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3,298,951
STABILIZED POLYBUTENE COMPOSITION
Roman D. Guminski, "The Croft," Banbury Road,
Bloxham, England

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11 Claims. (Cl. 252-52)

This application is a continuation-in-part of my copending application, Serial No. 449,330, filed April 19, 1965, now abandoned, which was a continuation-in-part of my application Serial No. 241,475, filed December 3, 1962, now abandoned.

The present invention is a stabilized lubricant composition, particularly useful with aluminum, copper, magnesium and other light metals susceptible to lubricant staining, which composition comprises (a) a polybutene having an approximate number average molecular weight between about 500 and about 5000; and (b) oil-soluble, ethylenically unsaturated organic compound having a molecular weight below about 300, characterized by the ability to substantially stabilize the viscosity of said composition, when said composition is subjected to heavy loads and shearing forces, said organic compound being present in an amount of not more than 5 weight percent.

The invention relates to polybutene lubricants and in particular to polybutene lubricants which may or do come into contact with aluminum during cold rolling or other cold working process.

It is found that the viscosity of certain high viscosity lubricant compositions, containing substances of the polyolefin type, becomes materially reduced in a relatively short space of time (i.e., within a few hours) when subjected to heavy working conditions under which they are subjected to heavy pressures and shear. It is usual for the manufacturers of rolling mills for hot- or cold-reduction of metals to specify a minimum viscosity for lubricants for use in the roll bearings of such equipment. The particular disadvantage of those polybutenes that have adequate viscosity for use in lubricants for this class of equipment is that their viscosity is dynamically unstable so that it is difficult to predict the actual viscosity of these compositions under the working conditions to which they would be subjected as lubricants. This is a very substantial drawback to the use of such compositions as lubricants in heavy duty applications.

On the other hand, polybutenes have certain advantages for use in lubricants in apparatus performing certain metal working processes on aluminum.

It has been explained in my U.S. Patent No. 2,962,401 that if the surface of aluminum bears a film of previously known rolling lubricants it is subject to severe staining when it is annealed even under the most favourable conditions for carrying out the annealing process. Patent No. 2,962,401 disclosed rolling lubricants which overcome that problem. However, it has been found in practice that, with many rolling mills, the bearing lubricant tends to seep into the rolling lubricant system and contaminate the rolling lubricant.

The conventional roll bearing lubricants are petroleum fractions of a high boiling range of a high viscosity, which depends on the boiling range. These conventional lubricants have the advantage for use in rolling mills that their viscosity is dynamically stable, but in mills for the cold rolling of aluminum they have the disadvantage that they are heavily staining of aluminum, and if such roll bearing lubricants leak into the rolling lubricant to any substantial extent, the advantage arising from the use of the new stain-free or low-staining rolling lubricants described in U.S. Patent No. 2,962,401 is destroyed.

It is known to make rolling lubricants by compounding polybutenes with a light, thermally stable mineral oil, because of the relatively low staining effect of the poly-

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butenes when heated in contact with metal. These rolling lubricants are of relatively low viscosity and contain only about 1-3% polybutenes of a molecular weight of 50,000-60,000.

When a lubricant is compounded from a commercially available polybutene and a light mineral oil to produce a lubricant having a viscosity greater than 400 seconds, Saybolt Universal at 100° F., its viscosity falls away under an application of shearing forces and becomes permanently reduced within a few hours.

An object of the invention is a lubricant for aluminum rolling mill bearings which is substantially non-staining of aluminum sheet and which maintains a substantially constant viscosity in use.

Other objects of the invention will become apparent in the course of the detailed description of the invention.

Broadly, the composition of the invention comprises a polybutene and a viscosity stabilizer; in some cases a light mineral oil may be present to adjust the viscosity of the composition to a desired value. Any of the butene polymers having an approximate number average molecular weight between about 500 and about 5000 may be utilized in the composition. The polybutenes are available commercially from several chemical companies and their preparation need not be described herein. Illustrative polybutenes are:

	Molecular Weight	SSU 100° F.	Viscosity Index	Pour Off Point
Oronite No. 8.....	440	560	87	-30
Oronite No. 16.....	640	5,700	96	-10
Oronite No. 24.....	950	40,000	112	+20
Oronite No. 128.....	2,700	890,000	122	+65

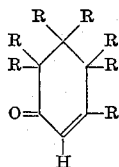
The mineral oil, with which the polybutenes may be compounded, is a light mineral oil, derived from petroleum and having a very low bromine number, so that it contains very few unsaturated groupings which are believed to lead to some staining problems. Gulf Mineral Seal Oil and Mineral Colza Oil have similar characteristics, typically a boiling range of 428-536° F. and a low viscosity of about 37.5 SSU at 100° F. and a bromine number of 0.4. Broadly the light mineral oil has a viscosity between about 30 and 100 SSU at 100° F. and usually about 30-50 SSU at 100° F. and a bromide number not in excess of 0.8.

The viscosity stabilizer(s) present in the composition of the invention are highly reactive organic substances (compounds) of low molecular weight, which by virtue of ethylenically unsaturated bond in their molecules can be easily polymerised. The molecular weight of the viscosity stabilizer is preferably below 250 and should not exceed about 300. Subject to this qualification of maximum molecular weight it appears that all oil-soluble, ethylenically unsaturated carboxylic acids, esters, aldehydes, ketones and alcohols are, to a greater or lesser degree, suitable viscosity stabilizers. Preferably, these should not contain substituents such as halogens or sulphur or nitrogen-containing groups. The especially preferred viscosity stabilizer additive is propylene tetramer in an amount of 1-3%, but other branched chain alkenes (either monomer or lower polymer) are suitable. Among other preferred stabilizers are: styrene, acrylic acid, mesityl oxide, isophorone, acrolein, crotonaldehyde, vinyl acetate, methacrylic acid, methyl methacrylate, methyl acrylate and other alkyl esters of acrylic acid and methacrylic acid, dipentene, butylene tetramer, and butylene pentamer.

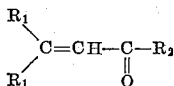
Illustrative of other classes of compounds suitable for

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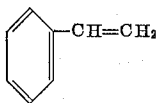
use as viscosity stabilizers are those having the general formula:



in which R is a hydrogen, lower alkyl or acyl group;



in which R₁ and R₂ are a hydrogen, lower alkyl or aryl group; and



in which the nucleus is substituted at one or more positions with alkyl or acyl groups or is unsubstituted.

The mechanism by which the viscosity stabilizer performs its function is not fully understood, but it is postulated that it reacts rapidly with "free radical"-like substances formed temporarily when the polybutene chain is broken under heavy shearing forces which occur in rolling mill bearings. Since the stabilizer tends itself to polymerize and since its reaction with the degraded polybutene tends to form compounds of longer chain lengths, it is important that the percentage of the stabilizer incorporated in a lubricant composition should be regulated, so that there is no excessive increase in viscosity as a result during the service life of the lubricant. It follows that the content of viscosity stabilizer will be regulated by a number of factors, such as the duty to which the lubricant composition is to be subjected and the molecular weight and type of polybutene used in the lubricant composition, and the reactivity of the chosen viscosity stabilizer.

The viscosity stabilizer is preferred to be used in an amount of not more than 5% and more preferably in the amount of 1-3%. (All percentages herein are based on composition.)

The reason for preferring propylene tetramer to styrene as an additive arises out of the somewhat toxic nature of styrene. On the other hand, propylene tetramer has the slight disadvantage that a polybutene lubricant composition stabilized with it gives rise to slight brown staining when heated in contact with aluminum, although this staining is negligible when compared with that due to conventional roll bearing lubricants.

The staining tendency of a polybutene bearing lubricant stabilized by alkene or lower polyalkene, can be largely suppressed by the use of conventional anti-oxidant additives, such as 0.1% para-tertiary-butyl catechol or para-tertiary-butyl phenol.

Antioxidants, such as Santolube AR and Topanol BHT can be added to prevent the development of acidity in the roll lubricant, as explained in Patent No. 2,962,401, should be free from acidity and hence it is also important that any bearing oil which leaks into it should not be acidic. Polybutenes dissolved in a petroleum fraction tend to develop acidity during service, but this difficulty can be obviated by the addition of a suitable anti-oxidant. The best choice of antioxidant depends on the grade of polybutene, on the type of petroleum fraction and on the viscosity stabilizer used. Topanol BHT and Santolube AR are only two of many antioxidants that could be used.

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Load bearing additives may be included in small amount in the composition. The load bearing additives preferred for use in the composition of the inventions are: saturated fatty alcohols having 9-8 carbon atoms; saturated fatty acids having 5-9 carbon atoms; esters of alkanols or alkanic acids which esters have a boiling point of not more than about the boiling point of stearyl alcohol. The load bearing additives must not leave any heavy residues on the metal during heat treatment after the rolling or other cold working operations.

Illustrative of the above classes of load bearing additives are: decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, and stearyl alcohol; valeric acid, caproic acid, caprylic acid, and pelargonic acid; propyl acetate, decyl acetate, isoamyl valerate and ethyl n-heptylate, ethyl pelargonate, butyl laurate and butyl stearate. Lauryl alcohol, cetyl alcohol and stearyl alcohol are preferred additives.

