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QUENCHING COMPOSITION

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This invention relates to improved quenching oil compositions for use in the metallurgical industries and to the method of quenching metals therewith.

In the process of hardening metals such as steel, it is common practice to use as the quenching medium water, oil or compressed air, according to the type of steel. Recently salts or aqueous solutions of salts have also been used for this purpose but these have the disadvantage that they solidify or deposit solids on cooling to room temperature. Fatty oils, especially rapeseed oil, are used as quenching oils, but these have been gradually superseded by mineral quenching oils. It has also been proposed to harden and temper steels using baths containing naphthalene mono- or di-sulfonic acids or salts thereof or anthracene mono- or di-sulfonic acids or salts thereof. Sulfonic acids or their salts are mixed with water or oil to form the treating bath and the oils generally used are linseed oil, cotton seed oil and other fatty substances.

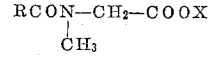
Quenching compositions of the above types are defective in a number of respects among which are that water or emulsion quenching causes stress and strains in the metal such as steel which results in warping and cracking thereof, rendering the metal unusable. Oil quenching, although essentially obviating this objectionable characteristic of water or emulsion quenching compositions, tend to leave adherent deposits on quenching metal surfaces which must be removed by relatively expensive buffing or machining operations prior to further processing of the metal. This, plus the fact that oil quenching is expensive and the life of such oil is short because of thermal and oxidation deterioration, thereby requiring continuous replacement with fresh oils, presents a pressing problem to the industry.

An object of the present invention is an improved process for quenching metals. A further object is to provide a quenching oil composition of superior speed and stability. Another object is to provide a quenching oil composition capable of producing bright quenched metal surfaces. Still other objects will be apparent from the following description of the invention.

The above objects may be attained in accordance with the present invention by quenching a metal in a thermally and oxidatively stable mixture of particular petroleum fractions which contains a critical amount within the range of from about 0.1% to about 2%, preferably between 0.2% and 0.5% by weight of a non-ash forming oil-soluble N—C_{10-24} acyl sarcosine and nitrogen-base salts or esters thereof. By the particular petroleum mixture is meant a blend of 50–95% (preferably 60–70%) of (1) a mineral oil fraction in the viscosity range of 80–250 SUS at 100° F., a viscosity index of at least 90, preferably between 95 and 120 and an aromatic content of at least 15%, preferably between 30 and 60%, such as a 100 SUS at 100° F. HVI neutral or 250 SUS at 100° F. HVI neutral and the balance of the blend being (2) a highly refined medium VI (70–80 VI) light mineral oil such as a spray base oil or transformer oil in the viscosity range of from 40 to 100 SUS at 100° F. and/or a heavy residue fraction such as a 150–210 bright stock or an asphalt or derivatives thereof. The surprising discovery made resides in the fact that both the mineral oil blend and the additive of the present invention exert a profound effect on both the quenching speed and surface brightness of the metal being treated. Thus using a conventional or ordinary quenching oil such as described in U.S. Patents 2,866,729, 2,485,103 or 2,340,724 with the additives of the present invention results in poor quick-quenching and only fair surface brightness and the same holds true when well known quenching additives such as metal sulfonates or certain polymeric compounds are used in the oil base blend of the present invention.

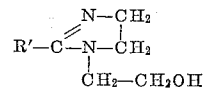
The N—C_{10-24} acyl sarcosines and derivatives thereof have the general formula

(I)



where R is a C_{10-24} saturated or unsaturated alkyl radical, preferably a C_{13-24} unsaturated alkyl radical, and X is the same as R or is a hydrogen or is an amine, preferably a heterocyclic amine. Thus R may be decyl, tetradecyl, dodecyl, tetradecenyl, hexadecenyl, oleyl, ricinoleyl radicals and the amine may be a C_{10-18} alkyl amine such as mono- or di-decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and octadecenyl amines; heterocyclic amines such as substituted imidazolines having the formula

