United States Patent [19]

Wilpers

[11] **3,853,638**

[45] **Dec. 10, 1974**

[54] **QUENCHING OIL COMPOSITION**

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[22] Filed: **June 25, 1973**

[21] Appl. No.: **373,065**

[52] **U.S. Cl.** **148/29,** 148/20.6, 148/27, 252/77, 252/47.5

[51] **Int. Cl.** **B23k 35/24**

[58] **Field of Search** 148/29, 28, 27, 20.6; 252/47, 78, 75, 71, 47.5, 77

[56] **References Cited**

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[57] **ABSTRACT**

A quenching oil composition with an improved rate of cooling for the quenching of ferrous metals comprises a major portion of a hydrocarbon mineral oil containing a minor proportion of a vic-dihydrocarbyl substituted thiazole having in its 2-position a mercapto group.

6 Claims, No Drawings

QUENCHING OIL COMPOSITION

BACKGROUND OF THE INVENTION

The method of hardening ferrous materials by heating them to a temperature above 1,600°F and then rapidly cooling them in order to increase the hardness is well known. The cooling step in this procedure is termed "quenching." It is also known that an increase in the speed of quenching results in increased metallic hardness. Hydrocarbon oils, in particular mineral oils, are commonly used as quenching liquids. But straight mineral oils do not usually form satisfactory quench media since the initial rate of cooling is too slow. Hence, the development of the quenching oil art has been in the direction of modifying hydrocarbon oils by incorporating certain additives therein. The state of the art is such that many various different additives have been used for this purpose; see, for example, U.S. Pat. No. 3,729,417, issued Apr. 24, 1973. Illustrative of these additives for improving cooling rate are ash-forming materials such as oil-soluble alkali metal and/or alkaline earth metal petroleum sulfonates, e.g., calcium, sodium, or barium sulfonates. Such materials leave behind on the metal an "ash" or deposit which affects the brightness or cleanliness of the metal surface. These deposits are difficult to wipe off or remove from the metal surface. Consequently, it would be an advance in the art to have an oil composition containing an effective additive that facilitates rapid heat exchange between the metal and the oil composition in the heat treating process, such as the hardening of steel, and to have such a composition which leaves on heat-treated metal surfaces an easily removable deposit.

SUMMARY OF THE INVENTION

It has now been found that a quenching oil with an improved rate of cooling consists essentially of a mineral oil having a viscosity of from about 15 to about 200 SUS at 100°F which contains dissolved therein a critical amount within the range of from about 0.005 to about 0.04 percent, preferably between 0.01 and 0.03 percent, by weight of a vicinal dihydrocarbyl-substituted 2-mercaptothiazole. An improved process for quenching metals, especially steel, is obtained by use of the above-defined quenching oil. In addition to the advantageously improved speed of quenching achieved with the composition of the invention, an added advantage resides in the phenomenon that any deposit left on the metallic surface quenched with said composition is deposited in the form of an easily removable flake; for example, simply wiping off the metallic surface removes the flaky deposit.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The mineral oil base which in addition to the additive is a critical feature of the invention must have thermal and oxidative resistant properties capable of meeting the requirements desired in a quenching oil. Furthermore, viscosity of an oil affects its quenching properties. Usually higher viscosity oils have slower quenching times than lower viscosity oils. In order to achieve the advantageous effects of the invention, the base oil is preferably a mineral oil having a viscosity of from about 15 to about 200 SUS at 100°F and an aromatic content of 8–60 percent. A preferred viscosity range of

the mineral oil is one of from about 40 to about 100 SUS at 100°F. Such oils may be illustrated by, inter alia, a HVI 100 neutral having the following properties:

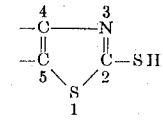
Gr. API	31.6
Color NPA	+1
Flash, °F	370
Pour Point, °F	0
Viscosity at 100°F SUS	103
Viscosity index	90
Aromatics, %	15.5
Naphthenes, %	68.9
Paraffins, %	15.6,

a MVI 60 having the following properties:

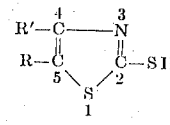
Gr. API	30.8
Color Sayboldt	+25
Flash, °F	300
Pour Point, °F	−65
Viscosity at 100°F SUS	58.4
Viscosity index	58
Aromatics, %	8.2
Saturates, %	91.4
Resins, %	0.4,

and the like.

The additive component required for the composition of the invention is a vicinal dihydrocarbyl-substituted thiazole having in its 2-position a mercapto or sulfhydryl group and has the general formula

