



US 20130338049A1

(19) **United States**

(12) **Patent Application Publication**
King et al.

(10) **Pub. No.: US 2013/0338049 A1**

(43) **Pub. Date: Dec. 19, 2013**

(54) **NOVEL LIGNIN BASED COMPOSITION**

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(21) Appl. No.: **13/095,821**

(22) Filed: **Apr. 27, 2011**

Publication Classification

(51) **Int. Cl.**
C10M 159/02 (2006.01)

(52) **U.S. Cl.**
CPC **C10M 159/02** (2013.01)
USPC **508/181**; 508/220; 508/216

(57) **ABSTRACT**

A novel and environmentally friendly lignin based lubricant composition in the form of oil, gel, grease, paste, solid, or water/glycol emulsion comprising lignin and/or its derivatives with a dosage ranging from 0.01 to 95 wt %, preferably 0.1% to 80 wt %, or even more preferably 0.5 to 60 wt % dispersed in at least one or more components selected from 1) base oils, 2) surfactants or coupling agents, 3) lubricant additives, or 4) grease thickeners of soap or non-soap type whereupon the said composition was found to exhibit novel and synergistic performance benefits such as, but not limited to, antioxidancy, extreme pressure, antiwear, lubricity as well as a rheology modifying characteristics, e.g. thickening effect, for a broad range of lubricant, grease, or oil field drilling applications.

NOVEL LIGNIN BASED COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation in-part of Ser. No. 61/328,873, Filed on Apr. 28, 2010 and titled "Lignin Derivatives for lubricant and grease applications" and Ser. No. 61/533,227, filed on Sep. 11, 2011, titled "Lignin based grease improvements".

BACKGROUND

[0002] Lignin is the main structural component of the plant and is nature's most abundant organic polymers with varying content of aromatic/Phenolic/ether functionalities. Lignin is isolated as the by-products in the traditional paper pulping industry as well as from biomass conversion technologies or solvent pulping process and through which lignin is physically modified or chemically derivativized into sulfonates (e.g. Sulfite process), thio-lignin (Kraft process), or sulfur-free lignins (e.g. Soda process). For a comprehensive review on the commercial processes in isolating/modifying lignin, see J. Polymer and the environment, vol. 10, nos. 1-2, April 2002, page 39-48. The use of lignin and its derivatives, collectively called "Lignin Derivatives" hereinafter, has been limited primarily to polymeric systems such as resin/adhesive applications (see U.S. Pat. No. 5,656,733) where lignin is used as fillers/binders to cross link through its phenolic/hydroxy functionalities to provide the structural strength. Other use of lignin has been disclosed in the rubber processing (U.S. Pat. No. 5,196,460), for instance, as tackifier and antioxidants, and as emulsifiers/surfactants (lignin sulfonates: Asphalt emulsion: U.S. Pat. No. 5,683,497, Oil field enhanced oil recovery: U.S. Pat. No. 5,114,599) or cleaning detergents (modified lignin polymers containing anionic, cationic, and/or alkoxy substitution, US 2010/0075878). Lignins are practically insoluble in hydrocarbon oils with generally high softening points or glass transition temperature, e.g. in the range of 100-170° C. (Wood Sci. Technol. 19: 139-149 (1985) that do not allow them to be easily melted and/or blended into lubricant products. It is therefore rather surprising to find that Lignin Derivatives as disclosed in the present invention can be readily incorporated into compositions in the form of oil, gel, grease, paste, or solid under relatively mild or even ambient conditions yielding the products with good uniformity and stability and novel performance characteristics as disclosed hereinafter.

SUMMARY OF THE INVENTION

[0003] The present invention relates to a novel lubricant composition in the form of oil, gel, grease, paste, solid, or water/glycol based emulsion, comprising Lignin Derivatives with a dosage ranging from 0.01 to 95 wt %, preferably 0.1% to 80 wt %, or even more preferably 0.5 to 60 wt % dispersed in base oils, thickener, or additive components with at least one or more components selected from the following categories:

1) Base oil

[0004] 2) Surfactants or coupling agents,

3) Lubricant additives,

4) Grease thickeners of soap or non-soap type, whereupon the Lignin Derivatives were found to function as multifunctional additives exhibiting improved and synergistic performance

such as antioxidancy, extreme pressure, antiwear, lubricity, as well as rheology modifying characteristics, e.g. thickening effect, for a broad range of lubricant, grease, or oil field drilling applications

[0005] One embodiment of the present invention relates to a lubricant composition comprising Lignin Derivatives that is used in the range of 0.01 to 95 wt %, preferably 0.1% to 80%, or even more preferably 0.5% to 60%, wherein the desired dosage range is determined by what is required for the compositions to perform under specific applications.

