



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 172 430 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
16.01.2002 Bulletin 2002/03

(21) Application number: **01305635.3**

(22) Date of filing: **28.06.2001**

(51) Int Cl.7: **C10M 173/00**, B29D 30/38,
B29B 15/14, B21C 9/02,
C10M 135/12, C10M 135/28,
C10M 135/18, C10M 159/18,
C10M 135/36, C10M 129/06,
C10M 129/10, C10M 135/14,
C10M 139/00, C10M 137/10,
C10M 129/32, C10M 129/40,
C10M 135/22, C10M 135/26,
C10M 125/10, C10M 125/12,
C10M 125/14, C10M 125/16,
C10M 125/18, C10M 125/20,
C10M 125/22, C10M 125/24,
C10M 125/26, C07C 321/14

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **29.06.2000 JP 2000195648**
29.06.2000 JP 2000196243
29.06.2000 JP 2000196244
29.06.2000 JP 2000196245
11.06.2001 JP 2001175826

(71) Applicant: **Bridgestone Corporation**
Tokyo (JP)

(72) Inventors:
• **Fukushima, Yasuo,**
Bridgestone Corp. Tech. Center
Kodaira City, Tokyo (JP)
• **Kondo, Hajime, Bridgestone Corp. Tech. Center**
Kodaira City, Tokyo (JP)

(74) Representative: **Whalley, Kevin et al**
MARKS & CLERK, 57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) **Lubricant composition for steel filament and rubber-steel filament composite body**

(57) A lubricant composition for a surface treatment
of a steel filament comprises at least one specified com-

pound as a lubricant component and a rubber-steel fil-
ament composite body is prepared by using a steel fil-
ament treated with the lubricant composition.

EP 1 172 430 A2

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates to a lubricant composition used in a drawing treatment of a steel filament constituting a steel cord for the reinforcement of rubber articles, a steel filament treated with such a lubricant composition, and a rubber-steel filament composite body using such a treated steel filament.

2. Description of Related Art

[0002] Heretofore, steel cords have been used as a reinforcing member for rubber articles such as tires for automobiles, hoses, conveyor belts and the like.

In order to adhere such a cord to rubber, a surface of a steel filament constituting the cord is subjected to a brass plating. However, the corrosion resistance, adhesion stability, wet adhesion property, thermoresistance adhesion property and the like are not sufficiently improved only by a simple brass plating.

[0003] In order to solve this problem, there are proposed various methods.

As one of these methods, there is a method of treating a surface of a steel filament with a lubricant composition at a drawing step of the filament. For instance, the surface treatment with a lubricant composition containing a triazine thiol derivative is disclosed in JP-A-5-185136, JP-A-6-341073 and the like. However, the adhesion property to rubber is not yet sufficient even in the thus surface-treated steel filament.

[0004] On the other hand, there is a method of using a rubber composition compounded with a cobalt salt of an organic acid having an adhesion promoting action in rubber as a coating rubber for the steel filament. However, the cobalt salt of the organic acid indicates a high adhesion force just after vulcanization, but has a drawback of degrading rubber properties in heat aging.

SUMMARY OF THE INVENTION

[0005] It is, therefore, an object of the invention to solve the aforementioned problems and to provide a lubricant composition useful in the drawing treatment of the steel filament and a rubber-steel filament composite body using such a treated steel filament.

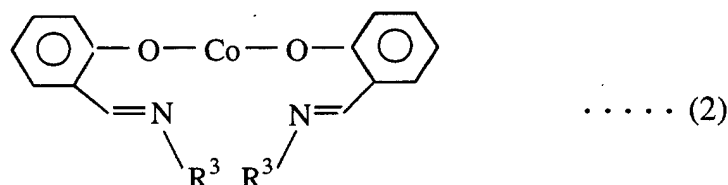
[0006] It is another object of the invention to provide an emulsion type lubricant composition useful for wet drawing having a higher heat resistance.

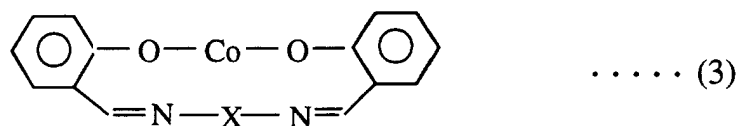
[0007] The inventor has examined various substances to be added to the lubricant composition used in the drawing step of the steel filament and found that steel filaments having an excellent adhesion property to rubber are obtained by adding a compound(s) as mentioned later to the lubricant composition as a lubricant component and treating the steel filament with such a composition and as a result the invention has been accomplished.

[0008] According to a first aspect of the invention, there is the provision of a lubricant composition for steel filament comprising at least one compound selected from the group consisting of sodium 1,6-hexamethylenediamine-dithiosulfate dihydrate, a compound represented by the following formula (1):



(wherein A is an alkylene group having a carbon number of 2-10, and each of R^1 and R^2 is a monovalent organic group containing at least one nitrogen atom), a monoalkali metal salt of triazine thiol, a thiadiazole compound, bivalent or trivalent cobalt salt of an inorganic acid, a Schiff base complex represented by the following formula (2) or (3):

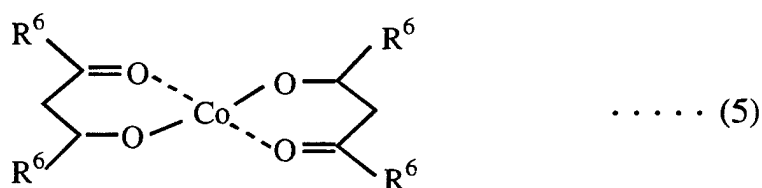




(wherein R^3 is an alkyl group having a carbon number of 1-10 and X is $-R^4-$ or $-R^4\text{-NH-}R^4-$ in which R^4 is an alkylene group having a carbon number of 1 to 10), a cobalt alcoholate represented by the following formula (4):



(wherein R^5 is an alkyl group having a carbon number of 1-20, a phenyl alkyl group or an alkyl phenyl group provided that a carbon number of the alkyl group is 1-10), a cobalt complex represented by the following formula (5):



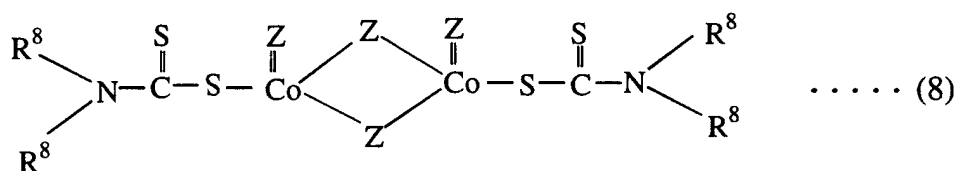
(wherein R^6 is an alkyl group having a carbon number of 1-20 or a -NHR^7 group or a -OR^7 group in which R^7 is an alkyl group having a carbon number of 1-20), a metal borate derivative represented by the following formula (6):