(II)



where R' is the same as R in Formula I. Examples of N-acyl sarcosines used as quenching speed additive and surface brighteners are illustrated by the following: N-lauroyl sarcosine, N-stearoyl sarcosine, N-caproyl sarcosine, N-myristol sarcosine, n-oleoyl sarcosine, N-palmitoyl sarcosine, and N-arachidoyl sarcosine, amine salts of such acid as monodecylamine, didecylamine, monotetradecylamine, ditetradecylamine, monooctadecylamine, dioctadecylamine, 1-hydroxyethyl-2-undecylimidazoline, 1-hydroxyethyl-2-heptadecylimidazoline and 1-hydroxyethyl-2-heptadecylimidazoline salts of N-lauroyl sarcosine or N-cocoyl or N-oleoyl sarcosine or N-stearyl sarcosine, particularly preferred compounds are the free acids such as N-oleoyl sarcosine, octadecylamine salts of N-oleoyl sarcosine and 1-hydroxyethyl-2-heptadecenyl imidazoline salt of N-oleoyl sarcosine. The esters include the N—C_{10-24} acyl sarcosinates of C_{8-20} alkanols such as octyl, decyl, dodecyl and octadecyl alcohols, e.g., N-oleoyl sarcosinate of octyl alcohol, N-oleoyl sarcosinate of octadecyl alcohol. Mixtures of the free acid, ester or amine salts may be used such as a mixture of N-oleoyl sarcosine and 1-hydroxyethyl-2-heptadecenyl imidazoline salt of N-oleoyl sarcosine.

The oil base blend which is a critical feature of the invention must have thermal and oxidative resistant properties capable of meeting the requirements desired in a quenching oil. Thus the oil of part (1) of the blend must be high viscosity index oil (90–120 VI) in the viscosity range of 80–250 SUS at 100° F., preferably 100–150 SUS at 100° F. and an aromatic content of 15–60%.

Such oils may be illustrated by a HVI 100 neutral having the following properties (*Ia*):

Gr. API	31.6
Color NPA	+1
Flash, ° F	370
Pour point, ° F	0
Viscosity at 100° F. SUS	103
Viscosity index	90
Aromatics, percent	15.5
Naphthenes, do	68.9
Paraffins, do	15.6

The petroleum fractions of (2) may be illustrated by a mineral spray oil (*IIa*) of viscosity 45–80 SUS at 100° F., a viscosity index of 70–80 and having 14.7% aromatics, 85.2% naphthenes and 0.1% paraffins or refined transformer oil and the heavy oils (*IIc*) may be illustrated by 150 HVI bright stock, 170 HVI bright stock having a viscosity index of 90–110 or propane asphalt, petroleum resins, asphaltenes, short residues, etc. Oil blends which are particularly useful are:

(A) 60% HVI 100 neutral (*Ia*)
30% transformer oil (100 SUS 100° F., PP, ° F. —60, color NPA 1)
10% unfiltered HVI 150 bright stock (VI 95)

(B) 60% HVI 100 neutral (*Ia*)
30% spray base oil (*IIa* 45 SUS at 100° F.)
10% unfiltered HVI 150 bright stock

(C) 95% HVI 100 neutral (*Ia*)
5% propane asphalt

(D) 50% HVI 100 neutral (*Ia*)
40% spray base oil (80 SUS at 100° F.)

(E) 90% HVI neutral (*Ia*)
10% transformer oil

The compositions of the present invention which contain as the essential additive N-acyl sarcosines and derivatives thereof can be further improved with respect to oxidation stability by addition thereto of from 0.01% to 2%, preferably from 0.1% to 2%, of polymeric ashless dispersants such as nitrogen-containing polymers described in U.S. Patents 2,737,496, 2,839,512, 2,889,282, 2,944,974, or British 808,665 or polyhydric polymeric compounds described in U.S. Patents 2,800,450–2. Polymers of this type having a molecular weight of from 20,000–800,000 can be illustrated by copolymer of lauryl methacrylate/diethylaminoethyl methacrylate, copolymer of 2-methyl-5-vinylpyridine/lauryl methacrylate/stearyl methacrylate, copolymer of 2-methyl-5-vinylpyridine/lauryl methacrylate/stearyl methacrylate/methyl methacrylate, copolymer of vinyl pyrrolidone/lauryl methacrylate, hydrolyzed copolymer of C_{10-18} alpha-olefin/vinyl acetate. Also desirable is the presence of small amounts (0.1–1%) of phenolic anti-oxidants such as mono or bisphenols, preferably phenols which contain at least one tertiary alkyl radical. Alkyl phenols of this type include 2,4,6-triethyl-, tributyl-, trioctyl-, 2,4-ditert-butyl-6-methyl, 2,6-ditert-butyl-4-methyl, 2,4,6-ditert-butyl-, 2,6-dicyclohexyl-4-methyl, 2,6-dimethyl-4-cyclohexylphenols, 2,6-ditert-butyl, 2,2-ditert-butyl, 2,6-tert-butylcyclohexyl, 2-methyl-6-tert-butyl-4-methylphenols. The alkyl bisphenols include 1,1-bis-(2-hydroxy-3-tert-butyl-5-methylphenyl)methane; bis(2-hydroxy-3-tert-butyl-5-methylphenyl)ethane; 1,1-bis(2-hydroxy-3-tert-butyl-5-methylphenyl)propane; bis(2-hydroxy-3-tert-butyl-5-methylphenyl)butane; bis(2-hydroxy-3-tert-butyl-5-methylphenyl)isobutane; 1,1-bis(6-hydroxy-5-tert-butyl-3-methylphenyl)methane; bis(2-hydroxy-5-tert-butyl-3-methylphenyl)ethane; 1,1-bis(2-hydroxy-5-tert-butyl-3-methylphenyl)propane; 1,1-bis(2-hydroxy-5-tert-amyl-3-methylphenyl)butane; 1,1-bis(2-hydroxy-5-tert-amyl-3-methylphenyl)isobutane; etc. The 2,4,6-trialkyl phenols containing two tertiary alkyl groups in the 2,4- or 2,6-positions are preferred, such as 2,4-ditert-butyl-6-methyl-, 2,6-ditert-butyl-4-methylphenol or 2,6-ditert-butyl-4-methylolphenol or 4,4'-methylene bis(2,6-dibutylphenol).

The following compositions illustrate the invention:

	Percent wt.
Composition I—	
N-oleoyl sarcosine	0.2
2,6-ditert-butyl-4-methylphenol	0.1
Base oil blend (A)	Balance
Composition II—	
N-oleoyl sarcosine	0.25
2,6-di-tert-butyl-4-methylphenol	0.1
Copolymer of lauryl methacrylate (90)/diethylamine ethyl methacrylate (10) (M.W. 600,000)	0.5
Base oil blend (A)	Balance
Composition III—	
N-oleoyl sarcosine	0.2
Base oil blend (A)	Balance
Composition IV—	
N-oleoyl sarcosine	0.3
Hydrolyzed copolymer of C_{16-18} alpha-olefin/vinyl acetate (3:1) (M.W. 27,000)	1
Base oil blend (D)	Balance
Composition V—	
1-hydroxyethyl-2-heptadecenyl imidazoline N-oleoyl sarcosine	0.2
Base oil blend (A)	Balance
Composition VI—	
Octadecylamine N-oleoyl sarcosine	0.5
Base oil blend (B)	Balance
Composition VII—	
N-lauroyl sarcosine	0.2
2,6-di-tert-butyl-4-methylphenol	0.1
Base oil blend (A)	Balance
Composition VIII—	
N-cocoyl sarcosine	0.3
Hydrolyzed copolymer of C_{16-18} alpha-olefin/vinyl acetate (3:1) (M.W. 27,000)	1
Base oil blend (D)	Balance
Composition IX—	
1-hydroxyethyl-2-heptadecenyl imidazoline N-stearoyl sarcosine	0.2
Base oil blend (A)	Balance
Composition X—	
Octadecylamine N-oleoyl sarcosine	0.1
N-oleoyl sarcosine	0.1
Base oil blend (C)	Balance

The effectiveness of compositions of this invention as quenching media is demonstrated by the data presented in Table I in which the compositions were subjected to the following tests:

