

# (11) **EP 1 785 473 A1**

(12)

### **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

16.05.2007 Bulletin 2007/20

(51) Int Cl.:

C10M 141/10 (2006.01)

C10M 171/02 (2006.01)

(21) Application number: 06023448.1

(22) Date of filing: 10.11.2006

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

Designated Extension States:

AL BA HR MK YU

(30) Priority: 12.11.2005 US 271294

(71) Applicant: Afton Chemical Corporation Richmond, VA 23219 (US)

(72) Inventors:

- Milner, Jeffrey L.
   Chesterfield
   Virginia 23838 (US)
- Iyer, Ramnath N.
   Glen Allen
   Virginia 23059 (US)
- Tersigni, Samuel H. Glen Allen Virginia 23060 (US)
- (74) Representative: Schwabe Sandmair Marx Stuntzstrasse 16 81677 München (DE)

### (54) Relatively low viscosity transmission fluids

(57) A relatively low viscosity transmission fluid composition, transmissions containing the fluids, and methods of operating motor vehicles with the fluids are described. The transmission fluid composition includes a lubricant basestock, at least one active sulfur-containing component, and at least one phosphorus-containing

compound. An active sulfur atom content of the composition is greater than about 0.02 wt.%, and a ratio of active sulfur atoms to phosphorus atoms in the composition is above about 5. The composition has a viscosity at 100° C ranging from about 4 to less than about 7 centistokes.

EP 1 785 473 A1

#### Description

#### **FIELD**

5

10

20

30

35

40

45

50

55

**[0001]** The present disclosure relates to lubricating fluid compositions having relatively low viscosity for use in transmission applications, in particular for use in automated manual transmissions. The fluid compositions have enhanced extreme pressure and antiwear properties despite the relatively low viscosity of the fluid compositions.

#### **BACKGROUND AND SUMMARY**

**[0002]** New and advanced transmission systems are being developed by the automotive industry that are useful for high fuel economy vehicles such as hybrid vehicles. Such transmissions include continuously variable transmissions (CVTs) and automated manual transmissions, e.g. dual clutch transmissions (DCTs) and double-sided clutch transmissions (DSCTs). Fuel economy is one of the primary benefits that DCTs, DSCTs and CVTs can offer. Relatively lower viscosity fluids may provide greater fuel economy. However, antiwear, and extreme pressure characteristics of the fluids are influenced to a great extent by the viscosity of the transmission fluid being used. In order for lower viscosity fluids to achieve similar antiwear and extreme pressure performance provided by higher viscosity fluids, improved transmission fluids are needed.

**[0003]** For the purposes of this disclosure, a relatively low viscosity transmission fluid is a transmission fluid have a viscosity ranging from about 3 to less than about 7 centistokes at 100° C.

**[0004]** In an embodiment, a relatively low viscosity transmission fluid composition is provided. The transmission fluid composition includes a lubricant basestock, at least one active sulfur-containing component, and at least one phosphorus-containing compound. An active sulfur atom content of the composition is greater than about 0.02 wt.%, and a ratio of active sulfur atoms to phosphorus atoms in the composition is above about 5. The composition has a viscosity at 100° C ranging from about 4 to less than about 7 centistokes.

**[0005]** In another embodiment, there is provided an additive concentrate for a transmission fluid. The additive concentrate includes at least one sulfur-containing component and at least one phosphorus-containing compound sufficient to provide more than about 0.02 wt.% active sulfur to a finished transmission fluid, and a ratio of active sulfur atoms to phosphorus atoms in the finished transmission fluid of greater than about 5. The finished transmission fluid containing the additive concentrate has a viscosity at 100° C ranging from about 4 to less than about 7 centistokes.

**[0006]** Yet another embodiment provides a method for improving fuel economy of a motor vehicle. The method includes providing a transmission fluid to a transmission of the motor vehicle and operating the motor vehicle with the transmission fluid. The transmission fluid contains a lubricant basestock, at least one sulfur-containing component, and at least one phosphorus-containing compound. An active sulfur atom content of the transmission fluid is greater than about 0.02 wt. %, and a ratio of active sulfur atoms to phosphorus atoms in the transmission fluid is above about 5. The transmission fluid has a viscosity at 100° C ranging from about 4 to less than about 7 centistokes.

**[0007]** An advantage of the compositions described herein is that the compositions may be effective to provide fuel economy benefits for motor vehicles. Another advantage is that the fluids may provide lower viscosity fluids having similar antiwear and extreme pressure benefits as higher viscosity fluids for the same applications. The disclosed compositions may provide excellent friction durability for steel-paper applications and provide good steel-on-steel friction for synchronizer performance similar to fluids having higher viscosities. A further advantage of the embodiments described herein is the provision of suitable active sulfur to phosphorus ratios in lubricant compositions that enable compositions having desirable antiwear and extreme pressure properties to be formulated in a variety of lubricating fluids.

### DETAILED DESCRIPTION OF EMBODIMENTS

**[0008]** As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

- (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
- (3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Hetero-

atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituent in the hydrocarbyl group.

**[0009]** In exemplary embodiments described herein, the transmission fluid compositions include a lubricant basestock, at least one active sulfur-containing component and at least one phosphorus-containing compound. In other embodiments, the transmission fluid composition also includes other conventional lubricant additive components including, but not limited to at least one antioxidant, at least one friction modifier, at least one corrosion inhibitor, at least one surfactant, and at least one antifoam agent. Other components in conventional amounts, such as pour point depressants and metal deactivators may also be included in the compositions described herein.