(wherein M is Co or Ni and Y is an acid residue of a monocarboxylic acid having a carbon number of 2-21 or an aromatic group containing monocarboxylic acid having a carbon number of 2-21 provided that Ys are the same or different), a metal aluminate derivative represented by the following formula (7):



(wherein M is Co or Ni and Y is an acid residue of a monocarboxylic acid having a carbon number of 2-21 or an aromatic group containing monocarboxylic acid having a carbon number of 2-21 provided that Ys are the same or different), a cobalt, nickel or iron salt of dithiocarbamate or dithiocarbonate, a cobalt dithiocarbamate represented by the following formula (8):



(wherein R^8 is an alkyl group having a carbon number of 1-20 and Z is an oxygen atom or a sulfur atom provided that Zs are the same or partly different), a cobalt dithiophosphate represented by the following formula (9) or (10):



15



35



45

50

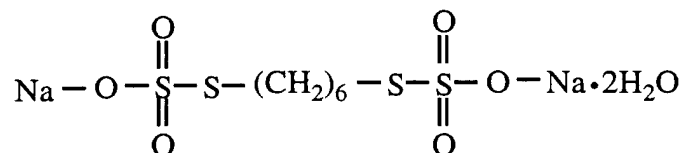
55

4

[0012] The lubricant composition is so-called emulsion-formed by dispersing a high-pressure preventive, an oiling agent, an emulsifying agent, a foam controlling agent and so on in a solvent. These agents used can properly be selected from those usually used in the wet drawing. In addition to these agent, the lubricant composition used in the invention is characterized by compounding at least one of the compounds as defined above as a lubricant component.

The details of these compounds will be described below.

[0013] Sodium 1,6-hexamethylenediamine-dithiosulfate dihydrate (hereinafter abbreviated as HTS) is represented by the following chemical formula:

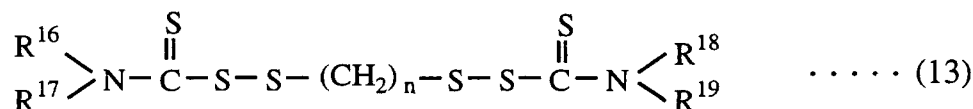


[0014] HTS is radically cleaved by heat to form $\cdot\text{S}-(\text{CH}_2)_6-\text{S}\cdot$, which reacts with a surface of a metal and a double bond in a polymer. Therefore, when the steel filament is drawn in the HTS-containing lubricant composition, a layer of such a lubricant composition is formed on the surface of the steel filament. A preferable amount of HTS compounded is 1-40 parts by weight based on 100 parts by weight of the lubricant composition.

[0015] In the compound of the formula (1), the alkylene group represented by symbol A may be a straight chain, a branched chain or a cyclic structure, and it is preferably a straight chain alkylene group. As an example of the straight chain alkylene group, mention may be made of ethylene group, trimethylene group, tetramethylene group, pentamethylene group, hexamethylene group, heptamethylene group, octamethylene group, decamethylene group and the like. Among them, hexamethylene group is preferable from a viewpoint of the effect.

[0016] In the formula (1), a nitrogen-containing monovalent organic group containing at least one aromatic ring or a nitrogen-containing monovalent organic group having a group of bonding a carbon atom to a dithio group or a $=\text{N}-\text{C}(=\text{S})$ -group is preferable as the organic group represented by symbol R^1 , R^2 . Moreover, R^1 and R^2 may be the same or different, but it is favorable that they are the same from a viewpoint of production easiness or the like.

[0017] As the compound of the formula (1), α,ω -bis(N, N'-dihydrocarbylthiocarbamoyldithio) alkane represented by the following formula (13):



(wherein each of R^{16} to R^{19} is an alkyl group, an aryl group or an aralkyl group, provided that at least one of R^{16} and R^{17} and at least one of R^{18} and R^{19} are an aryl group having a carbon number of 6-20 or an aralkyl group having a carbon number of 7-20, and n is an integer of 2 to 10).

[0018] The alkyl group in the formula (13) is favorable to have a carbon number of 1-20 and includes methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, various pentyl groups, various hexyl groups, various octyl groups, various decyl groups, various dodecyl groups, various tetradecyl groups, various hexadecyl groups, various octadecyl groups, cyclopentyl group, cyclohexyl group, cyclooctyl group and so on.

[0019] The aryl group in the formula (13) is favorable to have a carbon number of 6-20 and may have a proper substituent such as lower alkyl group or the like.

As the aryl group, mention may be made of phenyl group, tolyl group, xylyl group, naphthyl group, methylnaphthyl group and so on.

[0020] The aralkyl group in the formula (13) is favorable to have a carbon number of 7-20 and may have a proper substituent such as lower alkyl group or the like.

As the aralkyl group, mention may be made of benzyl group, methylbenzyl group, dimethylbenzyl group, phenetyl group, methylphenetyl group, dimethylphenetyl group, naphthylmethyl group, (methylnaphthyl)methyl group, (dimethylnaphthyl)methyl group, naphthylethyl group, (methylnaphthyl)ethyl group, (dimethylnaphthyl)ethyl group and so on.

[0021] In the formula (13), it is favorable that all of R^{16} to R^{19} are the above aryl group or aralkyl group. Particularly, they are preferable to be benzyl group from a viewpoint of prevention of heat aging, production easiness and the like. As an example of such compounds, there are 1,2-bis(N, N'-dibenzylthiocarbamoyldithio)ethane, 1,3-bis(N, N'-dibenzylthiocarbamoyldithio)propane, 1,4-bis(N, N'-dibenzylthiocarbamoyldithio)butane, 1,5-bis(N, N'-dibenzylthiocarbamoyldithio)pentane, 1,6-bis(N, N'-dibenzylthiocarbamoyldithio)hexane, 1,7-bis(N, N'-dibenzylthiocarbamoyldithio)

heptane, 1,8-bis(N, N'-dibenzylthiocarbamoyldithio)octane, 1,9-bis(N, N'-dibenzylthiocarbamoyldithio)nonane, 1,10-bis(N, N'-dibenzylthiocarbamoyldithio)decane and so on. Among them, 1,6-bis(N, N'-dibenzylthiocarbamoyldithio)hexane (hereinafter abbreviated as KA9188) is preferable from a viewpoint of the effect.

[0022] The compound of the formula (1) causes the cutting of crosslink for the rubber composition on the surface of the steel filament at a high temperature but also efficiently produces monosulfide crosslink having a higher heat-resistant stability as compared with polysulfide crosslink. A preferable amount of the compound of the formula (1) compounded is 1-40 parts by weight based on 100 parts by weight of the lubricant composition.

[0023] The monoalkali metal salt of triazine thiol is represented by the following formula (14):



(wherein M is an alkali metal selected from lithium, sodium and potassium) and reacts with a surface of a metal and a double bond of a polymer to adhere them to each other.

[0024] On the contrary, a di- or a tri-alkali metal salt of triazine thiol is high in the hygroscopicity (or deliquescence) to chemicals and degrades the adhesion property, particularly initial adhesion property, so that the use of such a compound is unfavorable.

[0025] A preferable amount of the monoalkali metal salt of triazine thiol compounded is 1-40 parts by weight based on 100 parts by weight of the lubricant composition.

[0026] And also, the monoalkali metal salt of triazine thiol may be used together with boric acid or boric ester because boric acid or boric ester forms a film by reacting with the surface of the metal and blocks a corrosion factor to develop a rust prevention and improve a waterproof adhesion property. As the boric ester, there are $(\text{CH}_3\text{O})_3\text{B}$, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_3\text{B}$, $(\text{CH}_3-(\text{CH}_2)_8-\text{O})_3\text{B}$, $(\text{CH}_3-(\text{CH}_2)_9-\text{O})_3\text{B}$ and so on. Moreover, the carbon number of the boric ester is favorable to be a range of 9-12. A preferable amount of boric acid or boric ester compounded is 1-40 parts by weight based on 100 parts by weight of the lubricant composition.

[0027] The thiadiazole compound includes thiadiazole, dimercaptothiadiazoles and monosubstituted bodies thereof. Since the thiadiazole compound has -SH group in its molecule, it reacts with a surface of a metal and a double bond of a polymer to adhere them to each other. As the dimercaptothiadiazole, 2,5-dimercapto-1,3,4-thiadiazole is favorable. As the monosubstituted body, there are sodium salt, potassium salt, lithium salt, ammonium salt and zinc salt of the dimercaptothiadiazole. A preferable amount of the thiadiazole compound compounded is 1-40 parts by weight based on 100 parts by weight of the lubricant composition.

[0028] In the bivalent or trivalent cobalt salt of the inorganic acid, hydrochloric acid, sulfuric acid, nitric acid and carbonic acid are used as the inorganic acid.

[0029] As the Schiff base complex of the formula (2), N, N'-disalicylideneethylenediamine is preferable.

[0030] In the Schiff base complex of the formula (3), X is preferable to be ethylene group or -propylene-NH-propylene-. For example, there is N,N-disalicylaryl- γ,γ' -diaminopropylamine cobalt (II).

[0031] As the cobalt alcoholate of the formula (4), cobalt oleyl alcoholate, cobalt palmityl alcoholate, cobalt stearyl alcoholate and cobalt nonylphenyl alcoholate are preferable.

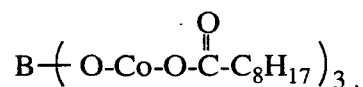
[0032] In the cobalt complex of the formula (5), R^7 is preferable to be methyl group, ethyl group, propyl group, benzyl group or phenyl group. For example, there are cobalt acetylacetonate (II), cobalt acetylacetonate (III) and cobalt acetanilide (II).

[0033] As the monocarboxylic acid constituting the acid residue Y in the formulae (6) and (7), mention may be made of acetic acid, propionic acid, butyric acid, valeric acid, pivalic acid (trimethylacetic acid), n-heptanoic acid, 2,2-dimethyl pentanoic acid, 2-ethyl pentanoic acid, 4,4-dimethyl pentanoic acid, n-octanoic acid, 2,2-dimethyl hexanoic acid, 2-ethyl hexanoic acid, 4,4-dimethyl hexanoic acid, 2,4,4-trimethyl pentanoic acid, n-nonanoic acid, 2,2-dimethyl heptanoic acid, 6,6-dimethyl heptanoic acid, 3,5,5-trimethyl hexanoic acid, n-decanoic acid, 2,2-dimethyl octanoic acid, 7,7-dimethyl octanoic acid, n-undecanoic acid, Versatic 10 (trade name, made by Shell International Co., Ltd. synthetic mixture mainly composed of neodecanoic acid), lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, palmitic acid, heptadecanoic acid, linoleic acid, linolenic acid, oleic acid, stearic acid, arachidonic acid and so on. The acid residue is preferable to have a carbon number of 9-12.

[0034] As the aromatic group-containing monocarboxylic acid in the formulae (6) and (7), mention may be made of phenylacetic acid, toluic acid, methylbenzenecarboxylic acid, 3-phenylpropionic acid, 2-phenylpropionic acid, tolylace-

tic acid, 4-ethylbenzoic acid, 2,4,6-trimethylbenzoic acid, 4-isopropylbenzoic acid, 3-pyridylacetic acid and so on.

[0035] As the cobalt borate derivative of the formula (6) is preferable



[0036] In the formula (8), R⁸ is preferable to be an alkyl group having a carbon number of 8-13 for providing excellent lubricity and workability.

[0037] In the formulae (8) and (9), a ratio of sulfur atom/oxygen atom in all of Xs is particularly favorable to be 1/3-3/1 considering the lubricity and corrosion resistance.

[0038] As the cobalt salt of dithiocarbamate is preferable cobalt bis(diethyldithiocarbamate).

[0039] As the cobalt salt of dithiocarbonate is preferable cobalt bis(o-ethyldithiocarbonate).

[0040] In the formulae (9) and (10), the hydrocarbon residue of R⁹ or R¹⁰ may be a straight chain, a branched chain or a cyclic structure and be aliphatic, alicyclic or aromatic, and may contain at least one element selected from nitrogen, oxygen and sulfur in its molecule. As the hydrocarbon residue, there are mentioned an alkyl group, an alkenyl group, an aromatic ring-containing group, a cycloalkyl group and a cycloalkenyl group.

[0041] As the alkyl group, mention may be made of methyl group, ethyl group, propyl group, isopropyl group, butyl group, isobutyl group, t-butyl group, pentyl group, isopentyl group, neopentyl group, t-pentyl group, hexyl group, heptyl group, octyl group, 2-ethylhexyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, isotridecyl group, myristyl group, palmityl group, stearyl group, icosyl group, docosyl group, tetracosyl group, triacontyl group, 2-octyldodecyl group, 2-dodecylhexadecyl group, 2-tetradecyloctadecyl group, monomethyl branched isostearyl group and so on.

[0042] As the alkenyl group, mention may be made of vinyl group, allyl group, propenyl group, isopropenyl group, butenyl group, isobutenyl group, pentenyl group, isopentenyl group, hexenyl group, heptenyl group, octenyl group, nonenyl group, decenyl group, undecenyl group, dodecenyl group, tetradecenyl group, oleyl group and so on.