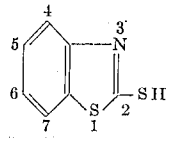


As can be seen from the general formula the hydrocarbyl substituents are always on adjacent ring carbons and in the 4 and 5 positions of the thiazole ring since the covalent bonds of the 1,2 and 3 positions of the thiazole ring are completely satisfied or filled. Although the dihydrocarbyl substituents on the thiazole ring may be any hydrogen and carbon-containing group such that the resultant molecule is oil-soluble, it is preferred that these substituents be of low-molecular weight, preferably containing from one to six carbon atoms. For the purposes of this invention, the vicinal dihydrocarbyl substituent may be joined to complete a ring structure and, therefore, encompasses also the concept of the substituent being a divalent hydrocarbylene moiety. Thus a preferred substituted thiazole has the formula



where R and R′ are lower hydrocarbyl, especially alkyl, groups of one to six carbon atoms or R and R′ may be joined to form a divalent hydrocarbylene group of four to six carbon atoms. For example, if the hydrocarbylene group forming the ring is a butadienylene group, then R and R′ may be considered as furnishing two carbon atoms each. Representative examples of vic-hydrocarbyl substituted 2-mercaptothiazoles used as

improved quenching speed additives include the following: 2-mercapto-4,5-dimethylthiazole, 2-mercapto-4,5-diethylthiazole, 2-mercapto-4-ethyl-5-methylthiazole, 2-mercapto-4-methyl-5-propylthiazole, 2-mercapto-4-methyl-5-butylthiazole, 2-mercapto-4-butyl-5-methylthiazole, 2-mercapto-4-butyl-5-ethylthiazole, 2-mercapto-4-methyl-5-isoamylthiazole, 2-mercaptobenzothiazole, 2-mercapto-4-methylbenzothiazole, 2-mercapto-5-methylbenzothiazole, 2-mercapto-6-methylbenzothiazole, 2-mercapto-7-methylbenzothiazole, and the like. It is to be understood that the benzothiazoles are named according to the position isomers given in the following general formula



Most preferred are the 2-mercaptobenzothiazole and the 2-mercapto-4,5-dimethylthiazole.

The concentration of the 2-mercaptothiazole additive component required for the oil compositions of the invention is a critical amount falling within the range of from about 0.005 percent to about 0.04 percent by weight, based on the amount of the base mineral oil in which the additive is dissolved. A preferred range is from about 0.01 percent to about 0.03 percent by weight.

The compositions of the present invention, which contain as the essential additive the above-defined 2-mercaptothiazole can be further improved with respect to oxidation stability by addition thereto of phenolic antioxidants, amine antioxidants and the like.

EXAMPLE I

The base mineral oil alone and the base mineral oil together with the indicated concentration of additive given below and the effectiveness thereof as improved quenching speed oils is demonstrated by testing the compositions in the GMC Magnetic Quenchometer Test. This test takes advantage of the fact that metals lose their magnetic properties when heated above a critical temperature called the "Curie point" and regain it when cooled. Polished nickel balls, preheated to 1,625°F in a muffle furnace, are dropped past a photoelectric cell into a measured volume of oil located in a magnetic field. When the nickel ball cools to its "Curie point," approximately 670°F for pure nickel, it regains its magnetic properties and is drawn to a magnet. An electric timer, which is engaged when the nickel ball passes the photoelectric cell, is automatically stopped when the ball is drawn to the magnet. The recorded time in seconds is reported as the quenching time of the sample or oil being tested. The lower the quenching time reported, i.e., the smaller the number of seconds, the faster is the speed of the quenching oil and the greater its cooling effectiveness. Table 1 below indicates the effectiveness of the additives of the invention as compared with the mineral oil without additives. Table 2 below containing additives not according to the invention is included to show how additives of similar chemical content to the 2-mercaptothiazoles of the inventions are far less effective than the additives of the invention in speed of quenching. The mineral oil used as base oil in Tables 1 and 2 below is a MVI 60 oil having the following properties:

Gravity, lbs/gal	7.2
Color ASTM	0.5
Flash, °F	300
Pour Point, °F	−65
Viscosity at 100°F SUS	58.4
Viscosity index	58
Aromatics, %	8.2
Saturates, %	91.4
Resins, %	0.4

Table 1

Test Oil	GMC Quenching Time (sec)
Base oil	32
Base oil + 0.01%w 2-mercaptobenzothiazole	11
Base oil + 0.03%w 2-mercapto-4,5-dimethylthiazole	9

Table 2

Test Oil	GMC Quenching Time (sec)
Base oil	32
Base oil + 0.125%w oil-soluble sulfur	19
Base oil + 0.48%w dibenzyl disulfide	17
Base oil + 0.83%w tert-dodecyl mercaptan	32
Base oil + 0.52%w benzothiophene	32
Base oil + 0.02%w benzotriazole	33
Base oil + 0.1%w hydrogenated benzotriazole	33
Base oil + 0.66%w butylthiocresol	30
Base oil + 0.22%w thiophenol	30
Base oil + 0.50%w thiobetanaphthol	27

I claim as my invention:

1. A quenching oil composition consisting essentially of a mineral oil, having a viscosity of from about 15 to about 200 SUS at 100°F and an aromatic content of from 8 to 60 percent, and from about 0.01 to about 0.03 percent by weight of a vicinal dehydrocarbyl-substituted 2-mercaptothiazole, each hydrocarbyl substituent having from one to six carbon atoms.

2. The composition of claim **1** wherein said dihydrocarbyl is dialkyl.

3. The composition of claim **1** wherein said vicinal dihydrocarbyl substituent is joined to form a divalent hydrocarbylene moiety of four to six carbon atoms.

4. The composition of claim **1** wherein the viscosity of the mineral oil is from about 40 to about 100 SUS at 100°F.

5. The composition of claim **2** wherein dialkyl is dimethyl and the 2-mercaptothizole is 2-mercapto-4,5-dimethylthiazole.

6. The composition of claim **3** wherein the hydrocarbon moiety is butadienylene and the 2-mercaptothiazole is 2-mercaptobenzothiazole.

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