#### **Basestock**

5

10

15

20

30

35

40

45

50

**[0010]** Base oils suitable for use in formulating transmission fluid compositions according to the disclosure may be selected from any of the synthetic or natural oils or mixtures thereof including, but not limited to, gas to liquid base oils, Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also suitable. The base oil typically has a viscosity of about 2 to less than about 7 cSt at 100° C.

**[0011]** The synthetic base oils include alkyl esters of dicarboxylic acids, polyglycols and alcohols, poly-alpha-olefins, including polybutenes, alkyl benzenes, organic esters of phosphoric acids, and polysilicone oils. Synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); poly(1-hexenes), poly-(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, di-nonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl-ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0012] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils that may be used. Such oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3-8</sub> fatty acid esters, or the C<sub>13</sub> Oxo acid diester of tetraethylene glycol. [0013] Another class of synthetic oils that may be used includes the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

**[0014]** Esters useful as synthetic oils also include those made from  $C_5$  to  $C_{12}$  monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

**[0015]** Hence, the base oil used which may be used to make the transmission fluid compositions as described herein may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines, as well as gas to liquid base oils. Such Group I-V base oil groups are as follows:

Base Oil Group <sup>1</sup>	Sulfur (wt.%)		Saturates (wt.%)	Viscosity Index	
Group I	> 0.03	and/or	< 90	80 to 120	
Group II	≤ 0.03 And		≥ 90	80 to 120	
Group II	≤ 0.03	And	≥ 90 ≥ 120		
Group IV all polyalphaolefins (PAOs)					

#### (continued)

Base Oil Group <sup>1</sup>	up <sup>1</sup> Sulfur (wt.%) Saturates (wt.%)		Viscosity Index			
Group V	all others not included in Groups I-IV					
<sup>1</sup> Groups I-III are mineral oil base stocks.						

**[0016]** The amount of base oil in the finished transmission fluid composition may range from about 40 to about 99 percent by weight of the finished transmission fluid composition.

### Extreme Pressure Agent

mission fluid compositions described herein.

5

10

20

30

35

40

45

50

55

[0017] The compositions disclosed herein contain at least one active sulfur-containing component. One suitable active sulfur-containing component is a sulfur-containing extreme pressure agent. Typical sulfur-containing extreme pressure additives include, but are not limited to dihydrocarbyl polysulfides, sulfurized olefins, sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins, trithiones, sulfurized thienyl derivatives, sulfurized terpenes, sulfurized oligomers of C<sub>2</sub>-C<sub>8</sub> monoolefins, and sulfurized Dieis-Alder adducts such as those disclosed in reissue U.S. Pat. No. 27,331, the disclosure of which is incorporated herein by reference. Specific examples include sulfurized polyisobutene, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl polysulfide, diphenyl and dibenzyl polysulfide, di-tert-butyl polysulfide, and dinonyl polysulfide, among others.

[0018] Phosphorus-containing extreme pressure agents may also be used. Generally speaking there are two principal categories of phosphorus-containing extreme pressure agents: metal salts of phosphorus acids and metal-free phosphorus compounds. The metal salts are the oil-soluble salts of a metal such as copper, cadmium, calcium, magnesium, and most notably, zinc, and of a suitable acidic compound of phosphorus, such as a thiophosphoric acid, a dithiophosphoric acid, a trithiophosphoric acid, a tetrathiophosphoric acid or of a complex acidic product formed by phosphosulfurizing a hydrocarbon such as one or more olefins or terpenes with a reactant such as phosphorus pentasulfide and hydrolyzing the resultant product. Methods of forming such metal salts are well known to those skilled in the art and are extensively described in the patent literature.

[0019] The oil-soluble metal-free phosphorus-containing extreme pressure agents are for the most part partially or fully esterified acids of phosphorus. Such compounds include for example phosphates, phosphites, phosphonates, phosphonites, and their various sulfur analogs. Examples include monohydrocarbyl phosphates, monohydrocarbyl mono-, di-, tri-, and tetrathiophosphites, monohydrocarbyl mono-, di-, tri-, and tetrathiophosphates, dihydrocarbyl phosphates, dihydrocarbyl phosphates, dihydrocarbyl mono-, di-, tri-, and tetrathiophosphites, trihydrocarbylphosphites, trihydrocarbylphosphates, trihydrocarbyl mono-, di-, tri-, and tetrathiophosphites, trihydrocarbyl mono-, di-, tri-, and tetrathiophosphites, trihydrocarbyl phosphonates and thiophosphonates, the various hydrocarbyl phosphonates and thiophosphonates, and analogous oil-soluble derivatives of polyphosphoric and polythiophosphoric acids, and many others. A few specific examples of such compounds are tricresyl phosphate, tributyl phosphite, triphenyl phosphite, tri-(2-ethylhexyl) phosphate, dihexyl thiophosphite, diisooctyl butylphosphonate, tricyclohexyl phosphate, cresyl diphenyl phosphate, tris(2butoxyethyl) phosphite, diisopropyl dithiophosphate, tris(tridecyl)tetrathiophosphate, tris(2-chloroethyl) phosphate, and like compounds.

[0020] In one embodiment, the sulfur-containing extreme pressure agent is at least one dimercaptothiadiazole or an oil-soluble derivative thereof. Such materials provide extreme pressure and/or antiwear properties to exemplary trans-

**[0021]** Dimercaptothiadiazoles which may be used in the transmission fluid compositions include, but are not limited to, 2,5-dimercapto-1,3,4-thiadiazoles (DMTD) of the following formula:

wherein  $R^1$  and  $R^2$  are selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3. DMTD may be prepared by reacting one mole of hydrazine, or a hydrazine salt, with two moles of carbon disulfide in an alkaline medium, followed by acidification.