(I) General Motors magnetic quench test for quenching steel and quenched metal brightness rating, (II) Thermal and oxidation stability tests (*a*) 250° F. oven stability test, (*b*) 150° F. quench oxidation test. Test I exploits the magnetic properties of nickel to measure quenching speeds of various liquids. Nickel loses its ferro magnetic properties when heated above 670° F. and regains them when cooled below this temperature. In this test the time necessary for a quenching fluid to cool a ⅞-inch diameter nickel ball from 1625° F. to its Curie temperature of 670° F. is measured automatically. The quenching time is a measure of the heat extracting power of the quenchant, i.e., a low quench time represents a high metal cooling rate or high quenching speed. Quench brightness is determined visually by noting deposits and ease of removal on nickel ball after quenching and rated as follows:

A=zero to trace
B=trace to light
C=light
D=moderate
E=heavy

(II) The 250° F. oven stability test is conducted as follows: A steel rod is immersed in the test oil and placed in an oven for 1 week at 250° F. Oil stability is evaluated by (1) measuring the quenching speed and quenched metal brightness of oils after varying periods of over storage,

(2) inspection of the immersed steel rods after oven storage for evidence of tarnish or sludge formation, and (3) viscosity and acid number increases for oxidized oil samples as a function of time of storage.

Table I

Composition	Quench Time (sec.)	Quench Brightness Rating	Oven Oxidation Test
Composition I	12.7	A	Excellent.
Composition II	13.1	B	Do.
Composition V	13.2	B	Do.
Composition VI	13.8	A	Do.
Base oil blend (A)	12.2	E	Poor.
HVI 100 neutral	16.6	C	Fair.
Base oil blend (C)	13.2	C	Poor.
Spray base oil	12.2	E	Do.
Base oil blend (A) plus 2% dioctadecylamine plus 1% hydrolyzed copolymer of C 18-18 alpha-olefin/vinyl acetate	11.4	D	Fair.
Base oil blend (A) plus 0.25% copolymer lauryl methacrylate (90)/diethylaminoethyl methacrylate (11)	13.0	D	Poor.

Compositions VII to X also are excellent quenching speed oils and leave the surface bright and clean for immediate further processing.

We claim as our invention:

1. A process for heat treating steel comprising heating the metal to a quench hardening temperature and thereafter quenching the metal by immersion in an oil blend containing from 0.1% to 2% of an oil-soluble N—C_{10-24} acyl sarcosine, said oil blend consisting of a predominant amount of a high viscosity index mineral oil having a viscosity index of from 90 to 120, and an aromatic content of from 20 to 60% and the balance of the blend being selected from the group consisting of a light mineral oil having a viscosity range of from 40 to 100 SUS at 100° F., a heavy residue fraction and mixtures thereof.

2. The process of claim 1 wherein the oil blend consists of a mixture of from 50 to 95% of 80–250 SUS at 100° F. HVI neutral mineral oil and the balance being bright stock.

3. The process of claim 1 wherein the oil blend consists of a mixture of from 50 to 95% of 80–250 SUS at 100° F. HVI neutral mineral oil and the balance being propane asphalt.

4. The process of claim 1 wherein the oil blend consists of a mixture of from 50 to 95% of 80–250 SUS at 100° F. HVI neutral mineral oil and the balance being spray base oil.

5. The process of claim 1 wherein the oil blend consists of a mixture of from 50 to 95% of 80–250 SUS at 100° F. HVI neutral mineral oil and the balance being refined transformer oil.

6. A process for heat treating steel comprising heating the metal to a quench hardening temperature and thereafter quenching the oil by immersion in an oil blend containing from 0.1 to 2% of N—C_{10-24} acyl sarcosine, said blend consisting of 60–70% of HVI neutral mineral oil having a viscosity range of from 80–250 SUS at 100° F., a viscosity index of 90–120 and an aromatic content of 20–60% and the balance being a mixture of a highly refined transformer oil and 5–10% bright stock.

7. A process for heat treating steel comprising heating the metal to a quench hardening temperature and thereafter quenching the oil by immersion in an oil blend containing from 0.1 to 2% of amine salt of N—C_{10-24} acyl sarcosine, said blend consisting of 60–70% of HVI neutral mineral oil having a viscosity range of from 80–250 SUS at 100° F., a viscosity index of 90–120 and an aromatic content of 20–60% and the balance being a mixture of a highly refined transformer oil and 5–10% bright stock.