[0043] As the aromatic ring-containing group, mention may be made of phenyl group, tolyl group, xylyl group, cumenyl group, mesityl group, benzyl group, phenyl group, styryl group, cinnamyl group, benzhydryl group, tolythyl group, ethylphenyl group, propylphenyl group, butylphenyl group, pentylphenyl group, hexylphenyl group, heptylphenyl group, octylphenyl group, nonylphenyl group, decylphenyl group, undecylphenyl group, dodecylphenyl group, styrenated phenyl group, cumylphenyl group, α-naphthyl group, β-naphthyl group, furyl group, propyl group, pyridyl group and so on.

[0044] As the cycloalkyl group, mention may be made of cyclopentyl group, cyclohexyl group, cycloheptyl group, methylcyclopentyl group, methylcyclohexyl group, methylcycloheptyl group and so on.

[0045] As the cycloalkenyl group, mention may be made of cyclopentenyl group, cyclohexenyl group, cycloheptenyl group, methylcyclopentenyl group, methylcyclohexenyl group, methylcycloheptenyl group and so on.

[0046] Among the aforementioned hydrocarbon residues, alkyl groups having a carbon number of 8-20 such as octyl group, 2-ethylhexyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, isotridecyl group, myristyl group, palmityl group, stearyl group and the like are favorable. Particularly, primary alkyl group having a carbon number of 10-14 such as decyl group, undecyl group, dodecyl group, tridecyl group, isotridecyl group and myristyl group are preferable because they are small in the bad odor, high in the decomposition temperature and good in the lubricity.

[0047] In any case, the preferable amount of each of the compounds used as a lubricant component as defined above is 1-40 parts by weight based on 100 parts by weight of the lubricant composition.

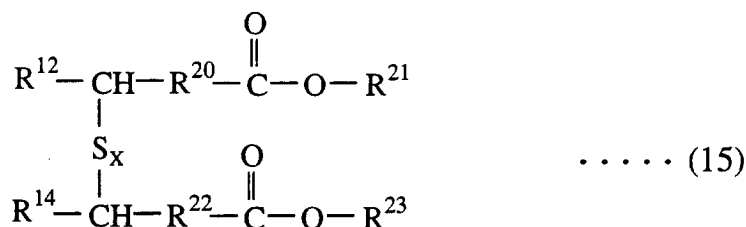
[0048] As the molybdenum salt of the formula (11), mention may be made of molybdenum plamitate, molybdenum behenate, molybdenum stearate, molybdenum palmitate, molybdenum oleate, molybdenum linolate and so on.

[0049] As the alkyl group in R¹², R¹³, R¹⁴, R¹⁵ of the formula (12), mention may be made of methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, t-butyl group, various pentyl groups, various hexyl groups, various octyl groups, various decyl groups, various dodecyl groups, various tetradecyl groups, various hexadecyl groups, various octadecyl groups and so on.

[0050] As the cycloalkyl group in R¹², R¹³, R¹⁴, R¹⁵ of the formula (12), mention may be made of cyclopropyl group, cyclobutyl group, various methylcyclopentyl groups, various dimethylcyclopentyl groups, various ethylcyclopentyl groups, various diethylcyclopentyl groups, various propylcyclopentyl groups, various butylcyclopentyl groups, various pentylcyclopentyl groups, cyclohexyl group, various methylcyclohexyl groups, various dimethylcyclohexyl groups, various ethylcyclohexyl groups, various diethylcyclohexyl groups, various propylcyclohexyl groups, various butylcyclohexyl groups, cyclooctyl group, various methylcyclooctyl groups, various ethylcyclooctyl groups, various dimethylcyclooctyl groups and so on.

[0051] As the monovalent aromatic ring-containing group in R^{12} , R^{13} , R^{14} , R^{15} of the formula (12), mention may be made of phenyl group, tolyl group, ethylphenyl group, xylyl group, benzyl group, naphthyl group, methylnaphthyl group, furyl group, pyrrolyl group, pyridyl group and so on.

[0052] Among the compounds represented by the formula (12), the use of compounds represented by the following formula (15) is preferable:



(wherein R^{12} , R^{14} and x are the same as in the formula (12), and R^{20} , R^{22} are independently an alkylene group having a carbon number of 1-19, a cycloalkylene group having a carbon number of 3-19 or a bivalent aromatic ring-containing group having a carbon number of 3-19, direct bond, and R^{21} , R^{23} are independently hydrogen atom, methyl group or ethyl group).

[0053] As the alkylene group in R^{20} , R^{22} of the formula (15), mention may be made of ethylene group, trimethylene group, tetramethylene group, pentamethylene group, hexamethylene group, heptamethylene group, octamethylene group, decamethylene group, dodecamethylene group, tetradecamethylene group, hexadecamethylene group, octadecamethylene group and so on.

[0054] As the cycloalkylene group in R^{20} , R^{22} of the formula (15), mention may be made of cyclopropylene group, various cyclobutylene groups, various cyclopentylene groups, various methylcyclopentylene groups, various dimethylcyclopentylene groups, various ethylcyclopentylene groups, various diethylcyclopentylene groups, various propylcyclopentylene groups, various butylcyclopentylene groups, various cyclohexylene groups, various methylcyclohexylene groups, various dimethylcyclohexylene groups, various propylcyclohexylene groups, various octylene groups, various methylcyclooctylene groups and so on.

[0055] As the bivalent aromatic ring-containing group in R^{20} , R^{22} of the formula (15), mention may be made of various phenylene groups, various xylylene groups, various naphthylene groups and so on.

[0056] As an example of the compounds represented by the formula (15), there are mentioned various thiodidecanoic acids, various thiodidodecanoic acids, various thioditradecanoic acids, various thiodihexadecanoic acids, various thiodioctadecanoic acids, various thiodiicosanoic acids, various dithiodidecanoic acids, various dithiodidodecanoic acids, various dithioditradecanoic acids, various dithiodihexadecanoic acids, various dithiodioctadecanoic acids, various dithiodiicosanoic acids, various trithiodidecanoic acids, various trithiodihexadecanoic acids, various trithiodioctadecanoic acids, various trithiodiicosanoic acids, various tetrathiodidecanoic acids, various tetrathiodidodecanoic acids, various tetrathioditradecanoic acids, various tetrathiodihexadecanoic acids, various tetrathiodioctadecanoic acids, various tetrathiodiicosanoic acids, various pentathiodidecanoic acids, various pentathiodidodecanoic acids, various pentathioditradecanoic acids, various pentathiodihexadecanoic acids, various pentathiodioctadecanoic acids, various pentathiodiicosanoic acids, methyl esters and ethyl esters thereof and so on.

[0057] Among the compounds of the formula (15), it is particularly preferable to use compounds wherein the carbon number in each of R^{12} and R^{14} is 6-10, and the carbon number in each of R^{20} and R^{22} is 5-9, and each of R^{21} and R^{23} is hydrogen and x is 2-4.

[0058] The compound of the formula (12) efficiently produces a monosulfide crosslink having a higher heat-resistant stability than polysulfide crosslink on the surface of the steel filament in parallel to the crosslink scission to the rubber composition at a higher temperature. Therefore, the preferable amount of the compound of the formula (12) is within a range of 10-100 g per 1000 g of the lubricant composition.

[0059] According to the invention, the surface of the steel filament is treated with the lubricant composition of the above construction during the drawing in the wet drawing machine to form a layer of the lubricant composition, particularly a coating layer of the compound according to the invention as the lubricating component in the lubricant composition. Although the mechanism of forming such a coating layer is not clear, it is guessed as follows. That is, as the steel filament passes through the lubricant composition, the lubricating component in the lubricant composition is adsorbed on the surface of the steel filament. When the steel filament is drawn by passing through the die in the wet drawing machine at such a state, the lubricating component is strongly adhered to the surface of the steel filament to form the coating layer.

[0060] Particularly, when the steel filament is drawn at a drawing rate of not less than 700 m/min in the wet drawing

machine, an interface between the steel filament and the die becomes a high temperature and high pressure state. In the invention, when the compound of the formula (12) is particularly used as a lubricating component in the lubricant composition, a higher lubrication effect can be maintained at such a state to prevent the baking of a plated portion of the steel filament onto the die. And also, as the steel filament is drawn at a very high drawing rate, there can be obtained

a drawn steel filament having a high tensile strength of, for example, not less than 4000 MPa.
[0061] The thus treated steel filament is used as a monofilament cord or as a steel cord formed by twisting a plurality of these treated steel filaments. In the steel cord, a non-treated steel filament may be used as a part of steel filaments, but the desired effects becomes large when all are treated steel filaments. When such a cord is used as a reinforcing member for rubber articles, it is coated with a coating rubber to form a rubber-steel filament composite body. The coating rubber is not particularly restricted and can use a rubber composition usually used in the art. According to the invention, the coating layer of the lubricant component is existent at an interface between the steel filament and rubber in the composite body for strongly adhering them to each other.

[0062] As the rubber-steel filament composite body according to the invention is used as a reinforcing member for rubber articles, since the adhesion property between rubber and steel filament is excellent, there is caused no peeling of the steel filament from rubber and the durability of the rubber article is considerably improved

[0063] The following examples are given in illustration of the invention and are not intended as limitations thereof.

[0064] A lubricant composition and a rubber composition are prepared according to a compounding recipe shown in Tables 1 to 4. At first, a steel filament subjected to a brass plating (Cu: 63 wt%, Zn: 37 wt%) is drawn to a filament diameter of 0.25 mm by passing through the above lubricant composition in a wet drawing machine. The thus treated steel filaments are used to form a steel cord (1x5 construction). The thus obtained steel cords are arranged side by side at an interval of 12.5 mm and sandwiched with two rubber sheets made of the above rubber composition to prepare a sample of a rubber-cord composite body.

[0065] After the sample is cured at 160°C for 10 minutes, the steel cord is pulled out according to ASTM D-2229 to measure a pulling force. The measured results are shown in Tables 1 to 4 as an initial adhesion property by an index on the basis that control is 100, wherein the larger the index value, the stronger the adhesion force and the better the initial adhesion property.

[0066] Then, the sample is cured at 160°C for 20 minutes and further subjected to a heat aging treatment at 60°C for 10 minutes to measure a tensile strength of rubber. The measured results are shown in Tables 1 to 4 by an index on the basis that control is 100, wherein the larger the index value, the higher the strength.

Examples 1-6, Comparative Examples 1-3

[0067] Various experiments are carried out by using HTS or KA9188 as a lubricating component. In this case, Comparative Example 1 is set to be the control for initial adhesion property and tensile strength after heat aging.

Table 1

	Comparative Example 1	Example 1	Example 2	Comparative Example 2	Example 3	Example 4	Comparative Example 3	Example 5	Example 6
Lubricant composition (parts by weight)									
ethylenediamine phosphate	4	4	4	4	4	4	4	4	4
oleic triethanolate	8	8	8	8	8	8	8	8	8
laurylamine octaethylene glycol	4	4	4	4	4	4	4	4	4
octadecane	3	3	3	3	3	3	3	3	3
octylic tetraethylene glycol	2	2	2	2	2	2	2	2	2
methyl p-oxybenzoate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
methyl benzotriazole	1	1	1	1	1	1	1	1	1
HTS		5			5			5	
KA9188			5			5			5
ion-exchanged water	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Rubber composition (parts by weight)									
natural rubber	100	100	100	100	100	100	100	100	100
carbon black HAF	50	50	50	50	50	50	50	50	50
zinc oxide	5	5	5	5	5	5	5	5	5
antioxidant (6C) *1	2	2	2	2	2	2	2	2	2
cobalt naphthenate	2	2	2	1	1	1	0	0	0
vulcanization accelerator (DZ) *2	1	1	1	1	1	1	1	1	1
sulfur	5	5	5	5	5	5	5	5	5
Initial adhesion property (index)	100	110	115	85	100	100	70	85	85
Tensile strength after heat aging (index)	100	100	100	110	110	110	115	115	115

*1 : N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

*2 : N,N'-dicyclohexyl-2-benzothiazolyl sulfeneamide

Examples 7-13, Comparative Examples 4-6

[0068] Various experiments are carried out by using a triazine thiol as a lubricating component. In this case, Comparative Example 4 is set to be the control for initial adhesion property and tensile strength after heat aging.

5

10

15

20

25

30

35

40

45

50

55

Table 2

	Comparative Example 4	Example 7	Example 8	Example 9	Example 10	Example 11	Comparative Example 5	Example 12	Comparative Example 6	Example 13
Lubricant composition (parts by weight)										
ethylenediamine phosphate	4	4	4	4	4	4	4	4	4	4
oleic triethanolate	8	8	8	8	8	8	8	8	8	8
laurylamine octaethylene glycol	4	4	4	4	4	4	4	4	4	4
octadecane	3	3	3	3	3	3	3	3	3	3
octylic tetraethylene glycol	2	2	2	2	2	2	2	2	2	2
methyl p-oxybenzoate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
methyl benzotriazole	1	1	1	1	1	1	1	1	1	1
lithium triazine thiol		5			5	5		5	5	5
sodium triazine thiol			5							
potassium triazine thiol				5						
boric acid					3			3		3
trimethoxy borane						3				
ion-exchanged water	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Rubber composition (parts by weight)										
natural rubber	100	100	100	100	100	100	100	100	100	100
carbon black HAF	50	50	50	50	50	50	50	50	50	50
zinc oxide	5	5	5	5	5	5	5	5	5	5
antioxidant (6C) *1	2	2	2	2	2	2	2	2	2	2
cobalt naphthenate	2	2	2	2	2	2	1	1	0	0
vulcanization accelerator (DZ) *2	1	1	1	1	1	1	1	1	1	1
sulfur	5	5	5	5	5	5	5	5	5	5
Initial adhesion property (index)	100	110	110	105	115	115	90	100	80	90
Tensile strength after heat aging (index)	100	100	100	100	100	100	110	110	120	120

*1 : N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

*2 : N-N'-dicyclohexyl-2-benzothiazolyl sulfeneamide

Examples 14-20, Comparative Examples 7-9

[0069] Various experiments are carried out by using a thiaziazole as a lubricating component. In this case, Comparative Example 7 is set to be the control for initial adhesion property and tensile strength after heat aging.