**[0022]** Transmission fluid compositions described herein may include DMTD or derivatives of DMTD as set forth in the foregoing formula. For example, U.S. Pat. Nos. 2,719,125; 2,719,126; and 3,087,937 describe the preparation of various 2,5-bis(hydrocarbon dithio)-1,3,4-thiadiazoles.

**[0023]** The total amount of sulfur- and/or phosphorus-containing extreme pressure agent in the transmission fluid compositions described herein may range from about 0.01 to about 12.0 weight percent of the total finished transmission fluid composition, provided the active sulfur content of the finished transmission fluid composition is greater than about 0.02 wt.% and the active sulfur atom to phosphorus atom ratio does not fall below about 5. In another example, the active sulfur content of the finished transmission fluid composition may be greater than about 0.04 wt.%, and as a further example, the active sulfur content of the finished transmission fluid composition may be greater than about 0.05 wt.%.

#### Dispersant

10

20

30

35

40

45

50

55

**[0024]** The dispersant may comprise a mannich or succinimide dispersant. Further, the dispersant may be a phosphorylated, boronated, or boronated/phosphorylated dispersant. The dispersant used in the transmission fluid compositions described herein is typically an oil-soluble phosphorus-containing ashless dispersant. The phosphorus-containing ashless dispersants can be formed by phosphorylating an ashless dispersant having basic nitrogen and/or at least one hydroxyl group in the molecule, such as a succinimide dispersant, succinic ester dispersant, succinic ester-amide dispersant, Mannich base dispersant, hydrocarbyl polyamine dispersant, or polymeric polyamine dispersant. Polyamine succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms are described for example in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435.

**[0025]** As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between one or more polyamine reactants and a hydrocarbon-substituted succinic acid or anhydride (or like succinic acylating agent), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

**[0026]** Alkenyl succinic acid esters and diesters of polyhydric alcohols containing 2-20 carbon atoms and 2-6 hydroxyl groups may be used in forming the phosphorus-containing ashless dispersants. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179.

**[0027]** Hydrocarbyl polyamine dispersants that may be phosphorylated are generally produced by reacting an aliphatic or alicyclic halide (or mixture thereof) containing an average of at least about 40 carbon atoms with one or more amines, for example polyalkylene polyamines. Examples of such hydrocarbyl polyamine dispersants are described in U.S. Pat. Nos. 3,275,554; 3,394,576; 3,438,757; 3,454,555; 3,565,804; 3,671,511; and 3,821,302.

**[0028]** Mannich polyamine dispersants which can be used in forming the phosphorylated ashless dispersant is a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines). Examples of Mannich condensation products, and methods for their production are described in U.S. Pat. Nos. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

**[0029]** Polymeric polyamine dispersants suitable for preparing phosphorylated ashless dispersants are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials are illustrated by interpolymers formed from various monomers such as decyl methacrylate, vinyl decyl ether or relatively high molecular weight olefins, with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300.

**[0030]** In another exemplary embodiment, the phosphorus-containing dispersants are also boronated. Methods that can be used for boronating (borating) the various types of ashless dispersants described above are described in U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069; 3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; and 4,652,387.

**[0031]** The amount of phosphorylated ashless dispersant on an "active ingredient basis" (i.e., excluding the weight of impurities, diluents and solvents typically associated therewith) is generally within the range of about 0.1 to about 10.0 weight percent (wt.%), typically within the range of about 0.5 to 5.0 wt % of the total weight of the transmission fluid composition.

### Friction Modifiers

[0032] Friction modifiers are used in power transmission fluids to decrease friction between surfaces (e.g., the members of a torque converter clutch or a shifting clutch) at low sliding speeds. The result is a friction-vs.-velocity (u-v) curve that has a positive slope, which in turn leads to smooth clutch engagements and minimizes "stick=slip" behavior (e.g., shudder, noise, and harsh shifts). Many conventional organic friction modifiers, however, are thermally unstable. Upon prolonged exposure to heat, these additives decompose, and the benefits they confer on clutch performance are lost. Friction-modifying succinimides, as described herein, show unusual thermal stability. Compositions containing such friction modifiers show little change in friction behavior upon thermal stressing.

**[0033]** Friction modifiers include such compounds as aliphatic amines or ethoxylated aliphatic amines, ether amines, alkoxylated ether amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, polyol esters, aliphatic carboxylic ester-amides, imidazolines, tertiary amines, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphonates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia primary amines.

**[0034]** One useful group of friction modifiers includes the N-aliphatic hydrocarbyl-substituted diethanol amines in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms.

**[0035]** A particularly suitable friction modifier system is composed of a combination of at least one N-aliphatic hydrocarbyl-substituted diethanol amine and at least one N-aliphatic hydrocarbyl-substituted trimethylene diamine in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms. Further details concerning this friction modifier system are set forth in U.S. Pat. Nos. 5,372,735 and 5,441,656.

[0036] Another particularly useful friction modifier system is based on the combination of (i) at least one di(hydroxyalkyl) aliphatic tertiary amine in which the hydroxyalkyl groups, being the same or.different, each contain from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms, and (ii) at least one hydroxyalkyl aliphatic imidazoline in which the hydroxyalkyl group contains from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms. For further details concerning this friction modifier system, reference should be had to U.S. Pat. No. 5,344,579. Generally speaking, the transmission fluid compositions described herein will contain up to about 5.0 wt % one or more of the foregoing friction modifiers.

### Antioxidants

20

30

50

55

[0037] Antioxidant compounds may be included in the transmission fluid compositions. Antioxidants include phenolic antioxidants, aromatic amine antioxidants, sulfurized phenolic antioxidants, and organic phosphites, among others. Examples of phenolic antioxidants include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol),2,2'-methylenebis(4-methyl6-ter t-butylphenol), mixed methylene-bridged polyalkyl phenols; and 4,4'-thiobis(2-methyl-6-tert-butylphenol). N,N'-di-sec-butyl-phenylenediamine, 4-isopropylaminodiphenylamine, phenyl-.alpha.-naphthyl amine, phenyl-.alpha.-naphthyl amine, and ring-alkylated diphenylamines. Suitable examples are the sterically hindered tertiary butylated phenols, bisphenols and cinnamic acid derivatives and combinations thereof. The amount of antioxidant in the transmission fluid compositions described herein may range from about 0.01 to about 1.0 weight percent based on the total weight of the fluid composition.

### 45 Rust or corrosion inhibitors

[0038] Rust or corrosion inhibitors are another type of inhibitor additive for use in fluid compositions described herein. Such materials include monocarboxylic acids and polycarboxylic acids. Examples of suitable monocarboxylic acids are octanoic acid, decanoic acid and dodecanoic acid. Suitable polycarboxylic acids include dimer and trimer acids such as are produced from such acids as tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources.

[0039] Another useful type of rust inhibitor is comprised of the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable rust or corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; aminosuccinic acids or derivatives thereof, and the like. Materials of these types are available as articles of commerce. Mixtures

of such rust or corrosion inhibitors may be used. The amount of corrosion inhibitor in the transmission fluid formulations described herein may be up to about 0.5 weight percent based on the total weight of the formulation.

#### Viscosity Index Improvers

5

15

20

25

30

35

40

45

50

55

**[0040]** Viscosity index improvers for use in the above described transmission fluid compositions may be selected from polyisoalkylene compounds and conventional viscosity index improvers. A particularly suitable polyisoalkylene compound for use as a viscosity index improver includes polyisobutylene having a weight average molecular weight ranging from about 700 to about 2,500.

**[0041]** Commercially available materials for use as viscosity index improvers may also be used either alone or in combination with the polyisoalkylene viscosity index improver. Such commercially available materials include styrene-maleic esters, polyalkylmethacrylates; and olefin copolymer viscosity index improvers. Mixtures of the foregoing products may also be used as well as dispersant and dispersant-antioxidant viscosity index improvers. The amount of viscosity index improver in the transmission fluid formulations described herein may be up to about 1.5 weight percent based on the total weight of the formulation.

#### Antifoam agents

**[0042]** A foam inhibitor forms another component suitable for use in the compositions described herein. Foam inhibitors may be selected from silicones, polyacrylates, surfactants, and the like. The amount of antifoam agent in the transmission fluid formulations described herein may range from about 0.01 to about 0.1 weight percent based on the total weight of the formulation.

#### Seal swell agents

[0043] The seal swell agent which may be used in the transmission fluid compositions described herein is selected from oil-soluble diesters, oil-soluble sulfones, and mixtures thereof. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of  $C_8$ - $C_{13}$  alkanols (or mixtures thereof), and the phthalates of  $C_4$ - $C_{13}$  alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and tridecyl diesters of phthalic acid. Other esters which may give generally equivalent performance are polyol esters. Suitable sulfone seal swell agents are described in U.S. Pat. Nos. 3,974,081 and 4,029,587. Other suitable seal swell agents are the oil-soluble dialkyl esters of (i) adipic acid, (ii) sebacic acid, or (iii) phthalic acid. Typically these products are employed at levels in the range of up to about 1 wt % in the finished power transmission fluid.

### **Detergents**

[0044] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion. Detergents generally comprise a polar head with a long hydrophobic tail where the polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal, in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as measured by ASTM D2896) of from 0 to less than 150. Large amounts of a metal base may be included by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises micelles of neutralized detergent surrounding a core of inorganic metal base (e.g., hydrated carbonates). Such overbased detergents may have a TBN of 150 or greater, and typically ranging from 250 to 450 or more.

**[0045]** Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, and salicylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present. Mixtures of calcium and/or magnesium with sodium are also useful. Particularly convenient metal detergents are neutral and overbased calcium or magnesium sulfonates having a TBN of from 20 to 450 TBN, neutral and overbased calcium or magnesium phenates and sulfurized phenates having a TBN of from 50 to 450, and neutral or overbased calcium or magnesium salicylates having a TBN of from 130 to 350. Mixtures of such salts may also be used. When used, the presence of at least one overbased detergent is desirable.

**[0046]** The amount of detergent in a finished lubricant composition according to the disclosed embodiments may range from about 0.01 to about 1.0 percent by weight based on the total weight of the finished lubricant composition.

[0047] Additives used in formulating the fluid compositions described herein can be blended into the base oil individually

or in various sub-combinations. Further, all of the components may be blended concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). The use of an additive concentrate takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also, the use of a concentrate reduces blending time and lessens the possibility of blending errors.

**[0048]** The transmission fluid compositions disclosed herein may include fluids suitable for any automatic, manual, or automated manual transmission application. For example, embodiments disclosed herein may be suitable for use in a step automatic transmission, a manual transmission, a continuously variable transmission, a dual clutch transmission, a double-sided clutch transmission, and the like. Further, the presently disclosed power transmission fluids may be suitable for use in transmissions with a slipping torque converter, a lock-up torque converter, a starting clutch, and/or one or more shifting clutches. Such transmissions include four-, five-, six-, and seven-speed transmissions, and continuously variable transmissions (chain, belt, or disk type).

[0049] An exemplary transmission fluid composition as described above may contain the following components in the amounts indicated:

Component	Amount		
Base oil	Balance		
active sulfur-containing component(s)	0.1 to 2.0 wt.%		
phosphorus-containing compound(s)	0.01 to 10.0 wt.%		
boron-containing compound(s)	0 to 10.0 wt.%		
antioxidant(s)	0.01 to 1.0 wt.%		
friction modifier(s)	0.05 to 5.0 wt.%		
antifoam agent(s)	0.001 to 0.1 wt.%		
detergent(s)	0.01 to 1.0 wt.%		
process oil(s)	1.0 to 30.0 wt.%		
Total	100.00 wt.%		

15

20

25

30

35

40

45

50

55

[0050] In order to evaluate transmission fluid compositions having relatively lower viscosities, the load carrying characteristics of various fluids having different viscosities and different total sulfur to phosphorus and/or boron ratios were evaluated on an FZG test rig using A and A10 gears according to ASTM D 5182 and CED-L-84-A-04, respectively. Themaximum load stage fail of the fluids was 8 for the A10 gears at 16.6 RPM and 90 °C and was>12 for the A gears at 8.3 RPM and 90 °C. The kinematic viscosities of the fluids were determined according to ASTM D 445 and the Brookfield viscosities of the fluids were determined according to ASTM D 5182.

[0051] In the following table, relatively low viscosity fluids (Fluid A and Fluid B) were formulated according to the above formulation and were compared to a commercially available dual clutch transmission fluid (DCTF) (Fluid C) having a relatively higher viscosity.

Table 1

<u>rable i</u>			
Fluid Property	Fluid A	Fluid B	Fluid C
Kinematic viscosity at 100° C (centistokes) (ASTM D 445)	6.52	4.95	7.24
Brookfield viscosity at -40° C (centipoises) (ASTM D 2983)	14,000	9,500	9,960
A10/16.6R/90° C, Load stage fail (CEC-L-84-A-04)	8	8	6
A/8.3/90° C, Load stage fail (ASTM D 5182)	>12	>12	11

**[0052]** As shown by the results in the foregoing table, Fluid A and Fluid B, having relatively lower viscosities than commercially available DCTF (Fluid C), exhibited significantly improved extreme pressure performance despite the lower viscosities of Fluid A and Fluid B.

[0053] It is believed that the sulfur to phosphorus and/or sulfur to boron ratios in the lower viscosity fluids have a significant impact on the load carrying capability of the fluids. Accordingly, fluids were prepared according to the above

formulation so that the fluids had a range of sulfur, phosphorus, and boron ratios, and kinematic viscosities ranging from about 5 to about 7. The sulfur content for fluid Nos. 1, 3, 5, and 7 was 256 ppm and for fluid Nos. 2, 4, 6, and 8 was about 2511 ppm. The FZG test rig results are given in the following table.

Table 2

5

10

15

20

35

45

50

55

Fluid	KV	A10/16.6R/90	A/8.3/90	S/P ratio	S/B ratio
No.	(cSt @100°C)	Load Stage Fail	Load Stage Fail		
1	5.40	5	9	0.58	1.38
2	5.28	6	>12	5.70	13.57
3	5.09	4	9	1.24	3.46
4	4.95	8	>12	12.19	33.93
5	6.67	6	11	0.58	1.38
6	7.15	6	>12	5.70	13.57
7	6.49	4	9	1.24	3.46
8	6.42	8	>12	12.19	33.93

**[0054]** As shown by the FZG test results using the A/8.3/90 gear and test conditions, higher levels of sulfur (Fluid Nos. 2, 4, 6, and 8) improved load state performance at all viscosities irrespective of the phosphorus and boron levels in the compositions.

[0055] By contrast, the A10/16.6R/90 gear and test conditions illustrated in the above Table 2 provided a different response to sulfur and phosphorus levels compared to the A/8.3/90 gear and test conditions. For the A10/16.6R/90 gear and test conditions, a higher level of sulfur (Fluid Nos. 4 and 8) improved the extreme pressure performance of the fluids only at a lower level of phosphorus, i.e., higher S/P ratios. For example, Fluid No. 2 had a tenfold increase in sulfur but the same phosphorus content as Fluid No. 1 and Fluid No. 5 had a tenfold increase in sulfur but the same phosphorus content as Fluid No. 6. The A10/16.6R/90 performance of Fluid Nos. 2 and 6 were the same or only slightly better than Fluid Nos. 1 and 5. Fluid Nos. 4 and 8 having an S/P ratio of about 12 had significantly better extreme pressure performance than Fluid Nos. 2 and 6 due to the lower level of phosphorus in the fluids.