[0006] Another embodiment of the present invention relates to the chemical and physical natures of the Lignin Derivatives that are employed or sourced, e.g., from one or more of the following processes:

1) Isolation/purification through industrial paper pulping processes, such as, but not limited to, paper pulping process including Sulfite, Kraft, or Soda, or solvent pulping ("organosolve") and the alike,

2) Physical modification of lignin, e.g. milling to reduce particle size, or

3) Chemical modification of Lignin, e.g. Lignin sulfonates

[0007] Another embodiment of the present invention relates to a lubricant composition being in the form of oil, gel, grease, paste, solid, or water/glycol based emulsion wherein the Lignin Derivatives with particle sizes ranging from 0.001 micron (1 nm) to 200 micron are uniformly dispersed within the lubricant media yielding the compositions that are haze free suitable for lubricant applications.

[0008] In yet another embodiment of the present invention relates to the forms (oil, gel, grease, or paste) of the lubricant composition may be defined by the following table according to the worked penetration ranges (e.g. from NLGI grade 000 to NLGI Grade 5, see web link: http://en.wikipedia.org/wiki/NLGI_Grade):

NLGI Grade	Worked penetration after 60 Strokes at 25° C. (0.1 mm)	Appearance	Consistency food analog
000	445-475	Fluid	cooking oil
00	400-430	semi-fluid	Applesauce
0	355-385	very soft	brown mustard
1	310-340	Soft	tomato paste
2	265-295	"normal" grease	peanut butter
3	220-250	Firm	vegetable shortening
4	175-205	very firm	frozen yogurt
5	130-160	Hard	smooth paste
6	85-115	very hard	cheddar cheese

[0009] Another embodiment of the present invention, Lignin based composition can be in the form of solid or paste lubricants where they can be used for wiring drawing or deep drawing applications for various metals.

[0010] In yet another embodiment of the present invention, Lignin Derivatives may be micronized so it may further enhance the emulsion stability, e.g. through air/jet milling or through the use of supercritical fluids, e.g. the RESS process (Rapid Expansion of Supercritical Solutions), the SAS method (Supercritical Anti-Solvent), or the PGSS method (Particles from Gas Saturated Solutions), or any other methods that are intended to reduce and particle sizes of Lignin Derivatives.

[0011] Another embodiment of the present disclosure relates to the base oil, thickener, or additive used in the lubri-

cant composition is in the range of 5 to 99.99%, preferably from 20 to 99.9 wt %, or even more preferably from 40 to 99.5 wt %:

- 1) Surfactants or coupling agents,
- 2) Lubricant additives,
- 3) Grease thickeners of soap or non-soap type

[0012] Furthermore, these base oils, thickener, and additives are chosen in such a combination so that they provide the polarity and the dispersancy necessary to enhance the dispersion stability of Lignin Derivatives and to provide additive functions that may be required for the intended applications. Base oils that can be used may be synthetics such as PAO, alkyl aromatics, or esters, or mineral oils of Group I/II/III types. Thickeners may include soap thickener e.g. Li, Ca, or Al types, or non-soap thickener such as, but not limited to, Silica or PU types. Additives include those such as surfactants, coupling components such as, but not limited to, alcohols, phenols, glycols, or the alike. Lubricant additives such as, but not limited to, Antioxidants, EP/AW additives, or pour points depressants may also be used.

[0013] In accordance with one aspect of the present invention, the lubrication composition formulated as described above provides a stable dispersed system in the form of oil, gel, grease, paste, or solid, whereupon the Lignin Derivatives function as a multifunctional additive exhibiting significantly improved and synergistic performance such as antioxidancy, extreme pressure, antiwear, or lubricity properties that are of great values as heavy duty and environmentally friendly lubricants or greases to replace those formulated with traditional EP/AW additives such as Molybdenum disulfide, graphite, Molybdenum additives such as MOLYVAN A or L of R. T. Vanderbilt, or other S/P additives.

[0014] In yet another embodiment, according to the disclosures of the present invention, the Lignin Derivatives was shown surprisingly as a highly effective rheology control agent to control structural and/or viscosity enhancements/adjustments to the lubricant composition as disclosed in the examples of the present invention, which are particularly useful for grease and metal working applications as well as for oil field drilling fluid application, for instance, to prevent fluid loss or to enhance mud stability/integrity.