8. A process for heat treating steel comprising heating the metal to a quench hardening temperature and thereafter quenching the oil by immersion in an oil blend containing from 0.1 to 2% of octadecyl amine salt of N-oleoyl sarcosine, said blend consisting of 60–70% of HVI neutral mineral oil having a viscosity range of from 80–250 SUS at 100° F., a viscosity index of 90–120 and an aromatic content of 20–60% and the balance being a mixture of a highly refined transformer oil and 5–10% bright stock.

9. A process for heat treating steel comprising heating the metal to a quench hardening temperature and thereafter quenching the oil by immersion in an oil blend containing from 0.1 to 2% of 1-hydroxyethyl-2-heptadecenyl imidazoline salt of N-oleoyl sarcosine, said oil blend consisting of 60–70% of HVI neutral mineral oil having a viscosity range of from 80–250 SUS at 100° F., a viscosity index of 90–120 and an aromatic content of 20–60% and the balance being a mixture of a highly refined transformer oil and 5–10% bright stock.

10. A process for heat treating steel comprising heating the metal to a quench hardening temperature and thereafter quenching the oil by immersion in an oil blend containing from 0.1 to 2% of N—C_{10-24} acyl sarcosine, 0.01 to 2% of an ashless polymeric dispersant and 0.001 to 2% of a phenolic antioxidant, said blend consisting of 60–70% of HVI neutral mineral oil having a viscosity range of from 80–250 SUS at 100° F., a viscosity index of 90–120 and an aromatic content of 20–60% and the balance being a mixture of a highly refined transformer oil and 5–10% bright stock.

11. A quenching oil composition consisting essentially of a mineral oil blend containing from 0.1 to 2% of an oil-soluble N—C_{10-24} acyl sarcosine, said blend consisting of a predominant amount of a high viscosity index mineral oil having a viscosity index of from 90 to 120 and an aromatic content of from 20 to 60% and the balance of the blend being selected from the group consisting of a light mineral oil having a viscosity range of from 40 to 100 SUS at 100° F., a heavy residue fraction and mixtures thereof.

12. The composition of claim 11 wherein the oil blend consists of a mixture of from 50–95% of 80–250 SUS at 100° F. HVI neutral mineral oil having an aromatic content of from 20–60% and the balance being a bright stock.

13. The composition of claim 11 wherein the oil blend consists of a mixture of from 50–95% of 80–250 SUS at 100° F. HVI neutral mineral oil having an aromatic content of from 20–60% and the balance being a propane asphalt.

14. The composition of claim 11 wherein the oil blend consists of a mixture of from 50–95% of 80–250 SUS at 100° F. HVI neutral mineral oil having an aromatic content of from 20–60% and the balance being a spray base oil.

15. The composition of claim 11 wherein the oil blend consists of a mixture of from 50–95% of 80–250 SUS at 100° F. HVI neutral oil having an aromatic content of from 20–60% and the balance being a refined transformer oil.

16. A quenching oil composition consisting of a mixture of from 50–85% of 80–250 SUS at 100° F. HVI neutral mineral oil having an aromatic content of from 30–60% and the balance being a mixture of bright stock and spray base oil, said mineral oil blend containing from 0.1 to 2% of N-oleoyl sarcosine.

17. A quenching oil composition consisting of a mixture of from 50–85% of 80–250 SUS at 100° F. HVI neutral mineral oil having a viscosity index of from 90 to 120 and an aromatic content of from 30–60% and the balance being a mixture of bright stock and spray base oil, said mineral oil blend containing from 0.1 to 2% octadecyl amine salt of N-oleoyl sarcosine.

18. A quenching oil composition consisting of a mixture of from 50–85% of 80–250 SUS at 100° F. HVI neutral mineral oil having a viscosity index of from 90 to 120 and an aromatic content of from 30–60% and the balance being a mixture of bright stock and spray base oil, said mineral oil blend containing from 0.1 to 2%

of 1-hydroxyethyl-2-heptadecenyl imidazoline salt of N-oleoyl sarcosine.

19. The composition of claim 16 containing a small amount of a polymeric dispersant and a phenolic antioxidant.

20. The composition of claim 18 containing a small amount of a polymeric dispersant and a phenolic antioxidant.

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