**[0056]** In order to determine the levels of sulfur, phosphorus, and boron that provide desirable extreme pressure performance using the A10/16.6R/90 gear and test conditions, the FZG test rig results provided in Table 2 were subjected to regression analysis to provide correlation coefficients for the equation  $y = m_1x_1 + m_2x_2 \dots m_nx_n$  where x is the variable and y is the observed response. The regression analysis of the data indicated that the ratio of sulfur to phosphorus has the greatest effect on load stage fail of the fluids tested. The sulfur to boron ratio also had a statistically significant effect on the extreme pressure performance of the fluids tested. Accordingly, a transmission fluid of the above formulation having a viscosity of 6.47 centistokes at 100° C, 1400 ppm sulfur, 201 ppm phosphorus, and 74 ppm boron gave an A10/16.6R/90 load stage fail of 8 and an A/8.3/90 load stage fail of >12.

**[0057]** At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0058] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the embodiments disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

[0059] The invention also relates to the following embodiments (1) to (35):

(1.) A relatively low viscosity transmission fluid composition comprising a lubricant basestock, at least one active sulfur-containing component, and at least one phosphorus-containing compound, wherein an active sulfur atom content of the composition is greater than about 0.02 wt%, a ratio of active sulfur atoms to phosphorus atoms in the composition is above about 5, and the composition has a viscosity at 100 °C ranging from about 4 to less than about 7 centistokes.

5

10

15

25

- (2.) The composition of embodiment (1), wherein the at least one phosphorus-containing compound comprises a boronated/phosphorylated dispersant and wherein an active sulfur atom to boron atom ratio in the composition is greater than about 15.
- (3.) The composition of embodiment (1), wherein the composition has a Brookfield viscosity of less than about 30,000 centipoise at -40 °C.
- (4.) The composition of embodiment (1) wherein the basestock selected from the group consisting of Group II basestocks, Group III basestocks, gas to liquid basestocks, and mixtures thereof.
- (5.) The composition of embodiment (1), further comprising an antioxidant, a friction modifier, a corrosion inhibitor, a surfactant, and an antifoam agent.
- 20 (6.) The composition of embodiment (1), wherein the at least one phosphorus-containing compound is selected from the group consisting of phosphonates, phosphates, phosphate salts, phosphorylated succinimides, and mixtures thereof.
  - (7.) The composition of embodiment (1), wherein the composition has a viscosity index of greater than about 120.
  - (8.) The composition of embodiment (1), wherein the at least one active sulfur-containing component comprises an extreme pressure agent.
- (9.) The composition of embodiment (1). wherein the at least one active sulfur-containing component comprises a thiadiazole of the formula

$$R^{1}-S_{a}-C_{S}$$
 $C-S_{b}-R^{2}$ 

- wherein R<sup>1</sup> is selected from straight and branched chain alkyl groups having from 1 to 30 carbon atoms, R<sup>2</sup> is selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3.
- (10.) The composition of embodiment (1), wherein the at least one active sulfur-containing component comprises a compound selected from the group consisting of sulfonates, sulfurized olefins, sulfides, sulfates, and mixtures thereof.
  - (11.) The composition of embodiment (1), comprising a fluid suitable for use in a continuously variable transmission.
- 50 (12.) The composition of embodiment (1), comprising a fluid suitable for use in a dual clutch transmission.
  - (13.) The composition of embodiment (1), comprising a fluid suitable for use in an automatic transmission.
- (14.) An additive concentrate for a transmission fluid comprising at least one active sulfur-containing component and at least one phosphorus-containing compound sufficient to provide more than about 0.02 wt.% active sulfur to a finished transmission fluid, and a ratio of active sulfur atoms to phosphorus atoms in the finished transmission fluid of greater than about 5, wherein the finished transmission fluid of greater than about 5, wherein the finished transmission fluid containing the additive concentrate has a viscosity at 100 °C ranging from about 4 to less than

about 7 centistokes.

5

10

20

25

30

35

40

45

- (15.) The additive concentrate of embodiment (14), wherein the at least one phosphoruscontaining compound comprises a boronated/phosphorylated dispersant.
- (16.) The additive concentrate of embodiment (15), wherein a ratio of active sulfur atoms to boron atoms in the finished transmission fluid is greater than about 15.
- (17.) The additive concentrate of embodiment (14), wherein the finished transmission fluid containing the additive concentrate has a Brookfield viscosity of less than about 30,000 centipoise at -40 °C.
- (18.) The additive concentrate of embodiment (14), further comprising an antioxidant, a friction modifier, a corrosion inhibitor, a surfactant, and an antifoam agent.
- (19.) The additive concentrate of embodiment (14), wherein the at least one phosphorus containing compound is selected from the group consisting of phosphonates, phosphates, phosphates, phosphate salts, phosphorylated succinimides, and mixtures thereof.
  - (20.) The additive concentrate of embodiment (14), wherein the finished transmission fluid containing the additive concentrate has a viscosity index of greater than about 120.
  - (21.) The additive concentrate of embodiment (14), wherein the at least one active sulphur containing component comprises a thiadiazole of the formula

$$R^{1}-S_{a}-C \setminus S_{b}-R^{2}$$

wherein  $R^1$  is selected from straight and branched chain alkyl groups having from 1 to 30 carbon atoms,  $R^2$  is selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3.