5

10

15

20

25

30

35

40

45

50

55

Table 3

	Comparative Example 7	Example 14	Example 15	Example 16	Example 17	Example 18	Comparative Example 8	Example 19	Comparative Example 9	Example 20
Lubricant composition (parts by weight)										
ethylenediamine phosphate	4	4	4	4	4	4	4	4	4	4
oleic triethanolate	8	8	8	8	8	8	8	8	8	8
laurylamine octaethylene glycol	4	4	4	4	4	4	4	4	4	4
octadecane	3	3	3	3	3	3	3	3	3	3
octylic tetraethylene glycol	2	2	2	2	2	2	2	2	2	2
methyl p-oxybenzoate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
methyl benzotriazole	1	1	1	1	1	1	1	1	1	1
thiadiazole	5	5						5		5
sodium thiadiazole			5							
potassium thiadiazole				5						
thiadiazole dichloroamine					5					
zinc thiadiazole						5				
ion-exchanged water	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Rubber composition (parts by weight)										
natural rubber	100	100	100	100	100	100	100	100	100	100
carbon black HAF	50	50	50	50	50	50	50	50	50	50
zinc oxide	5	5	5	5	5	5	5	5	5	5
antioxidant (6C) *1	2	2	2	2	2	2	2	2	2	2
cobalt naphthenate	1	1	1	1	1	1	0.5	0.5	0	0
vulcanization accelerator (DZ) *2	1	1	1	1	1	1	1	1	1	1
sulfur	5	5	5	5	5	5	5	5	5	5
Initial adhesion property (index)	100	115	110	110	115	110	90	100	85	95
Tensile strength after heat aging (index)	100	100	100	100	100	100	110	110	120	120

*1 : N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

*2 : N-N'-dicyclohexyl-2-benzothiazolyl sulfeneamide

Examples 21-34, Comparative Examples 10-11

[0070] Various experiment are carried out by using a cobalt compound as a lubricating component. In this case, Comparative Example 10 is set to be the control for initial adhesion property and tensile strength after heat aging.

5

10

15

20

25

30

35

40

45

50

55

Table 4

	Compar- ative Example 10	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Compar- ative Example 11	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34
Lubricant composition (parts by weight)																
ethylenediamine phosphate	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
oleic triethanolate	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
laurylamine octaethylene glycol	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
octadecane	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
octylic tetraethylene glycol	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
methyl p-oxybenzoate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
methyl benzotriazole	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
chlorinated Co (II)	8	8							8							
cobalt N,N'-disalicylidene ethylene diamine			26.5								26.5					
cobalt stearyl alcoholate				23								23				
cobalt acetoanilide (II)					35								35			
cobalt borate derivative *1						12.6								12.6		
cobalt bis(diethyl- dithiocarbonate)(II)							31.9								31.9	
cobalt dithiophosphate									30							30
ion-exchanged water	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Rubber composition (parts by weight)																
natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
carbon black HAF	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
antioxidant (6C) *2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
cobalt naphthenate	2	2	2	2	2	2	2	0	2	0	0	0	0	0	0	0
vulcanization accelerator (DZ) *3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
sulfur	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Initial adhesion property (index)	100	110	110	110	110	110	110	85	110	100	100	100	100	100	100	100
Tensile strength after heat aging (index)	100	105	105	105	105	105	105	110	105	110	110	110	110	110	110	110

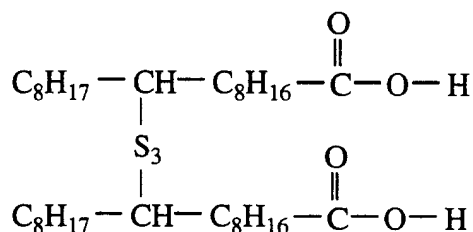
*1: cobalt borate derivative is $B\left(O-\text{Co}-O-\overset{\overset{O}{\parallel}}{C}-C_8H_{17}\right)_3$

*2: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

*3: N, N'-dicyclohexyl-2-benzothiazolyl sulfenamide

Examples 35-40, Conventional Examples 1-2, Comparative Examples 12-15

[0071] Various experiments are carried out by using a compound A (10,10'-trithiodioctadecanoic acid) represented by the following formula as a lubricating component:



In this case, a steel filament subjected to a brass plating (Cu: 63 wt%, Zn: 37 wt%) is drawn to a filament diameter of 0.25 mm by passing at a drawing rate of 800 m/min through the lubricant composition in a wet drawing machine. In addition to the compound A, the lubricant composition contains basic components as shown in Tables 5 and 6. In Table 6, HTS is chosen as an example of the lubricating compound of the first aspect of the invention.

[0072] The temperature of the steel filament just after the pass through a final die is measured for the evaluation of heat generation to obtain results as shown in Tables 5 and 6. In these tables, the term "filament temperature" means a temperature of steel filament just after passing through the final die. As the temperature becomes higher, the heat generation becomes larger.

[0073] The diameter of the steel filament just after passing through the final die is measured to compare the filament diameter before and after the drawing of 50000 m. The measured results are shown in Tables 5 and 6, in which difference of filament diameter before and after the drawing is indicated as an increment of filament diameter. As the increment of filament diameter becomes small, better lubricity is maintained.

Table 5

	Conventional Example 1	Example 35	Example 36	Example 37	Comparative Example 12	Comparative Example 13
Lubricant composition (part by weight)						
Ethylenediamine phosphate	4	4	2	1	2	1
Triethanol oleate	8	8	8	8	8	8
Laurylamine octaethylene glycol	4	4	4	4	4	4
Octadecane	3	3	3	3	3	3
Tetraethylene glycol octylate	2	2	2	2	2	2
Methyl p- oxybenzoate	0.5	0.5	0.5	0.5	0.5	0.5

EP 1 172 430 A2

Table 5 (continued)

	Conventional Example 1	Example 35	Example 36	Example 37	Comparative Example 12	Comparative Example 13
5 Methyl benzotriazole	1	1	1	1	1	1
HTS *1	0	0	0	0	0	0
Compound A	0	3	3	3	0	0
10 Ion-exchanged water	77.5	77.5	77.5	77.5	77.5	77.5
Filament temperature (°C)	178	170	181	187	226	245
15 Increment of filament diameter (mm)	0.000	0.000	0.000	0.001	0.009	0.012