[0015] While the present invention has been described with reference to one or more specific embodiments, the description is intended to be illustrative of the invention as a whole and is not to be construed as limiting the invention to the embodiments shown. It is appreciated that various modifications may occur to those skilled in the art that, while not specifically shown herein, are nevertheless within the true spirit and scope of the invention.

BRIEF DESCRIPTION OF THE DRAWING

[0016] FIG. 1 shows the unique and novel thickening/dosage effect of Star-shape glycols measured by the Slurry viscosity, in comparison with other glycol such as PEG400 and with the use of additive package.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Various preferred definitions/features and embodiments will be described below for illustrative purpose, and shall be in no way limit the scope of the present invention

[0018] As used herein, the term “Lignin Derivatives” includes lignin sulfonates, thio lignin, sulfur-free lignin,

[0019] As used herein, the term “lubricant composition” is used to describe a composition in the form of oil, gel, grease, or paste as may be described by NLGI grade ((e.g. from NLGI grade 000 to NLGI Grade 5, see web link: http://en.wikipedia.org/wiki/NLGI_Grade)

[0020] As used herein, the term “water/glycol based emulsion” relates to the lubricant composition comprises water and/or glycol emulsion. When properly formulated with emulsifiers, co-emulsifier, surfactants and coupling agents, and hydroxy containing components, Lignin Derivatives can be made into a stable emulsion concentrate that made be further diluted with water or glycol wherein the emulsion may be useful for metal working or for oil field applications.

[0021] As used herein, the term “base oil” includes base oils with low aniline points e.g., alkyl benzene, e.g. dialkylbenzene, or heavy alkylbenzene available from the bottom of LAB and BAB process, alkyl naphthalene, dialkyl phenyl ethers, and the alike, or base oils with oxygen or polar substituents, e.g. polyalkylene glycols such as ethylene oxide or propylene oxide block or copolymers, or esters such as polyol or aromatic esters, or with additional hydroxy functionalities such as castor oils and its derivatives, or dioleate, or sorbitan oleates and the alike,

[0022] As used herein, the term “surfactants or coupling agents” describes the components that will enhance the stability of the lubricant composition that is either in the form of oils, gels, greases, or water/glycol based emulsion. Examples of surfactants or coupling agents include polyalkylene glycol ethers or esters, fatty alkanol ether, ester, or amide, or glycerol esters such as glycerol mono or the combination of the above.

[0023] As used herein, the term of “lubricant additives” means additives that can be either inorganic or organic in nature, and is used to provide the necessary and additional functionalities and to improve the overall performance such as rust prevention, antioxidancy, lubricity, antiwear, or extreme pressure properties or to impart certain physical characteristics to the said lubricant composition such as low temperature properties desirable for low temperature applications.

[0024] As used herein, the term of “grease thickener of soap or non-soap types”, collectively called “Thickeners”, relates to the thickeners used in making metal (Li, Ca, or Al) soap or complex greases, or non-soap greases, e.g. clay, silica, polyurea, or other novel types.

[0025] As used herein, the term of “rheology modifying characteristics” relates to effects of viscosity thickening or thinning over shearing and mechanical stress that may be described as shear thickening (dilatants), thinning (pseudoplastic), or time-dependent viscosity responses (rheoplectic or thixotropic).

[0026] In one embodiment of the present invention, the said lubricant composition was found to exhibit good extreme pressure and antiwear performance while Lignin Derivative was used to replace partially or completely those additives that are traditionally used in grease industry such as S/P chemistry or molybdenum disulfide that are expensive to use and not considered environmentally friendly. Since Lignin Derivatives are originated from the plants and are abundantly available at a lower cost, the disclosures of the present invention are expected to be of great values while formulating cost effective and high performance EAL (environmentally Awareness Lubricant) lubricant products.

[0027] In yet another embodiment of the present invention, Lignin Derivative was found to exhibit novel rheological

modifying characteristics. For instance, it was found surprisingly that in some cases the some of the Lignin Derivatives provides the thickening effect in one type of grease thickener while the same Lignin Derivatives provides the thinning effect in another type of thickener as measured by grease consistency, e.g. penetration, or with rheology properties such as the storage modulus of the grease. Reducing the particle size (e.g. increased surface area) of Lignin Derivatives was found to play a key role to enhance the rheological modifying properties. Furthermore, the effects on thickening or thinning appear to vary based on the specific physical and chemical interactions among Lignin Derivatives, grease thickener, and base oils involved. Not to be bound by the theory that may be behind the rheology behaviors of the lignin-thickener blends, the present disclosure recognizes the full potentials and the utilities of Lignin Derivatives as the rheology control agent for applications in lubricants and in oil fields or others that employ greases gels, or other thicken matters.

EXAMPLES

[0028] Table 1 provides the list of Lignin examples cited in the present invention. After the isolations of these lignins and lignin derivatives, they are processed to give a certain and consistent particle sizes specifications ranging from submicron to 100 microns (see Table 1) prior to use.

TABLE 1

Characterization of Lignin examples	
Examples/Lignin Dosa Chemical Composition	Particle size (um)
Lignin Example 1 Lignin composition through soda process	20-40
Lignin Example 2 Lignin sourced from organosolve process	10-20
Lignin Example 3 Lignin composition through soda process, milled	2
Lignin Example 4 Calcium Lignosulfonate	<100

Example 1

The Preparation of Grease from Lignin Examples 1-3

[0029] Lignin Examples 1-3 (1-25% parts by weight) with a particle size of ~0 micron was mixed at ambient temperature with calcium 12-hydroxystearate soap grease (NLGI grade of 2) until homogeneous. The resulting grease samples exhibit higher grease consistency as the dosages increase (for details, see Table 2). Lignin 3 at a reduced particle size of 2 um is able to thicken the grease at a reduced dosage of 4%. The grease with 10% Lignin Example 1 was found to exhibit higher than 300 kg Four-Ball EP weld load as compared to 160 kg of the base grease.

Example 2

The Preparation of Grease from Lignin Example 3

[0030] Lignin Example 1 (20-40 um) and was mixed at 4 wt % at ambient temperature with calcium sulfonate grease (NLGI grade of 2) until homogeneous. The resulting grease sample is a gel, of NLGI grade of 000 or less, with excellent fluidity. Four-Ball weld load was unchanged from the sulfonate base grease.

Example 3

The Preparation of Stable Water Based Emulsion from Lignin 4

[0031] Lignin Example 4 with particle size of <100 microns was charged to a mixture of alkylbenzene oil (10 cSt with aniline point of 60 C), sodium alkylbenzene sulfonate, alkyl phenol ethoxylates, and butyl or methyl cellulose, and heated to 60 C whereupon the mixture thicken and form a stable emulsion concentrate that can be further diluted with water

Example 4

Preparation of Lubricating Solid Lubricants/Paste for Wire Drawing

[0032] Calcium stearates were first prepared by adding calcium oxides or lime to liquefied stearic acid at 190 C Lignin Example 1 (10-20 wt %) was then added with agitation to the cooling molten calcium stearates. The resulting powder mixture with high load carrying capacity is suitable for wire drawing operations. Also, the powder mixture can be suspended in an oil or aqueous medium in paste form and suitable as deep drawing lubricants for various metals.

Example 5

Preparation of Aluminum/Lithium Complex Grease Blends

[0033] Lignin Example 2 (1.5 wt % to 3 wt %) was blended into respective base greases. Tables 3-5 summarize the Oxygen Bomb test and Four-ball data with the blends made from commercial additives.

TABLE 2

thickening effect and EP (Four-ball weld) performance			
Examples/Lignin Dosage	NLGI Grade	Four Ball Weld Load	Dropping point
Base Grease*	0	160 KG	140 C.
3% Lignin Example 2	0		140 C.
10% Lignin Example 2	1		140 C.
25% Lignin Example 2	1		140 C.
10% Lignin Example 1	2	>300 KG	140 C.
4% Lignin Example 1	2		

*Base grease: Ca soap grease

TABLE 3

Synergistic AW/EP performance		
Example	Four-Ball Weld load	Four Ball Wear Scar
Base Grease*	160 KG	0.70
1% Example 2	200 KG	0.65
3% Example 2	315 KG	0.60

*Base grease: Li Soap grease

TABLE 4

Synergistic Antioxidant/AW/EP performance				
Example	Weld load	Wear Scar	Pressure drop* @100 hrs	Pressure drop* @500 hrs
Base Grease**	126 KG	0.85	>50 psi, end of test	N/A
3% Example 2	315 KG	0.60	0 psi	19 psi

*ASTM D942: Oxygen Bomb Test (100 C.)