- (22.) The additive concentrate of embodiment (14), wherein the at least one active sulphur containing component comprises a compound selected from the group consisting of sulfonates, sulfurized olefins, sulfides, sulfates, and mixtures thereof.
- (23.) A finished transmission fluid comprising the additive concentrate of embodiment (14) and a lubricant basestock selected from the group consisting of Group II basestocks, Group III basestocks, and gas to liquid basestocks.
- (24.) The finished transmission fluid of embodiment (23), comprising a fluid suitable for use in an automatic transmission.
- (25.) The finished transmission fluid of embodiment (23), comprising a fluid suitable for use in a continuously variable transmission.
- 50 (26.) The finished transmission fluid of embodiment (23), comprising a fluid suitable for use in a dual clutch transmission.
  - (27.) A method for improving fuel economy of a motor vehicle comprises the steps of:

providing a transmission fluid to a transmission of the motor vehicle wherein the transmission fluid comprises a lubricant basestock, at least one active sulfur-containing component, and at least one phosphorus-containing compound, wherein an active sulfur atom content of the transmission fluid is greater than about 0.02 wt.%, a ratio of sulfur atoms to phosphorus atoms in the transmission fluid is above about 5, and the

transmission fluid has a viscosity at 100° C ranging from about 4 to less than about 7 centistokes; and operating the motor vehicle.

- (28.) The method of embodiment (27), wherein the at least one phosphorus-containing compound comprises a boronated/phosphorylated dispersant.
  - (29.) The method of embodiment (28), wherein a ratio of active sulfur atoms to boron atoms in the transmission fluid is greater than about 15.
- 10 (30.) The method of embodiment (27), wherein the transmission fluid has a Brookfield viscosity of less than about 30,000 centipoise at -40 °C.
  - (31.) The method of embodiment (27), wherein the transmission fluid includes an antioxidant, a friction modifier, a corrosion inhibitor, a surfactant, and an antifoam agent.
  - (32.) The method of embodiment (27), wherein the at least one phosphorus containing compound is selected from the group consisting of phosphonates, phosphates, phosphate salts, phosphorylated succinimides, and mixtures thereof.
- 20 (33.) The method of embodiment (27), wherein the transmission fluid has a viscosity index of greater than about 120.
  - (34.) The method of embodiment (27), wherein the at least one active sulfur-containing component comprises a thiadiazole of the formula

$$R^{1}-S_{a}-C \setminus S_{b}-R^{2}$$

wherein R<sup>1</sup> is selected from straight and branched chain alkyl groups having from 1 to 30 carbon atoms, R<sup>2</sup> is selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3.

(35.) The method of embodiment (27), wherein the at least one active sulfur-containing component comprises a compound selected from the group consisting of sulfonates, sulfurized olefins, sulfides, sulfates, and mixtures thereof.

#### 40 Claims

5

15

25

30

35

45

- 1. A relatively low viscosity transmission fluid composition comprising a lubricant basestock, at least one active sulfur-containing component, and at least one phosphorus-containing compound, wherein an active sulfur atom content of the composition is greater than about 0.02 wt%, a ratio of active sulfur atoms to phosphorus atoms in the composition is above about 5, and the composition has a viscosity at 100°C ranging from about 4 to less than about 7 centistokes.
- 2. The composition of claim 1, wherein the at least one phosphorus-containing compound comprises a boronated/phosphorylated dispersant and/or wherein an active sulfur atom to boron atom ratio in the composition is greater than about 15.
- 3. The composition of claim 1 or 2, wherein the composition has a Brookfield viscosity of less than about 30,000 centipoise at -40 °C.
- The composition of any one of claims 1 to 3 wherein the basestock is selected from the group consisting of Group II basestocks, Group III basestocks, gas to liquid basestocks, and mixtures thereof.
  - 5. The composition of any one of claims 1 to 4, further comprising an antioxidant, a friction modifier, a corrosion inhibitor,

a surfactant, and an antifoam agent.

- **6.** The composition of any one of claims 1 to 5, wherein the at least one phosphorus-containing compound is selected from the group consisting of phosphonates, phosphates, phosphates, phosphate salts, phosphorylated succinimides, and mixtures thereof.
- 7. The composition of any one of claims 1 to 6, wherein the composition has a viscosity index of greater than about 120.
- **8.** The composition of any one of claims 1 to 7, wherein the at least one active sulfur-containing component comprises an extreme pressure agent.
  - **9.** The composition of any one of claims 1 to 8. wherein the at least one active sulfur-containing component comprises a thiadiazole of the formula

$$R^{1}-S_{a}-C_{S}-C_{S}-R^{2}$$

R'-S<sub>a</sub>-C<sub>\S</sub>C-S<sub>b</sub>-R

- wherein R<sup>1</sup> is selected from straight and branched chain alkyl groups having from 1 to 30 carbon atoms, R<sup>2</sup> is selected from hydrogen and straight and branched chain alkyl groups having from 1 to 30 carbon atoms, and a and b are independently selected from integers ranging from 1 to 3.
- **10.** The composition of any one of claims 1 to 9, wherein the at least one active sulfur-containing component comprises a compound selected from the group consisting of sulfonates, sulfurized olefins, sulfides, sulfates, and mixtures thereof.
- **11.** The composition of any one of claims 1 to 10, comprising a fluid suitable for use in one or more of the group consisting of a continuously variable transmission, a dual clutch transmission, and an automatic transmission.
- **12.** An additive concentrate for a transmission fluid comprising at least one active sulfur-containing component and at least one phosphorus-containing compound sufficient to provide a finished transmission fluid having a composition according to any one of claims 1 to 3 or 5 to 10.
  - **13.** A finished transmission fluid comprising the additive concentrate of claim 12 and a lubricant basestock selected from the group consisting of Group II basestocks, Group III basestocks, and gas to liquid basestocks.
  - **14.** The finished transmission fluid of claim 13, comprising a fluid suitable for use in one or more of the group consisting of an automatic transmission, a continuously variable transmission, and a dual clutch transmission.
- **15.** A method for improving fuel economy of a motor vehicle comprising the steps of: providing a transmission fluid to a transmission of the motor vehicle wherein the transmission fluid has a composition according to any one of claims 1 to 11; and operating the motor vehicle.

50

5

10

15

20

25

30

35

40



## **EUROPEAN SEARCH REPORT**

Application Number EP 06 02 3448

	DOCUMENTS CONSIDE	RED TO BE RELEVANT			
Category	Citation of document with indi of relevant passag		Rele to cla	vant aim	CLASSIFICATION OF THE APPLICATION (IPC)
Х	WO 2004/074414 A (NI TAKAHASHI MASATO [JP [JP]) 2 September 20 * tables 1,2 *	]; MATSUI SHIGEKI	1-15		INV. C10M141/10 C10M171/02
P,X	& EP 1 598 412 A (NI 23 November 2005 (20 * paragraphs [0001], tables 1,2 *	05-11-23)	1-15		
Х	EP 1 233 051 A (ETHY 21 August 2002 (2002 * paragraphs [0026] claim 1; tables *	-08-21)	1-14		
P,X	INC [US]; SULLIVAN W SHI-MING [) 2 Novemb			14	
A	US 5 358 650 A1 (SRI AL) 25 October 1994 * claims; examples *		Г 1-15		TECHNICAL FIELDS SEARCHED (IPC)
Х	US 4 212 753 A (HORO 15 July 1980 (1980-0 * examples; table 1	7-15)	1,4, 11-1		
A	US 5 225 093 A1 (CAM AL) 6 July 1993 (199 * column 19, lines 3	 PBELL DONALD G [US] ET 3-07-06) -15 *	Г 1-15		
А	US 4 507 215 A1 (SCH 26 March 1985 (1985- * the whole document	03-26)			
	The present search report has be	en drawn up for all claims  Date of completion of the search			Foundation
	Munich	19 March 2007		Ka <i>z</i>	emi, Pirjo
X : part Y : part docu A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another unent of the same category nological background -written disclosure mediate document	T : theory or princip E : earlier patent do after the filing da D : document cited L : document cited	ocument, b ate in the appl for other re	ng the ir ut publis lication easons	nvention shed on, or

### ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 06 02 3448

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-03-2007

	Patent document cited in search report		Publication date	Patent family member(s)		Publication date	
	WO 2004074414	Α	02-09-2004	EP KR :	1598412 20050098956 2006135378	Α	23-11-2005 12-10-2005 22-06-2006
	EP 1598412	Α	23-11-2005	WO KR :		A1 A A1	02-09-2004 12-10-2005 22-06-2006
	EP 1233051	A	21-08-2002	BR CN JP SG	0200492 1371964 2002285184 92829	A A	03-12-2002 02-10-2002 03-10-2002 19-11-2002
	WO 2006115666	Α	02-11-2006	NONE			
	US 5358650	A1		NONE			
	US 4212753	Α	15-07-1980	NONE			
	US 5225093	A1		NONE			
	US 4507215	A1		NONE			
-							

FORM P0459

© For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

### Patent documents cited in the description

US 27331 A [0017] US 2719125 A [0022] US 2719126 A [0022] US 3087937 A [0022] US 3172892 A [0024] US 3202678 A [0024] US 3216936 A [0024] US 3219666 A [0024] US 3254025 A [0024] [0030] US 3272746 A [0024] US 4234435 A [0024] US 3331776 A [0026] US 3381022 A [0026] US 3522179 A [0026] US 3275554 A [0027] US 3394576 A [0027] US 3438757 A [0027] US 3454555 A [0027] US 3565804 A [0027] US 3671511 A [0027] US 3821302 A [0027] US 2459112 A [0028] US 2962442 A [0028] US 2984550 A [0028] US 3036003 A [0028] US 3166516 A [0028] US 3236770 A [0028] US 3368972 A [0028] US 3413347 A [0028] US 3442808 A [0028] US 3448047 A [0028] US 3454497 A [0028] US 3459661 A [0028] US 3493520 A [0028] [0029] US 3539633 A [0028] US 3558743 A [0028] US 3586629 A [0028] US 3591598 A [0028] US 3600372 A [0028] US 3634515 A [0028] US 3649229 A [0028] US 3697574 A [0028]

US 3703536 A [0028] [0030]

US 3704308 A [0028]

US 3725277 A [0028]

US 3725480 A [0028] US 3726882 A [0028] US 3736357 A [0028] US 3751365 A [0028] US 3756953 A [0028] US 3793202 A [0028] US 3798165 A [0028] US 3798247 A [0028] US 3803039 A [0028] US 3872019 A [0028] US 3904595 A [0028] US 3957746 A [0028] US 3980569 A [0028] US 3985802 A [0028] US 4006089 A [0028] US 4011380 A [0028] US 4025451 A [0028] US 4058468 A [0028] US 4083699 A [0028] US 4090854 A [0028] US 4354950 A [0028] US 4485023 A [0028] US 3329658 A [0029] US 3449250 A [0029] US 3519565 A [0029] US 3666730 A [0029] US 3687849 A [0029] US 3702300 A [0029] US 3087936 A [0030] US 3281428 A [0030] US 3282955 A [0030] US 2284409 A [0030] US 2284410 A [0030] US 3338832 A [0030] US 3344069 A [0030] US 3533945 A [0030] US 3658836 A [0030] US 3718663 A [0030] US 4455243 A [0030] US 4652387 A [0030] US 5372735 A [0035] US 5441656 A [0035] US 5344579 A [0036] US 3974081 A [0043] US 4029587 A [0043]