The amount of load bearing additives present, if any, will be dependent on the ultimate conditions the composition must withstand and somewhat on the other components of the particular composition.

ROLL BEARING LUBRICANT

One aspect of the present invention is concerned with polybutene-containing lubricant compositions having a viscosity in the range of about 400-500 seconds Saybolt Universal at 100° F. which are especially suited for use in aluminum roll bearing lubrication where leakage would result in contact of the aluminum article with the roll lubricant, as this embodiment of the invention is non-staining to aluminum.

This embodiment consists essentially of polybutene, viscosity stabilizers and light mineral oil to adjust the viscosity of the composition to the desired point. Desirably the approximate number average molecular weight of the polybutene is between about 800 and about 5000 and preferably is between about 950 and about 2700. The light mineral oil and viscosity stabilizers are as defined earlier.

The amount of viscosity stabilizers present in the embodiment is as set out earlier, namely, not more than 5% of the composition and usually about 1-3%.

It is preferable that the bromine number of this compounded lubricant composition, including the viscosity stabilizer, should not exceed 6 and in any event must not exceed 25.

The following are examples of lubricant compositions which possess a high original viscosity, retain it after the application of shearing forces, and are free from or have only a small tendency to form brown stains on aluminum strip during annealing.

Composition 1¹

	Percent
Mineral Colza oil	24
Polybutene 24	75
Styrene	1

¹ Original viscosity 1850 seconds Saybolt Universal at 100° F., after the application of shearing forces for 15 hours, 2180 seconds Saybolt Universal at 100° F.

Composition 2²

	Percent
Mineral Colza oil	48
Polybutene 128	50
Styrene	2

² Original viscosity 1300 seconds Saybolt Universal at 100° F., after the application of shearing forces for 15 hours, 1550 seconds Saybolt Universal at 100° F.

Composition 3³

	Percent
Mineral Colza oil	48
Polybutene 128	50
Acrylic acid	2

³ Original viscosity 1300 seconds Saybolt Universal at 100° F., after the application of shearing forces for 15 hours, 1550 seconds Saybolt Universal at 100° F.

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Composition 4⁴

	Percent
Mineral Colza oil	46
Polybutene 128	50
Styrene	2
Lauryl alcohol	2

⁴ Original viscosity 1400 seconds Saybolt Universal at 100° F., after the application of shearing forces for 15 hours, 2050 seconds Saybolt Universal at 100° F.

Composition 5⁵

	Percent
Polybutene 128	52
Propylene tetramer	2
Stearyl alcohol	0.5
Cetyl alcohol	0.5
Santolube AR and Topanol BHT:	
Anti-oxidants	0.1
Gulf Mineral Seal oil, the balance.	

⁵ Original viscosity 1450 seconds Saybolt Universal at 100° F., after the application of shearing forces for 15 hours, 1700 seconds Saybolt Universal at 100° F.

It was found that by varying the polybutene content of Composition 5 the viscosity could be increased from 200 seconds SSU at 100° F. with 30% polybutene to 1140 seconds SSU at 100° F. with 50% polybutene and up to 3200 seconds SSU at 100° F. with 60% polybutene, the polybutene being polybutene 128 in each case. For this purpose a polybutene 128 content of 45–60% is preferred. It will be seen that the function of the light petroleum fraction is to reduce the viscosity of the polybutene to a desired value, at which it is stabilized by the viscosity stabilizer additive.

It will be observed that in all the above cases the viscosity of the stabilized roll bearing lubricants was actually increased after a number of hours service by virtue of the very small quantity of reactive unsaturated viscosity stabilizing additive present. The amount of styrene required to stabilize the lower molecular weight polybutene in Composition 1 was less than that required for the higher molecular weight polybutene of Composition 2.

The purpose of the addition of the long chain saturated fatty alcohols in Compositions 4 and 5 is to act as non-staining load bearing additives when the mill rolls are turning slowly. Under slow speed conditions the hydrodynamic lubrication due to polybutene is only partially developed and it is therefore found desirable to add load bearing additives to support the load under these conditions.

In general the bearing lubricant will include up to about 5% of load bearing additive and, more commonly between about 0.5–2% of the additive.

Example I

When a bearing lubricating composition of this type was tested in a foil-bearing apparatus, it was found that the lubricant behaved as a non-Newtonian fluid with a coefficient of friction in which it was designed to operate. The results obtained indicated that the lubricant composition was superior to the Newtonian mineral oils of comparable viscosity which are in standard general use as roll bearing lubricants in rolling mills.