**Base grease: Al complex grease

TABLE 5

Synergistic Effects with various additives										
	Example									
	A	B	C	D	E	F	G	H	I	J
Al complex base grease	100%	97%	97%	97%	97%	97%	97%	97%	97%	97%
Lignin - Example 2		3%		1.5%		1.5%		1.5%		1.5%
MoS ₂ , Tech fine			3%	1.5%						
Graphite, \$					3%	1.5%				
Desilube 88, %							3%	1.5%		
Sulfurized vegetable oil, %									3%	1.5%
Four-Ball EP*	100	250	160	250	160	200	400	400	400	400
Four-Ball Wear Scar**	0.85	0.6	0.63	0.5						

*ASTM D1596: 1800 rpm, 27 C. for 10 sec

**ASTM D2266: 1200 rpm, 40 kg, 27 C., for one hour

[0034] It should be understood that disclosures of the present invention as illustrated in Tables 1-5 are provided for illustration purpose only and should not be construed as the scope of the present invention. There are many and various kinds of lignin and lignin derivatives available from various industrial sources with a wide range of physical and chemical compositions. Base greases cited in Tables 2-5 can be easily extended to other types of greases such as metal complex grease, clay, silica, and calcium sulfonate greases and alike. Such variations are obvious and can be easily exercised by individuals that are skilled in the arts and thus, covered within the scope of the present invention.

What is claimed is:

1. A novel and environmentally friendly lignin based lubricant composition in the form of oil, gel, grease, paste, solid, or water/glycol based emulsion comprises Lignin Derivatives ranging from 0.01 to 95 wt %, preferably 0.1% to 80 wt %, or even more preferably 0.5 to 60 wt % dispersed in at least one or more components selected from the following categories:

- 1) Base oil
- 2) Surfactants or coupling agents,
- 3) Lubricant additives,
- 4) Grease thickeners of soap or non-soap type, whereupon the Lignin Derivatives were found to function as multifunctional additives exhibiting improved and synergistic performance such as antioxidant, extreme pressure, antiwear, lubricity, as well as rheology modifying characteristics, e.g. thickening effect, for a broad range of lubricant, grease, or oil field drilling applications.

2. The composition of claim 1, where the lubricant composition is in the form of oil, gel, grease, paste, solid, or water/glycol based emulsion

3. The composition of claim 1, wherein the lignin and its derivatives is used at a dosage from 0.01 to 95 wt %, preferably 0.1 to 80 wt %, or even more preferably 0.5 to 60 wt %

4. The composition of claim 1, where in the lignin and its derivatives are chosen from 1) isolation/purification through industrial paper pulping processes and the alike, 2) Physical modification of lignin, e.g. milling to reduce particle size, or 3) Chemical modification of Lignin, e.g. Lignin sulfonates

5. The composition of claim 1, where the lignin and its derivatives has a particle size ranging from 0.01 micron to 200 micron or more preferably from 0.5 micron to 100 micron or even more preferably from 1 micron to 50 micron.

6. The composition of claim 1, where the base oil, thickener, or additive together are used in the range of 5 to 99.99 wt %, preferably from 20 to 99.9 wt %, or even more preferably from 40 to 99.5 wt %,

7. The composition of claim 1, the surfactant or the coupling agent includes, but not limited to polyalkylene glycol ethers or esters, fatty alkanol ether, ester, or amide, or glycerol esters, or the combination of the above

8. The composition of claim 1, the lubricant additives is either organic (ashless) or inorganic (metal containing) type, including, but not limited to, antioxidants, rust preventive, antiwear, lubricity, extreme pressure, or pour point depressant, or defoamant

9. The composition of claim 1, the grease thickener is of soap such as Ca, Li, Al, or Na salts of simple soap, or complex type, or non-soap type such as polyurea, clay, silica, PTFE

10. The composition of claim 1, the water/glycol components includes water, glycols, or ethylene oxide or propylene oxide block of copolymers or carbonates of aliphatic or aromatic type and the alike

11. The composition of claim 1, the lignin and its derivatives is used as a multifunctional additive or a rheology control agent, e.g. grease thickener or co-thickener.

11. The composition of claim 1, the said composition is useful for lubricant and grease applications, and particularly useful for grease, metal working, and environmental sensitive industry requiring heavy metal free formulations

12. The composition of claim 1, the said composition may be used as solid lubricants or pastes for metal forming or drawing operations, e.g. wire drawing, cold forging and the alike

13. The composition of claim 1, the said composition may be used as oil based or a water/glycol based emulsion for applications as drilling fluids or service fluids/chemicals

14. The composition of claim 2, the said lubricant may contain lignin and its derivatives in such a finely dispersed state so it can be made into haze free oil based composition for lubricant applications

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