*1: Sodium 1,6-hexamethylene diamine dithiosulfate dihydrate

Table 6

	Conventional Example 2	Example 38	Example 39	Example 40	Comparative Example 14	Comparative Example 15
25 Lubricant composition (part by weight)						
30 Ethylenediamine phosphate	4	4	2	1	2	1
Triethanol oleate	8	8	8	8	8	8
35 Laurylamine octaethylene glycol	4	4	4	4	4	4
Octadecane	3	3	3	3	3	3
Tetraethylene glycol octylate	2	2	2	2	2	2
40 Methyl p- oxybenzoate	0.5	0.5	0.5	0.5	0.5	0.5
Methyl benzotriazole	1	1	1	1	1	1
45 HTS *1	5	5	5	5	5	5 5
Compound A	0	3	3	3	0	0
Ion exchanged water	77.5	77.5	77.5	77.5	77.5	77.5
50 Filament temperature (°C)	180	170	180	187	220	240
55 Increment of filament diameter (mm)	0.000	0.000	0.000	0.001	0.006	0.009

*1: Sodium 1,6-hexamethylene diamine dithiosulfate dihydrate

[0074] As seen from Tables 5 and 6, the rise of the filament temperature and the increment of filament diameter are controlled and the good lubricity is maintained in the examples as compared with the comparative examples.

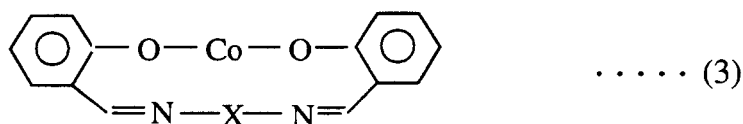
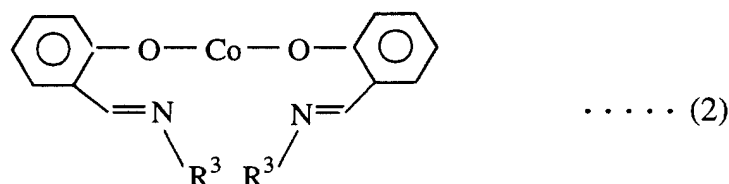
[0075] As mentioned above, according to the invention, steel filaments having an excellent adhesion property to rubber are obtained by compounding the compound(s) defined in the invention with the lubricant composition and surface-treating the steel filaments therewith during the drawing. And also, when the rubber-steel filament composite body using the thus treated steel filaments is used as a reinforcing member for the rubber article, it is possible to reduce the cobalt salt of the organic acid and hence the durability of the rubber article can largely be improved without damaging the adhesion property.

Claims

1. A lubricant composition for steel filament comprising at least one compound selected from the group consisting of sodium 1,6-hexamethylenediamine-dithiosulfate dihydrate, a compound represented by the following formula (1):



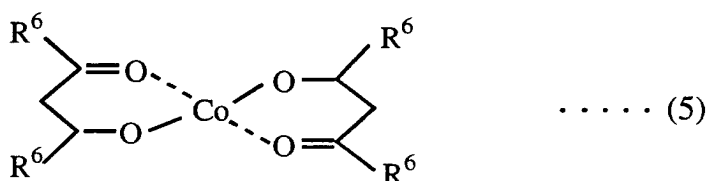
(wherein A is an alkylene group having a carbon number of 2-10, and each of R^1 and R^2 is a monovalent organic group containing at least one nitrogen atom), a monoalkali metal salt of triazine thiol, a thiadiazole compound, bivalent or trivalent cobalt salt of an inorganic acid, a Schiff base complex represented by the following formula (2) or (3):



(wherein R^3 is an alkyl group having a carbon number of 1-10 and X is $-R^4-$ or $-R^4-NH-R^4-$ in which R^4 is an alkylene group having a carbon number of 1 to 10), a cobalt alcoholate represented by the following formula (4):



(wherein R^5 is an alkyl group having a carbon number of 1-20, a phenyl alkyl group or an alkyl phenyl group provided that a carbon number of the alkyl group is 1-10), a cobalt complex represented by the following formula (5):



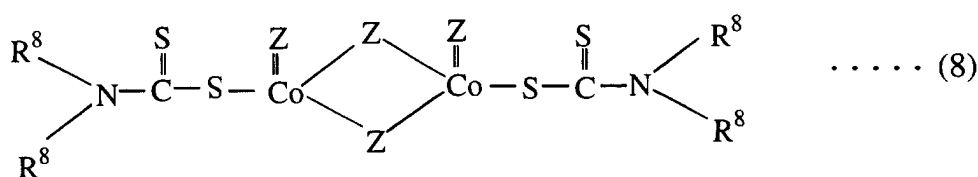
(wherein R^6 is an alkyl group having a carbon number of 1-20 or a $-NHR^7$ group or a $-OR^7$ group in which R^7 is an alkyl group having a carbon number of 1-20), a metal borate derivative represented by the following formula (6):



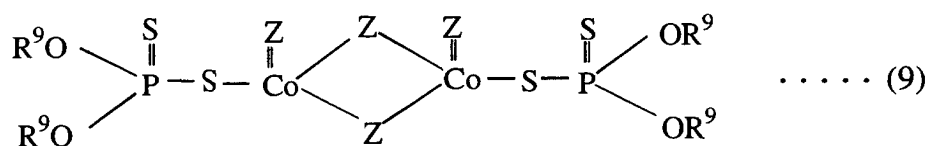
(wherein M is Co or Ni and Y is an acid residue of a monocarboxylic acid having a carbon number of 2-21 or an aromatic group containing monocarboxylic acid having a carbon number of 2-21 provided that Ys are the same or different), a metal aluminate derivative represented by the following formula (7):



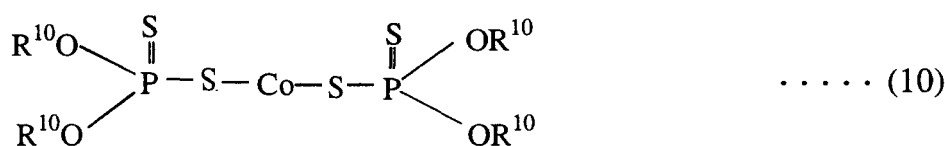
(wherein M is Co or Ni and Y is an acid residue of a monocarboxylic acid having a carbon number of 2-21 or an aromatic group containing monocarboxylic acid having a carbon number of 2-21 provided that Ys are the same or different), a cobalt, nickel or iron salt of dithiocarbamate or dithiocarbonate, a cobalt dithiocarbamate represented by the following formula (8):