Example II

The stabilizing effects of other unsaturated substances on the viscosity of polybutenes was tested.

The test was carried out in the following way. First, a quantity of high molecular weight polybutenes supplied by Oronite Chemical Company under their designation Oronite No. 128 was heated to about 160 F. and mixed with a light mineral oil such as mineral Colza oil, which has a viscosity of about 37.5 Saybolt Seconds Universal, a boiling range of about 425 to 535° F. and a low bromine number, to give a basic lubricant having a viscosity of about 1500 SSU at 100° F.

Second, some of this basic lubricant was mixed with 2% by weight of the viscosity stabilizer to be tested, the mix-

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ing being carried out by stirring manually at ambient temperature.

Third, the viscosity of a 500 gram sample of the lubricant-stabilizer mixture was measured at 100° F. using a Redwood No. 1 viscometer supplied by Messrs. Gallenkamp Limited, London. This measurement of the viscosity of the freshly made and substantially non-sheared sample of the lubricant-stabilizer mixture was made with an accuracy of 5 Saybolt Seconds Universal.

Fourth, the sample of the stabilized lubricant on which the viscosity determination had been carried out was placed immediately after that determination in the bowl of a Sunbeam "Mixmaster" food-mixing machine which was equipped for this purpose with 2 contra-rotating 4-bladed paddles (Part Nos. 10-1141 and 10-1142, one of which rotated the bowl. The speed of the paddles was set at 330 revolutions per minute and the sample of the stabilized lubricant was stirred continuously for 24 hours, during which time its temperature rose from its initial value of about 100° F. to about 125° F. On completion of the 24 hour stirring of the sample, its viscosity was measured at 100° F. using the abovementioned Redwood No. 1 viscometer.

The results of this test are set out in Table A.

TABLE A

Compound	Initial Viscosity SSU 100° F.	Final Viscosity SSU at 100° F.
Methyl methacrylate.....	1,150	1,200
Crotonaldehyde.....	1,160	1,205
Dipentene.....	1,157	1,208
Vinyl Acetate Monomer.....	1,100	1,120
Polybutene light polymer (Mixture of butylene tetramer and Pentamer in 1:1 ratio):		
Acrylic acid.....	1,200	1,200
Methyl acrylate.....	1,170	1,168
Iso-phorone.....	1,100	1,108
Mesityl oxide.....	1,150	1,175
Kerosene (control).....	1,130	1,140
	1,160	850

Example III

Using a lubricant with 50% polybutene 128 and other ingredients in the proportions given in Composition 5 excellent protection was given to white metal-steel bearings of a mill for cold-rolling aluminum strip.

Its leakage into the virtually non-staining cold rolling lubricant did not give rise to any staining tendency of the strip, even when the concentration of the bearing lubricant in the rolling lubricant was allowed to rise to the unusually high level of 15%. The lubricant in the rolling lubricant system of an aluminum cold rolling mill is usually discarded before this degree of contamination occurs.

I claim:

1. A stabilized lubricant composition which comprises:

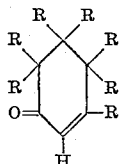
- a major amount of a base fluid selected from the class consisting of (I) a polybutene having an approximate number average molecular weight between about 500 and about 5000 and (II) a blend of I and a light mineral oil of low bromine number; and
- oil-soluble, ethylenically unsaturated organic compound having a molecular weight below about 300, characterized by the ability to substantially stabilize the viscosity of said composition, when said composition is subjected to heavy loads and shearing forces, said organic compound being selected from the class consisting of hydrocarbon carboxylic acids, hydrocarbon esters, hydrocarbon aldehydes, hydrocarbon ketones, hydrocarbon alcohols, aliphatic substituted aromatic hydrocarbons and branched chain alkenes, said organic compound being present in an amount of not more than 5 weight percent.

2. The lubricant composition of claim 1 wherein the viscosity stabilizer compound is selected from the class consisting of acrolein, crotonaldehyde, dipentene, butylene tetramer, butylene pentamer, propylene tetramer, styrene, acrylic acid, methacrylic acid, lower alkyl esters of acrylic

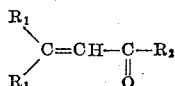
acid and methacrylic acid, vinyl acetate, mesityl oxide, and iso-phorone.

