desired viscosity index within this range, the aniline point will be determined by the given blend.

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The invention claimed is:

1. A lubricant composition which does not cause pin hole damage to cotton and which is useful as a lubricant for a spindle, a needle or a twister ring, said lubricant comprising an effective amount of a friction reducing additive and a base oil having an SUS viscosity at 100° F in the range of 60–600 and containing a major amount of at least one member selected from the group consisting of hydrorefined naphthenic petroleum oil, hydrorefined paraffinic petroleum oil, hydrocracked paraffinic petroleum oil, hydroisomerized paraffinic petroleum oil, solvent refined paraffinic petroleum oil and hydrogenated polyolefin oil, said additive containing an effective amount of trimethylamine of dilaurylphosphate.

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2. The composition of claim 1 wherein said base oil contains a major amount of a hydrocracked paraffinic petroleum oil having an ASTM viscosity index of at least 95.

3. The composition of claim 2 wherein said hydrocracked paraffinic petroleum oil has been stabilized against ultraviolet light degradation by solvent extraction or by hydrorefining.

4. The composition of claim 1 and which is useful as a twister ring oil, said composition comprising a major amount of a hydrocracked or hydrorefined paraffinic petroleum oil.

\* \* \* \* \*

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,816,346 Dated June 11, 1974

Inventor(s) Walter J. Coppock, James R. Amaroso & John Q. Griffith  
III

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, next to last line, after "trimethylamine" insert  
---salt---

Signed and sealed this 17th day of December 1974.

(SEAL)  
Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents