

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 466 023 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

26.10.2005 Bulletin 2005/43

(21) Application number: **02805163.9**

(22) Date of filing: **16.12.2002**

(51) Int Cl.7: **C21D 1/58**

(86) International application number:
PCT/US2002/040160

(87) International publication number:
WO 2003/052145 (26.06.2003 Gazette 2003/26)

(54) **QUENCHING OIL COMPOSITIONS**

ABSCHRECKÖLZUSAMMENSETZUNGEN

COMPOSITIONS D'HUILE DE TREMPÉ

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SI SK TR**

(30) Priority: **18.12.2001 US 341612 P**

(43) Date of publication of application:
13.10.2004 Bulletin 2004/42

(73) Proprietor: **The Lubrizol Corporation**
Wickliffe, Ohio 44092-2298 (US)

(72) Inventors:
• **SWEET, William, R.**
Richmond Hts., OH 44143 (US)

• **SIVIK, Matthew, R.**
Broadview Hts., OH 44147 (US)

(74) Representative: **Mallalieu, Catherine Louise et al**
D Young & Co
120 Holborn
London EC1N 2DY (GB)

(56) References cited:
EP-A- 0 113 157 **GB-A- 951 139**
US-A- 3 159 510 **US-A- 3 498 850**
US-A- 3 855 014 **US-A- 5 250 122**
US-A- 5 376 186 **US-B1- 6 239 082**
US-B1- 6 310 009

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 466 023 B1

DescriptionFIELD OF THE INVENTION

[0001] This invention relates to oil compositions that are useful as quenching oils used in heat treating of metals, particularly ferrous metals such as steel.

BACKGROUND OF THE INVENTION

[0002] Desired hardness and strength properties of metals, particularly ferrous metals and especially metal alloys such as carbon steel and alloy steel, are secured by heat treatment of the metal object. The properties usually depend upon establishment of certain physical structures in the metal. The production of the desired physical structures is obtained by heating the metal to a temperature where the structure is present, then by arresting at the desired point the changes in the internal structure which take place during cooling of the metal from high temperatures. Quick cooling by quenching the heated object in a quenching medium makes it possible to arrest the physical changes at the desired point during cooling.

[0003] Quenching in the quenching medium is carried out in such a manner that the physical changes in the metal are arrested at the desired point, usually at the point at which maximum hardness is obtained. Subsequently, the heat treated and quenched object may be subjected to treatment at lower temperature (annealing or tempering) to provide the desired degree of toughness and ductility.

[0004] For many years mineral oil based quenching fluids have been used. Previously, aqueous quenching media were employed. The aqueous fluids provided extremely rapid cooling setting up excessive amounts of internal stress in the object. Mineral oil based fluids avoided this difficulty, but often did not provide a sufficiently high cooling rate to secure desirable properties in pieces formed of materials having high critical cooling rates to develop maximum strength and hardness or to quench pieces of high mass to surface ratios to develop hardness and strength to maximum depth.

[0005] It is also desirable to provide quench oils that possess sufficient durability, cleanliness and consistency. Durability refers to additive lifetime after being exposed to thermal stressing while consistency relates to constant additive performance over time. Cleanliness is measured using a coker test.

[0006] A detailed description of heat treating of steel appears at pages 961 et seq of the Metals Handbook, Desk Edition, Second Edition, J.R. Davis, Ed., ASM International, Metals Park, OH, USA (1998). A discussion of quenching appears at pages 973-975 of that text.

[0007] U.S. Patent 2,340,724 relates to quenching oils comprising a light mineral quenching oil and an oil-soluble, heat stable, high molecular weight iso-olefin polymerization product in a controlled amount adequate to produce a quenching oil composition having an initial 5-second quenching speed of at least 22.0 percent without substantially modifying the stress-reducing characteristics of the oil. Polymers of molecular weight 1,000 to 10,000, and particularly, isobutylene polymerization product, are said to be particularly advantageous.

[0008] U.S. Patent 3,489,619 relates to oil compositions described as having good high temperature stability and useful as a heat transfer oil for the quenching of metals. The oil comprises a major proportion of a hydrocarbon lubricating oil into which has been dispersed a minor proportion of an alkali metal phosphate, silicate or borate with the aid of a minor proportion of a high molecular weight monocarboxylic acid, dicarboxylic acid or dicarboxylic acid anhydride.

[0009] U.S. Patent 3,567,640 describes a quenching oil composition comprised of a major portion of a petroleum oil having a viscosity within the range of about 40 to about 300 SUS at 100°F and a flash point in excess of 250°F and about 2% to about 15% by weight of a quench oil additive, which is an oil soluble petroleum resin produced from distillates of cracked petroleum stock having a melting point of at least 40°C and an aniline point value of less than 50°C.

[0010] U.S. Patent 3,855,014 describes an improved quenching oil composition comprising a major amount of a quench oil of lubricating viscosity; a minor amount of at least one carbon-linked poly-phenate metal compound sufficient to improve the anti-staining properties of the composition and at least one naphthyl amine sufficient to improve the resistance to oxidation of the composition. The composition may also include a minor amount of at least one of certain diamine components said to provide further improved oxidation resistance.

[0011] U.S. Patent 5,015,404 describes an oil composition containing 100 parts by weight of a base oil selected from the group consisting of mineral base oil, synthetic base oil and mixtures thereof, and 0.1 to 20 parts by weight of a hydrogenated oil obtained by hydrogenating an oil selected from the group consisting of coal type tar, oil produced by fractionating coal type tar, a hydrocarbon obtained by thermally cracking petroleum and having a boiling point of not lower than 200°C, a hydrocarbon obtained by catalytically cracking petroleum and having a boiling point of not lower than 200°C, a hydrocarbon obtained by catalytically reforming petroleum and having a boiling point of not lower than 200°C, and mixtures thereof, whereby the hydrogenated oil has the hydrogen-donating properties of not lower than three times the hydrogen-donating properties of the base oil at temperatures of not lower than 350°C.

[0012] U.S. Patent 5,250,122 discloses a heat treating oil composition which comprises (A) at least one base oil

selected from a mineral oil and a synthetic oil each having a sulfur content of not more than 300 ppm and (B) at least one member selected from alkaline earth metal salts of salicylic acid. There is also disclosed a heat treating oil composition which comprises (I) a base oil having a sulfur content of 3 to 1000 ppm consisting of said (A) component and (C) at least one member selected from a sulfur and a sulfur compound, along with (II) various additives for quenching. This heat treating oil composition is said to be suitable for quenching under the condition of a high oil temperature and capable of obtaining a treated metal excellent in brightness and having a minimized distortion.

[0013] U.S. Patent 5,376,186 describes a heat treating oil composition which comprises a base oil adjusted to have a total sulfur content of 3 to 1000 ppm comprising (A) at least one base oil selected from a mineral oil and a synthetic oil each having a sulfur content of not more than 300 ppm and (C) at least one member selected from a sulfur and a sulfur compound, and (B) at least one additive selected from an alkaline earth metal salt of sulfonic acid, that of a phenol, alkenyl succinic acid derivatives, fatty acid or its derivatives and phenol-based and amine-based antioxidants. The above-mentioned heat treating oil composition is said to be suitable for quenching under a condition of a high oil temperature to realize a treated metal product having a excellent brightness and little distortion.

[0014] U.S. Patent 5,487,796 relates to a method of quenching metals, in particular steel alloys includes treatment of the article being quenched in a boiling aqueous solution of sodium tetraborate, with gas being additionally introduced into the quench bath. The supply of gas enables a continuous operation in a wide range of application and avoids the use of conventional less environmentally friendly quenching media (oils).

[0015] U.S. Patent 5,879,743 describes a wear-resistant hardfacing and a method for applying such a hardfacing. A finely powdered, wear-resistant alloy and a polyvinyl alcohol (PVA) solution slurry is coated onto the metal surface of a tool, implement, or similar item to be hardfaced. Alternatively, a binding coating of PVA solution may be applied to the metal surface followed by application of a layer of a powdered alloy. After the slurry or PVA binding coating has dried, leaving a dry coat of alloy in a PVA matrix, the metal surface is heated to the fusion temperature of the alloy in vacuum, in an inert gas atmosphere, or in hydrogen atmosphere. The metal item with the fused coating is heat treated to impart desired mechanical properties to the part substrate material. The method of the present invention gives a smooth, dense coating of the wear-resistant hardfacing without nonmetallic inclusions.

[0016] U.S. Patent 6,239,082 describes petroleum quench oils described as effective for high speed cooling of heated metals and metal hardening. The petroleum quench oils contain natural or synthetic base oils having a minimum flash point of about 120°C and a combination of poly(iso)alkylene and poly(iso)alkylene succinic anhydride or succinic acid. A method for cooling heated metal to harden it, improve the metallurgical consistency, improve machinability and reduce residue on quenched metal parts is also disclosed comprising quenching the heated metal part in a quench oil containing natural or synthetic base oils having a minimum flash point of about 120°C and a combination of poly(iso)alkylene and poly(iso)alkylene succinic anhydride or succinic acid.

[0017] The quench oils of the instant invention afford durability, consistency and suitable quenching characteristics. Suitable quenching characteristics include a high maximum cooling rate and a high maximum cooling rate temperature signifying collapse of the vapor barrier between the workpiece and the quenching oil, and a lower cooling rate (6-8°C) after the workpiece has reached 300°C to prevent thermal distortion/cracking.

SUMMARY OF THE INVENTION

[0018] The instant invention is directed to a quenching oil composition comprising

(1) an oil having kinematic viscosity (ASTM Test Method D-445) at 40°C ranging from about 4 to about 45 mm²sec⁻¹ (about 40 to about 210 Saybolt Universal Seconds (SUS)) and having a saturated content from about 80% to about 100%;

(2) an aliphatic polyolefin having \bar{M}_n ranging from about 300 to about 10,000; and

(3) at least one member selected from members of the groups consisting of

(a) a metal salt of hydrocarbyl substituted phenols, salicylic acids, carboxylic acids, and sulfonic acids and alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives; and optionally, at least one member selected from members of the groups consisting of

(b) hydrocarbyl substituted succinic esters, amides, ester-amides, imides, amine salts, acid-esters, acid-amides ester-amine salts, amide-amine-salts and acid-amine salts.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] As used herein, the terms "hydrocarbyl" or "hydrocarbon based" mean that the group being described has predominantly hydrocarbon character within the context of this invention. These include groups that are purely hydrocarbon in nature, that is, they contain only carbon and hydrogen. They may also include groups containing substituents

or atoms which do not alter the predominantly hydrocarbon character of the group. Such substituents may include halo-, alkoxy-, nitro-, hydroxyl, etc. These groups also may contain heteroatoms. Suitable heteroatoms will be apparent to those skilled in the art and include, for example, sulfur, nitrogen and oxygen. Therefore, while remaining predominantly hydrocarbon in character within the context of this invention, these groups may contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

[0020] In general, no more than about three non-hydrocarbon substituents or heteroatoms, and preferably no more than one, will be present for every 10 carbon atoms in the hydrocarbon or hydrocarbon based groups. Most preferably, the groups are purely hydrocarbon in nature, that is, they are essentially free of atoms other than carbon and hydrogen.

[0021] It must be noted that as used in this specification and in the appended claims, the singular forms also include the plural unless the context clearly dictates otherwise. Thus the singular forms "a", "an", and "the" include the plural; for example "an amine" includes mixtures of amines of the same type. As another example the singular form "amine" is intended to include both singular and plural unless the context clearly indicates otherwise.

The Oil

[0022] The quenching oil compositions of this invention comprise at least one oil having kinematic viscosity (ASTM Test Method D-445) at 40°C ranging from about 4 to about 45 mm²sec⁻¹ (40 to about 210 SUS) and having a saturated content from about 80% to about 100%. Both mineral oils and synthetic oils are useful. Mixtures of these oils are useful. In one preferred embodiment, the oil is a paraffinic mineral oil, particularly a solvent refined paraffinic oil. In another preferred embodiment, the oil is a hydrotreated mineral oil having kinematic viscosity of about 60 to about 90 SUS. In yet another preferred embodiment, the oil is a poly-alphaolefin oligomer, preferably a polyoctene or polydecene oligomer.

[0023] Examples of useful oils include Excel/Paralube 70N, Excel/Paralube 75HC, (both from Pennzoil/Conoco) and Ergon® Hygold P70N.

The Polyolefin

[0024] The quenching oil compositions of this invention contain (2) a polyolefin having \bar{M}_n ranging from about 300 to about 10,000, preferably from about 500 to about 5,000 and more often from about 1,000 to about 3,000 and often ranging from about 1,500 to about 3,000.

[0025] In one preferred embodiment, the polyolefin is an aliphatic polyolefin derived from at least one alpha olefin containing from 3 to about 8 carbon atoms. Polyolefins derived from more than one olefin, for example ethylene-propylene copolymers, are useful. Polypropylene and polybutenes, especially polyisobutylene, are preferred. Polyisobutylene is particularly preferred.

[0026] In another preferred embodiment, the polyolefin is an olefin-polyene, preferably diene, especially preferred non-conjugated diene, copolymer, derived from at least one olefin, preferably an alpha olefin containing from about 3 to about 8 carbon atoms and the ratio of total number of moles of olefin to moles of polyene ranges from about 100:1 to about 1:1, preferably 25:1 to 1:2 and most preferably, 15:1 to 1:1. In a preferred embodiment, the olefin is isobutylene. Useful polymers of this type are commercially available, for example from BASF and BP Chemicals.

[0027] In one embodiment, the polyolefin is an olefin-diene copolymer comprising from about 0.5 to about 5 moles of units derived from diene per mole of copolymer based on \bar{M}_n of copolymer. In another embodiment, the polyolefin is an olefin-polyene copolymer, wherein the olefin contains from 3 to about 8 carbon atoms and weight ratio of olefin to polyene ranges from about 250:1 to about 1:4, preferably 25:1 to 1:2 and most preferably 15:1 to 1:1. In each of these embodiments, the olefin comprises isobutylene. Examples of olefin-diene copolymers include butyl rubbers (isobutylene-isoprene) and commercially available ethylene-propylene-diene terpolymers sold by Uniroyal Chemicals under the tradename TRILENE®.

The Metal Salt

[0028] The quenching oil compositions of this invention contain at least one member selected from the group consisting of a metal salt of hydrocarbyl substituted phenols, salicylic acids, carboxylic acids, and sulfonic acids and alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives. The metal salts may be acidic, neutral or basic, often referred to as 'overbased'.

[0029] The relative amount of metal present in "basic salts" is frequently indicated by the expression "metal ratio" (abbreviated MR), which is defined as the number of equivalents of metal present compared to a "normal", stoichiometric amount. Thus, for example, a basic salt containing twice the amount of metal compared to the stoichiometric amount, has a metal ratio (MR) of 2. For the purposes of this invention, the metal ratio of metal salts of phenols and salicylic acids ranges from about 0.5 to about 5, preferably from about 0.5 to about 2 and the metal ratio of metal salts

of sulfonic acids ranges from about 1 to about 20, preferably from about 1 to about 3.

[0030] The basicity of the metal salts used in the present invention generally is expressed in terms of a total base number (TBN). TBN is the amount of acid (perchloric or hydrochloric) needed to neutralize all of the metal salt's basicity. The amount of acid is expressed as potassium hydroxide equivalents. Total base number is determined by the procedure described in ASTM D-2896. Typically, the metal salt has TBN ranging from about 45 to about 900, preferably from about 100 to about 800.

[0031] Metal salts and techniques for preparing them are well known to those skilled in the art. Neutral and acidic salts are generally prepared by contacting the acidic reactant with a metal reactant to form the salt. Overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent for said acidic organic material, a stoichiometric excess of a metal base, and a promoter.

[0032] The acidic organic compounds useful in making the metal salts of the present invention include carboxylic acids, sulfonic acids, phenols and hydrocarbyl substituted saligenin derivatives or mixtures of two or more thereof.

[0033] Salicylic acids are considered as both phenols and carboxylic acids. Salicylic acids can be aliphatic hydrocarbon-substituted salicylic acids wherein each aliphatic hydrocarbon substituent contains an average of at least about 8 carbon atoms per substituent.

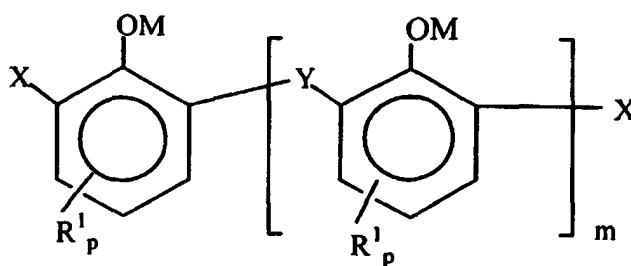
[0034] Sulfonic acids useful in the invention include the sulfonic and thiosulfonic acids. The sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. Illustrative examples of sulfonic acids include hydrocarbyl substituted naphthalene sulfonic acids, hydrocarbyl substituted benzene sulfonic acids, petroleum sulfonic acid and the like.

[0035] Phenols useful in making the metal salts used in this the invention can be represented by the formula $(R_1)_a-Ar-(OH)_b$, wherein R_1 is a hydrocarbon group; Ar is an aromatic group; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar.

[0036] While the term "phenol" is used herein, it is to be understood that this term refers to both mononuclear and polynuclear aromatic compounds. Polynuclear groups can be of the fused type wherein an aromatic nucleus is fused at two points to another nucleus or of the linked type wherein at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages to each other.

[0037] Saligenin, also known as salicyl alcohol and o-hydroxybenzyl alcohol and derivatives thereof are useful for preparing metal salts used in this invention.

[0038] The alkaline earth metal salts of saligenin derivatives of the present invention can be represented by the formula



where M is a valence of an alkaline earth metal, and the identity, description, and amounts of other symbols are as set forth hereinbelow.

[0039] The subscript "m" can be 0 to 10. This means that the number of rings can be 1 to 11, although it is to be understood that the upper limit of "m" is not a critical variable. Preferably, m is 2 to 9, more preferably 3 to 6.

[0040] At least one ring, and preferably most of the rings contain at least one R¹ substituent, which is a hydrocarbyl group, preferably an alkyl group, containing 1 to 60 carbon atoms, more preferably 7 to 18 carbon atoms. The R¹ groups will normally comprise a mixture of various chain lengths, so that the foregoing numbers usually represent an average number of carbon atoms in the R¹ groups (number average). Each ring in the structure will be substituted with 0, 1, 2, or 3 such R¹ groups (that is, each p is independently 0, 1, 2, or 3, most typically 1, and different rings in a given molecule may contain different numbers of such substituents. At least one aromatic ring in the molecule must contain at least one R¹ group, and the total number of carbon atoms in all the R¹ groups in the molecule should be at least 7, preferably at least 12.

[0041] In the above structure the X and Y groups may be seen as groups derived from formaldehyde or a formalde-

hyde source, by condensative reaction with the aromatic molecule. While various species of X and Y may be present in the molecules in question, the commonest species comprising X are CHO (aldehyde functionality) and CH₂OH (hydroxymethyl functionality); similarly the commonest species comprising Y are CH₂ (methylene bridge) and CH₂OCH₂ (ether bridge). The relative molar amounts of these species in a sample of the above material can be determined by ¹H/¹³C NMR as each carbon and hydrogen nucleus has a distinctive environment and produces a distinctive signal.

[0042] Alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives are described in detail in U.S. Patent 6,310,009 which is hereby incorporated herein by reference.

[0043] The metal compounds useful in making the metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements), including alkali metals (sodium, potassium, lithium, etc.) and Group 1b metals such as copper. Group 2 metals of the metal base include the Group 2a alkaline earth metals (magnesium, calcium, barium, etc.) as well as the Group 2b metals such as zinc or cadmium.

[0044] An acidic material is used to accomplish the formation of the basic metal salt. A promoter is a chemical employed to facilitate the incorporation of metal into the basic metal compositions. A particularly comprehensive discussion of suitable promoters is found in U.S. Patents 2,777,874, 2,695,910, and 2,616,904.

[0045] As noted hereinabove, the metal of the metal salt comprises at least one of Group 1 and Group 2 metal, preferably, an alkali and/or an alkaline earth metal. In one preferred embodiment, the metal salt is an alkaline earth metal salt.

[0046] In one preferred embodiment, the metal salt comprises a metal salt of sulfur or methylene coupled hydrocarbyl substituted phenols or salicylic acids. In one preferred embodiment, the composition comprises a metal salt of a hydrocarbyl substituted phenol. In another preferred embodiment, the composition comprises a metal salt of a Mg or Ca methylene coupled C₇₋₁₅ aliphatic group substituted phenate. In yet another preferred embodiment the composition comprises an alkaline earth metal salt of hydrocarbyl substituted saligenin derivatives.

[0047] In one preferred embodiment, the composition comprises a metal salt of a hydrocarbyl substituted salicylic acid. In another embodiment, the composition comprises a metal salt of a hydrocarbyl substituted sulfonic acid. In yet another embodiment, the composition comprises a metal salt of a hydrocarbyl substituted carboxylic acid.

[0048] Mixtures of two or more of these metal salts may be used.

Hydrocarbyl Substituted Succinic Derivatives

[0049] The quenching oil compositions of this invention may, in an optional embodiment, also contain hydrocarbyl substituted succinic derivatives selected from the group consisting of esters, amides, ester-amides, imides, amine salts, acid-esters, acid-amides ester-amine salts, amide-amine-salts and acid-amine salts. The hydrocarbyl substituent typically has \bar{M}_n ranging from about 500 to about 5000, preferably from about 900 to about 2500.

[0050] These succinic derivatives are well known to those skilled in the art.

[0051] The quenching oil compositions of this invention typically comprise from about 0.2% to about 10%, preferably to about 5% by weight of the aliphatic polyolefin (2), and a total of from 0.2% to about 10% by weight of a metal salt of hydrocarbyl substituted phenols, salicylic acids and sulfonic acids and alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives, and optionally at least one of hydrocarbyl substituted succinic esters, amides, ester-amides, imides, amine salts, acid-esters, acid-amides, ester-amine salts, amide-amine salts and acid-amine salts, provided that the composition comprises at least one of a metal salt and a succinic derivative. When used, the succinic derivatives are present in amounts ranging from about 0.1% to about 5% by weight.

[0052] In one preferred embodiment, the composition comprises from about 0.2% to about 5% by weight of the aliphatic polyolefin (2), and (3)(a) from about 0.2% to about 5% by weight of at least one metal salt wherein the weight ratio of (2):(3)(a) ranges from about 10: 1 to about 1: 10.

[0053] In another preferred embodiment, the composition comprises from about 0.2% to about 5% by weight of the aliphatic polyolefin (2), a total of from about 0.2% to about 4% by weight of (3)(a) at least one metal salt; and a total of from about 0.1 % to about 4% by weight of at least one hydrocarbyl substituted succinic derivative selected from the group consisting of amides, imides, amine salts, acid-amides and acid-amine salts wherein the weight ratio of polyolefin : metal salt : succinic derivative ranges from about (20-40) : (40-70) : (10-20).

[0054] This invention also relates to a method of heat treating metals comprising heating the metal to a temperature above its critical temperature and thereafter cooling the metal by immersion thereof into a quenching oil bath comprising the quenching oil composition of this invention.

[0055] The additive components may be incorporated into the base oil as individual components, added thereto in any order. Alternatively, and preferably, the additive components are added to the base oil as a concentrate which comprises the desired additives in appropriate ratios which, when incorporated into the base oil, provide a finished quenching oil composition containing the desired amount of each additive.

[0056] The following examples illustrate additive concentrates uses to prepare quenching oil compositions of this

invention. All parts are parts by weight and unless indicated otherwise, are on a neat chemical, i.e., oil and diluent free, basis.

TABLE 1

Example #	1	2	3	4	5	6	7	8	9
Parts by Weight									
Polyisobutylene ($\bar{M}_n \sim 1700$)	25	25	25	25	30	30	30	30	30
Ca (MR 0.85) Me C ₁₂ - Phenol (55% oil)						50		60	
Mg (MR<1) Me C ₁₂ - Saligenin (50% oil)		50	50	50	55		50		60
Ca (MR 0.8) Me C ₇ - Phenol (69% oil)	50								
Polyisobutenyl ($\bar{M}_n \sim 1700$) Succinimide (55% oil)	25	25	15	15		10	10		
Ca (MR 1.4) Petroleum Sulfonate (57% oil)			10						
Ca (MR 2.4) Petroleum Sulfonate (53% oil)				10	15	10	10	10	10
Me : methylene coupled									

[0057] The following examples illustrate compositions of this invention:

[0058] A series of quenching oil compositions is prepared, each member of the series containing 2% by weight of one of additive concentrates 1-5 in Pennzoil/Conoco Excel Paralube 75-HC (75N) oil. A second series is prepared, each member of the series containing 4% by weight of one of additive concentrates 1-2 and 4-5 in the same oil. A third series is prepared, each member containing 6% by weight of additive concentrates 1-2, and 4-5 in the same oil.

[0059] Two additional series of quenching oil compositions are prepared, each member of the first series containing 2% by weight of one of additive concentrates 6-9 and each member of the second series containing 4% by weight of one of additive concentrates 6-9 in Ergon Hygold P70N oil.

[0060] A portion of each of these oils as well as commercial quench oils is heat stressed by heating at 170°C for 22 hours while aerating at 10 liters per hour and tested with respect to the non-stressed quench oil samples.

[0061] Each sample is subjected to a one-minute quench test and a 3 hour panel coker test. The quench test quantifies the cooling characteristics of the quench oil sample and the panel coker test measures the tendency of the quench oil sample to stain and/or form deposits on hot metal surfaces. Similar results between corresponding heat stressed and unstressed oils samples provide an indication of durability and consistency of the test oils.

[0062] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

[0063] Except in the examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about". Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil that may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

[0064] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications that fall within the scope of the appended claims.

Claims

1. A quenching oil composition comprising

- (1) an oil having kinematic viscosity at 40°C ranging from 4 to 45 mm²sec⁻¹ (40 to 210 SUS) and having a saturated content from about 80% to about 100%;
 (2) an aliphatic polyolefin having \bar{M}_n ranging from about 300 to about 10,000; and
 (3) at least one member selected from members of the groups consisting of

(a) a metal salt of hydrocarbyl substituted phenols, salicylic acids, carboxylic acids, and sulfonic acids and alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives; and optionally
 (b) hydrocarbyl substituted succinic derivatives selected from the group consisting of esters, amides, ester-amides, imides, amine salts, acid-esters, acid-amides ester-amine salts, amide-amine-salts and acid-amine salts.

2. The composition of claim 1 wherein (1) the oil is a mineral oil and/or synthetic oil.
3. The composition of claim 1 or 2 wherein (2) the polyolefin is an olefin-polyene copolymer, wherein the olefin contains from about 3 to about 8 carbon atoms and the ratio of moles of olefin to moles of polyene ranges from about 100:1 to about 1:1.
4. The composition of any preceding claim comprising at least one member selected from the group consisting of (3) (a) a metal salt of hydrocarbyl substituted phenols, salicylic acids, carboxylic acids, and sulfonic acids and alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives.
5. The composition of claim 4 wherein (3)(a) comprises a metal salt of sulfur or methylene coupled hydrocarbyl substituted phenols or salicylic acids.
6. The composition of claim 4 wherein the metal ratio of metal salts of phenols, saligenin derivatives and salicylic acids ranges from about 0.5 to about 5 and the metal ratio of metal salts of sulfonic acids ranges from about 1 to about 20.
7. The composition of claim 4 wherein the metal salt (3)(a) has TBN ranging from about 45 to about 900, wherein TBN is the total base number determined in accordance with ASTM D-2896.
8. The composition of claim 4 wherein the metal salt is an alkaline earth metal salt.
9. The composition of claim 4 comprising a metal salt of a hydrocarbyl substituted phenol.
10. The composition of claim 9 wherein the metal salt is a Mg or Ca methylene coupled C₇₋₁₅ aliphatic group substituted phenate.
11. The composition of claim 4 comprising a metal salt of a hydrocarbyl substituted salicylic acid.
12. The composition of claim 4 comprising an alkaline earth metal salt of a hydrocarbyl substituted saligenin derivative.
13. The composition of claim 1 comprising from about 0.2% to about 10% by weight of the aliphatic polyolefin (2), and from 0.2% to about 10% by weight of (3)(a) a metal salt of hydrocarbyl substituted phenols, salicylic acids and sulfonic acids and alkaline earth metal salts of hydrocarbyl substituted saligenin derivatives; and from 0 to about 5% by weight of (3)(b) hydrocarbyl substituted succinic esters, amides, ester-amides, imides, amine salts, acid-esters, acid-amides, ester-amine salts, amide-amine salts and acid-amine salts.
14. A method of heat treating metals comprising heating the metal to a temperature above its critical temperature and thereafter cooling the metal by immersion thereof into a quenching oil bath comprising the quenching oil composition of any one of claims 1 to 13.

Patentansprüche

1. Abschreckölzusammensetzung, die umfaßt:

(1) ein Öl mit einer kinematischen Viskosität im Bereich von 4 bis 45 mm² sec⁻¹ (40 bis 210 SUS) bei 40°C

und einem Sättigungsgehalt von etwa 80% bis etwa 100%,

(2) ein aliphatisches Polyolefin mit \bar{M}_n im Bereich von etwa 300 bis etwa 10.000 und

(3) wenigstens einen Bestandteil, ausgewählt aus Bestandteilen der Gruppen, bestehend aus

(a) einem Metallsalz von Hydrocarbyl-substituierten Phenolen, Salicylsäuren, Carbonsäuren und Sulfonsäuren und Erdalkalimetallsalzen von Hydrocarbyl-substituierten Saligeninderivaten und optional

(b) Hydrocarbyl-substituierten Succinderivaten, ausgewählt aus der Gruppe, bestehend aus Estern, Amiden, Esteramiden, Imiden, Aminsäuren, Säureestern, Säureamiden, Esteraminsäuren, Amid-Amin-Salzen und Säureaminsäuren.

2. Zusammensetzung nach Anspruch 1, wobei (1) das Öl ein Mineralöl und/oder ein synthetisches Öl ist.

3. Zusammensetzung nach Anspruch 1 oder 2, wobei (2) das Polyolefin ein Olefin-Polyen-Copolymer ist, wobei das Olefin etwa 3 bis etwa 8 Kohlenstoffatome enthält und das Molverhältnis von Olefin zu Polyen im Bereich von etwa 100:1 bis etwa 1:1 liegt.

4. Zusammensetzung nach einem der vorangegangenen Ansprüche, welche wenigstens einen Bestandteil enthält, der aus der Gruppe ausgewählt ist, bestehend aus (3)(a), einem Metallsalz von Hydrocarbyl-substituierten Phenolen, Salicylsäuren, Carbonsäuren und Sulfonsäuren und Erdalkalimetallsalzen von Hydrocarbyl-substituierten Saligeninderivaten.

5. Zusammensetzung nach Anspruch 4, wobei (3)(a) ein Metallsalz von Schwefel- oder Methylen-gekoppelten, Hydrocarbyl-substituierten Phenolen oder Salicylsäuren umfaßt.

6. Zusammensetzung nach Anspruch 4, wobei das Metallverhältnis von Metallsalzen von Phenolen, Saligeninderivaten und Salicylsäuren im Bereich von etwa 0,5 bis etwa 5 liegt und das Metallverhältnis von Metallsalzen von Sulfonsäuren im Bereich von etwa 1 bis etwa 20 liegt.

7. Zusammensetzung nach Anspruch 4, wobei das Metallsalz (3)(a) eine TBN im Bereich von etwa 45 bis etwa 900 hat, wobei TBN die Gesamtbasenzahl ist, die gemäß ASTM D-2896 bestimmt wurde.

8. Zusammensetzung nach Anspruch 4, wobei das Metallsalz ein Erdalkalimetallsalz ist.

9. Zusammensetzung nach Anspruch 4, welche ein Metallsalz eines Hydrocarbyl-substituierten Phenols umfaßt.

10. Zusammensetzung nach Anspruch 9, wobei das Metallsalz ein Methylen-gekoppeltes, mit einer aliphatischen C₇₋₁₅-Gruppe substituiertes Mg- oder Ca-Phenolat ist.

11. Zusammensetzung nach Anspruch 4, welche ein Metallsalz einer Hydrocarbyl-substituierten Salicylsäure umfaßt.

12. Zusammensetzung nach Anspruch 4, welche ein Erdalkalimetallsalz eines Hydrocarbyl-substituierten Saligeninderivats umfaßt.

13. Zusammensetzung nach Anspruch 1, die etwa 0,2 Gew.-% bis etwa 10 Gew.-% des aliphatischen Polyolefins (2) und 0,2 Gew.-% bis etwa 10 Gew.-% von (3)(a), einem Metallsalz von Hydrocarbyl-substituierten Phenolen, Salicylsäuren und Sulfonsäuren und Erdalkalimetallsalzen von Hydrocarbyl-substituierten Saligeninderivaten, und 0 bis etwa 5 Gew.-% von (3)(b), Hydrocarbyl-substituierten Succinestern, Amiden, Esteramiden, Imiden, Aminsäuren, Säureestern, Säureamiden, Esteraminsäuren, Amid-Amin-Salzen und Säureaminsäuren, enthält.

14. Verfahren zur Wärmebehandlung von Metallen, welches das Erhitzen des Metalls auf eine Temperatur oberhalb seiner kritischen Temperatur und nachfolgend das Kühlen des Metalls durch Eintauchen in ein Abschreckölbad, das die Abschreckölzusammensetzung nach einem der Ansprüche 1 bis 13 enthält, umfaßt.

Revendications

1. Composition d'huile de trempe comprenant :

(1) une huile ayant une viscosité cinématique à 40°C comprise dans l'intervalle de 4 à 45 mm²s⁻¹ (40 à 210 SUS) et ayant une teneur en composés saturés d'environ 80 % à environ 100 % ;

(2) une polyoléfine aliphatique ayant une valeur de \overline{M}_n comprise dans l'intervalle d'environ 300 à environ 10 000 ; et

(3) au moins un membre choisi parmi des membres des groupes consistant en

(a) un sel métallique de phénols, acides salicyliques, acides carboxyliques et acides sulfoniques à substituants hydrocarbyle et des sels de métaux alcalinoterreux de dérivés de saligénine à substituant hydrocarbyle ; et facultativement

(b) des dérivés succiniques à substituants hydrocarbyle, choisis dans le groupe consistant en des esters, des amides, des ester-amides, des imides, des sels d'amines, des acides-esters, des acides-amides, des esters-sels d'amines des amides-sels d'amines et des acides-sels d'amines.

2. Composition suivant la revendication 1, dans laquelle (1) l'huile est une huile minérale et/ou une huile synthétique.

3. Composition suivant la revendication 1 ou 2, dans laquelle (2) la polyoléfine est un copolymère oléfine-polyène, dans lequel l'oléfine contient environ 3 à environ 8 atomes de carbone et le rapport du nombre de moles de l'oléfine au nombre de moles de polyène est compris dans l'intervalle d'environ 100:1 à environ 1:1.

4. Composition suivant l'une quelconque des revendications précédentes, comprenant au moins un membre choisi dans le groupe consistant en (3) (a) un sel métallique de phénols, acides salicyliques, acides carboxyliques et acides sulfoniques à substituants hydrocarbyle et des sels de métaux alcalinoterreux de dérivés de saligénine à substituant hydrocarbyle.

5. Composition suivant la revendication 4, dans laquelle (3) (a) comprend un sel métallique de phénols ou d'acides salicyliques à substituants hydrocarbyle couplés avec le soufre ou des groupes méthylène.

6. Composition suivant la revendication 4, dans laquelle le rapport des métaux des sels métalliques de phénols, de dérivés de saligénine et d'acides salicyliques est compris dans l'intervalle d'environ 0,5 à environ 5 et le rapport des métaux des sels métalliques d'acides sulfoniques est compris dans l'intervalle d'environ 1 à environ 20.

7. Composition suivant la revendication 4, dans laquelle le sel métallique (3) (a) a un IBT compris dans l'intervalle d'environ 45 à environ 900, le IBT étant l'indice de basicité total déterminé suivant la norme ASTM D-2896.

8. Composition suivant la revendication 4, dans laquelle le sel métallique est un sel de métal alcalinoterreux.

9. Composition suivant la revendication 4, comprenant un sel métallique d'un phénol à substituant hydrocarbyle.

10. Composition suivant la revendication 9, dans laquelle le sel métallique est un phénate de Mg ou Ca substitué avec un groupe aliphatique en C₇ à C₁₅ couplé avec des groupes méthylène.

11. Composition suivant la revendication 4, comprenant un sel métallique d'un acide salicylique à substituant hydrocarbyle.

12. Composition suivant la revendication 4, comprenant un sel de métal alcalinoterreux d'un dérivé de saligénine à substituant hydrocarbyle.

13. Composition suivant la revendication 1, comprenant environ 0,2 % à environ 10 % en poids de la polyoléfine aliphatique (2), et 0,2 % à environ 10 % en poids (3) (a) d'un sel métallique de phénols, acides salicyliques et acides sulfoniques à substituants hydrocarbyle et des sels de métaux alcalinoterreux de dérivés de saligénine à substituant hydrocarbyle ; et 0 à environ 5 % en poids (3)(b) de dérivés succiniques à substituants hydrocarbyle consistant en esters, amides, ester-amides, imides, sels d'amines, acides-esters, acides-amides, esters-sels d'amines, amides-sels d'amines et acides-sels d'amines.

14. Procédé pour le traitement thermique de métaux, comprenant le chauffage du métal à une température supérieure à sa température critique et ensuite le refroidissement du métal par son immersion dans un bain d'huile de trempe comprenant la composition d'huile de trempe de l'une quelconque des revendications 1 à 13.