3. A lubricant composition which comprises

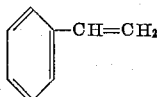
- (a) a major amount of a base fluid selected from the class consisting of (I) a polybutene having an approximate number molecular weight between about 500 and 5000 and (II) a blend of I and a light mineral oil of low bromine number; and
- (b) a viscosity stabilizer in an amount forming less than 5% of the composition, but sufficient to prevent substantial decrease of viscosity of the composition under shearing loads, without excessive increase of viscosity on ageing, said viscosity stabilizer, being an oil-soluble, ethylenically unsaturated compound having a molecular weight below about 300 and being selected from the class consisting of
- an ethylenically unsaturated aliphatic hydrocarbon carboxylic acid,
 - an aliphatic hydrocarbon ester of ethylenically unsaturated aliphatic hydrocarbon carboxylic acid,
 - an ethylenically unsaturated aliphatic hydrocarbon aldehyde,
 - an ethylenically unsaturated aliphatic hydrocarbon ketone,
 - an ethylenically unsaturated aliphatic hydrocarbon alcohol,
 - a branched chain alkene,
 - a substance having the general formula



in which R is selected from the class consisting of hydrogen, lower alkyl and acyl group, a substance having the general formula



in which R₁ and R₂ are selected from the class consisting of hydrogen, lower alkyl and aryl groups and at least one of R₁ and R₂ being aryl a substance having the general formula



in which the nucleus is unsubstituted or substituted in at least one position with a group selected from the class consisting of alkyl and acyl.

4. A high viscosity lubricant composition suitable for use in the bearings of mills for cold working aluminum, which lubricant composition has a bromine number not in excess of 25 and consists essentially of:

- (a) polybutene having an approximate number average molecular weight in the range of about 800 to about 5000;
- (b) light mineral oil of a low bromine number; said polybutene and said oil being blended in proportions to afford a lubricant composition viscosity, Saybolt Seconds Universal to 100° F., within the range of 400 to 5000; and
- (c) oil-soluble, ethylenically unsaturated organic compound having a molecular weight below about 300,

characterized by the ability to substantially stabilize the viscosity of said composition, when said composition is subjected to heavy loads and shearing forces, said organic compound being selected from the class consisting of hydrocarbon carboxylic acids, hydrocarbon esters, hydrocarbon aldehydes, hydrocarbon ketones, hydrocarbon alcohols, aliphatic substituted aromatic hydrocarbons and branched chain alkenes, said organic compound being present in an amount of not more than 5 weight percent.

5. The lubricant composition of claim 4 wherein said polybutene has an average molecular weight in the range of about 950 to 2700.

6. The lubricant composition of claim 4 further including not more than about 5% of saturated fatty alcohol having 9-18 carbon atoms as a load bearing constituent.

7. The lubricant composition of claim 4 wherein the viscosity stabilizer substance is selected from the class consisting of acrolein, crotonaldehyde, dipentene, butylene tetramer, butylene pentamer, propylene tetramer, styrene, acrylic acid, methacrylic acid, lower alkyl esters of acrylic acid and methacrylic acid, vinyl acetate, mesityl oxide and iso-phorone.

8. A lubricant composition having an original viscosity of about 1850 seconds Saybolt Universal at 100° F. which lubricant consists of:

- a light mineral oil having a bromine number not in excess of 0.8, about 24%;
- a polybutene having an approximate number average molecular weight of 950, about 75%; and
- styrene, about 1%.

9. A lubricant composition having an original viscosity of about 1300 seconds, SSU at 100° F. which lubricant consists of:

- a light mineral oil having a bromine number not in excess of 0.8, about 48%;
- a polybutene having an approximate number average molecular weight of 2750, about 50%; and
- styrene, about 2%.

10. A lubricant composition having an original viscosity of about 1300 seconds, SSU at 100° F., which lubricant consists of:

- a light mineral oil having a bromine number not in excess of 0.8, about 48%;
- a polybutene having an approximate number average molecular weight of approximately 2700, about 50%; and
- acrylic acid, about 2%.

11. A lubricant composition having an original viscosity of about 1450 seconds, SSU at 100° F., which lubricant consists of:

- polybutene having an approximate number average molecular weight of about 2700, about 52%;
- stearyl alcohol, about 0.5%;
- cetyl alcohol, about 0.5%;
- propylene tetramer, about 2%;
- anti-oxidant about 0.1%; and
- light mineral oil having a bromine number not in excess of 0.8, the balance.

References Cited by the Examiner

UNITED STATES PATENTS

2,256,603	9/1941	Wright	252-59 X
2,899,390	8/1959	Plemich	252-56
2,962,401	11/1960	Guminski	252-56 X

DANIEL E. WYMAN, *Primary Examiner*.

P. P. GARVIN, *Assistant Examiner*.