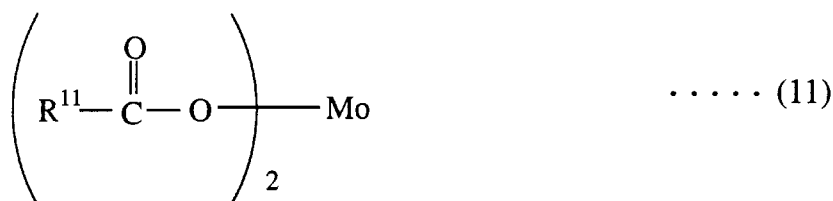
(wherein R^8 is an alkyl group having a carbon number of 1-20 and Z is an oxygen atom or a sulfur atom provided that Zs are the same or partly different), a cobalt dithiophosphate represented by the following formula (9) or (10):



or



(wherein R^9 or R^{10} is a hydrocarbon residue having a carbon number of 1-20 and Z is an oxygen atom or a sulfur atom provided that Zs are the same or partly different), and a molybdenum salt of a carboxylic acid represented by the following formula (11):



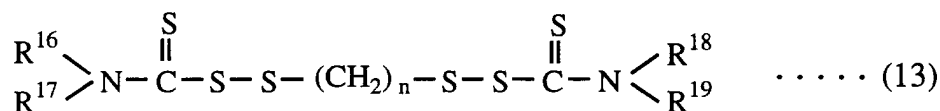
(wherein R¹¹ is an alkyl group having a carbon number of 1-20).

2. A lubricant composition for steel filament comprising at least one compound represented by the following formula (12):



(wherein R¹², R¹³, R¹⁴ and R¹⁵ are independently an alkyl group having a carbon number of 1-20, a cycloalkyl group having a carbon number of 3-20, a monovalent aromatic ring-containing group having a carbon number of 3-20 and, if necessary, containing at least one heteroatom selected from the group consisting of an oxygen atom, nitrogen atom and sulfur atom provided that at least one of R¹², R¹³, R¹⁴ and R¹⁵ contains at least one of carboxyl group and/or ester compound thereof in its molecule, and x is an integer of 1 to 5)

3. A lubricant composition according to claim 1, wherein A in the formula (1) is a hexamethylene group.
4. A lubricant composition according to claim 1, wherein each of R¹ and R² in the formula (1) is a nitrogen-containing monovalent organic group containing at least one aromatic ring.
5. A lubricant composition according to claim 1, wherein each of R¹ and R² in the formula (1) is a monovalent organic group having a group of bonding a carbon atom to a dithio group represented by =N-C(=S)- group.
6. A lubricant composition according to claim 1, wherein the compound of the formula (1) is α,ω -bis(N, N'-dihydro-carbylthiocarbamoyldithio) alkane represented by the following formula (13):



(wherein each of R¹⁶ to R¹⁹ is an alkyl group, an aryl group or an aralkyl group, provided that at least one of R¹⁶ and R¹⁷ and at least one of R¹⁸ and R¹⁹ are an aryl group having a carbon number of 6-20 or an aralkyl group having a carbon number of 7-20, and n is an integer of 2 to 10).

7. A lubricant composition according to claim 5, wherein the compound of the formula (12) is 1,6-bis(N, N'-dibenzylthiocarbamoyldithio)hexane.
8. A lubricant composition according to claim 1, wherein a metal in the monoalkali metal salt of triazine thiol is selected from lithium, sodium and potassium.
9. A lubricant composition according to claim 7, wherein at least one of boric acid and boric esters is added in addition to the monoalkali metal salt of triazine thiol.
10. A lubricant composition according to claim 8, wherein the boric ester has 1 to 3 boron elements per one molecule and an alcohol residue having a carbon number of 1 to 4.
11. A lubricant composition according to claim 1, wherein the thiadiazole compound is a dimercaptothiadiazole.
12. A lubricant composition according to claim 10, wherein the dimercaptothiadiazole is 2,5-dimercapto-1,3,4-thiadiazole.
13. A lubricant composition according to claim 10, wherein the dimercaptothiadiazole is a monosubstituted body selected from the group consisting of sodium salt, potassium salt, lithium salt, ammonium salt and zinc salt.

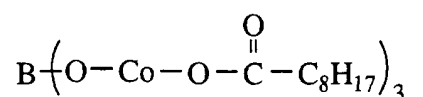
14. A lubricant composition according to claim 1, wherein an inorganic acid in the bivalent or trivalent cobalt salt of the inorganic acid is at least one of hydrochloric acid, sulfuric acid, nitric acid and carbonic acid.

15. A lubricant composition according to claim 1, wherein the Schiff base of the formula (2) is N, N'-disalicylidene ethylene diamine.

16. A lubricant composition according to claim 1, wherein the cobalt alcholate is cobalt stearyl alcholate or cobalt nonylphenyl alcholate.

17. A lubricant composition according to claim 1, wherein the cobalt complex of the formula (5) is at least one of cobalt acetylacetonate (II), cobalt acetylacetonate (III) and cobalt acetoanilide (II).

18. A lubricant composition according to claim 1, wherein the cobalt borate derivative of the formula (6) is



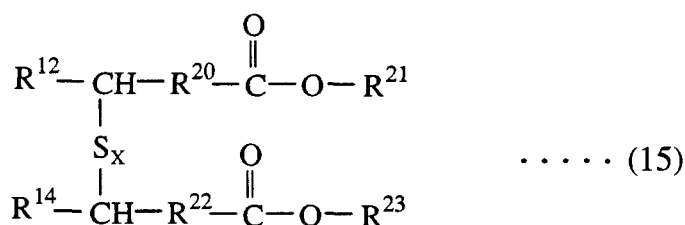
19. A lubricant composition according to claim 1, wherein the dithiocarbamate is cobalt bis(diethyldithiocarbamate)(II).

20. A lubricant composition according to claim 1, wherein the dithiocarbonate is cobalt bis(o-ethyldithiocarbonate)(II).

21. A lubricant composition according to claim 1, wherein the dithiocarbonate is cobalt bis(o-ethyldithiocarbonate)(II).

22. A lubricant composition according to claim 1, wherein the molybdenum salt of the formula (11) is molybdenum palmitate, molybdenum vehenate, molybdenum stearate, molybdenum palmitolate, molybdenum oleate or molybdenum linorate.

23. A lubricant composition according to claim 2, wherein the compound o: the formula (12) is a compound represented by the following formula (15):



(wherein R^{12} , R^{14} and x are the same as in the formula (12), and R^{20} , R^{22} are independently an alkylene group having a carbon number of 1-19, a cycloalkylene group having a carbon number of 3-19 or a bivalent aromatic ring-containing group having a carbon number of 3-19, direct bond, and R^{21} , R^{23} are independently hydrogen atom, methyl group or ethyl group).

24. A steel filament having on its surface a layer of a lubricant composition as claimed in any one of claims 1 to 23.

25. A rubber-steel filament composite body consisting of a rubber composition and a steel filament and having a layer of a lubricant composition as claimed in any one of claims 1 to 23 at an interface therebetween.