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(54) Titre : COMPOSITION D'HUILE POUR LE TRAITEMENT THERMIQUE
(54) Title: HEAT TREATING OIL COMPOSITION

(57) **Abrégé/Abstract:**

Disclosed is a heat treating oil composition which comprises: (I) a base oil having a sulfur content of 3 to 1,000 ppm and consisting of: (A) at least one member 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 (II) an additive for quenching. The additive may be an alkaline earth metal salt of salicylic acid, sulfonic acid or phenol, for example. The heat treating oil is useful for quenching a metal material at a high oil temperature to obtain treated metal material having improved brightness with minimum distortion.



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ABSTRACT

Disclosed is a heat treating oil composition which comprises: (I) a base oil having a sulfur content of 3 to 1,000 ppm and consisting of: (A) at least one member
5 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 (II) an additive for quenching. The additive may be an alkaline earth metal salt of salicylic acid, sulfonic acid
10 or phenol, for example. The heat treating oil is useful for quenching a metal material at a high oil temperature to obtain treated metal material having improved brightness with minimum distortion.

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HEAT TREATING OIL COMPOSITION

This is a divisional application of Canadian Patent Application Ser. No. 2,080,788 filed October 16, 1992.

The subject matter of the parent application was
5 restricted to certain embodiments of the invention disclosed
in the specification. Similarly, the subject matter of this
divisional application is restricted to certain embodiments
of the invention, not claimed in the parent application. It
should be understood, however, the expression "the present
10 invention" or the like in this specification encompasses the
embodiments of both the parent and divisional applications.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a heat treating
15 oil composition, particularly a quenching oil composition.
More particularly, it relates to a new type heat treating
oil composition excellent in the stability at high
temperature, suitable for quenching under the condition of a
high oil temperature and capable of providing an object to
20 be treated with excellent and long surviving brightness.

2. Description of Related Arts

Conventionally, a heat treatment, for example a
quenching treatment has been given by feeding a metal heated
to a high temperature into a quenching oil at 60 to 150°C
25 and quenching and hardening it. During the process of this
quenching treatment, the metal preferably is quenched even
at a higher oil temperature such as 170 to 250°C to make the
effective correction for a distortion.

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However, conventionally known heat treating oils, for example those which are mixed with mineral oil, fatty acid, alkenyl succinimide and the like (Japanese Patent Publication Nos. 52-4508 (published in 1977); 61-15913
5 (published in 1986); 61-106710 (published in 1986) and the like) have the poor stability at high temperatures. Thus, when they are used at high oil temperatures, they have encountered various problems that the metal is not hardened or does not have sufficiently high brightness or the life
10 span of the brightness is short. Meanwhile, inferior brightness has been

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blamed as one of the reasons for an increase of distortion associated with quenching.

On the other hand, the heat treating oil can have improved stability at high temperatures by comprising a highly purified base oil. It has been known, however, that unevenness is liable to occur in association with cooling because of this heat treating oil, resulting in an increase of inferior brightness, quenching unevenness and quenching distortion.

10 Moreover, a martempering treatment (at a liquid temperature around 230°C) using salt has also been known as suitable for decreasing the quenching distortion. But this treatment has been found to have poorer working efficiency than that of quenching oil, accompanied even by environmental problems.

Thus, the present inventors have made intensive studies with a view to finding a solution in these problems and developing a heat treating oil composition capable of quenching at high oil temperatures and obtaining a treated metal having excellent brightness and free of the distortion.

20 As the result, it has been found that the objects can be achieved by a heat treating oil composition comprising a highly purified mineral oil or synthetic oil as a base oil and an alkaline earth metal salt of salicylic acid or comprising a base oil consisting of a highly purified mineral oil or synthetic oil and a specific content of sulfur, along with various additives for quenching. The present invention has been completed on the basis of this finding.

SUMMARY OF THE INVENTION

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Therefore, the present invention provides 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 300ppm and (B) an alkaline earth metal salt of salicylic acid.

The present invention also provides a heat treating oil composition which comprises (I) a base oil having a sulfur content of 3 to 1000ppm consisting of (A) at least one member selected from a mineral oil and a synthetic oil each having a sulfur content of not more 300ppm and (C) at least one member selected from sulfur and a sulfur compound and (II) an additive for quenching.

Furthermore, the present invention also provides a method for quenching which comprises quenching with either of above-mentioned heat treating oil compositions at a high oil temperature.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The (A) component of the present invention is used as a base oil singly or with the adjustment of the sulfur content as will be described later. This (A) component includes at least one member selected from a mineral oil and a synthetic oil each having a sulfur content of not more than 300ppm. When the sulfur content of the mineral oil is more than 300ppm, inferior brightness or the quenching distortion is liable to occur in the object to be treated. On the other hand, when the mineral oil is even more highly purified to have the sulfur content of preferably not more than 100ppm, more preferably not more than

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30ppm, the object treated and quenched by using the composition of the present invention is provided with brightness having a longer span of life. These conditions of the sulfur content hold good for synthetic oil as well.

The kind of mineral oil and synthetic oil to be used as the (A) component is not particularly limited. Examples of the mineral oil to be used herein are the highly purified product of a paraffinic mineral oil, an intermediate mineral oil and a naphthenic mineral oil, each having the sulfur
10 content satisfying the aforesaid conditions. Examples of the synthetic oil to be used herein include various oils, for example an olefin (co) polymer having from 2 to 16 carbon atoms (including an oligomer),

alkylbenzene, alkyl naphthalene, a polyphenyl hydrocarbon, various esters including fatty acid esters of neopentylglycol, trimethylolpropane, pentaerythritol and the like. An olefin oligomer or its hydrogenated product having from 8 to 12 carbon atoms is the most suitable among them.

Of these mineral oils and synthetic oils, not only one
20 member can be singly but also two or more as their mixture at a discretionary ratio. The so obtained (A) component ordinarily has a kinematic viscosity of 2 to 100cSt at 100°C.

The (A) component when required, may be mixed with sulfur and a sulfur compound as the (C) component to obtain a base oil having a total sulfur content of 3 to 1000ppm, preferably 5 to 800ppm, capable of decreasing the quenching distortion, providing brightness having a longer span of life and improving brightness in the initial phase of quenching. It

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is even more preferable for the base oil to have a nitrogen content of not more than 30ppm, especially 20ppm, along with the total sulfur content of 3 to 1000ppm.

Of the sulfur and the sulfur compounds, not only one member can be used singly but also two or more in their discretionary combination.

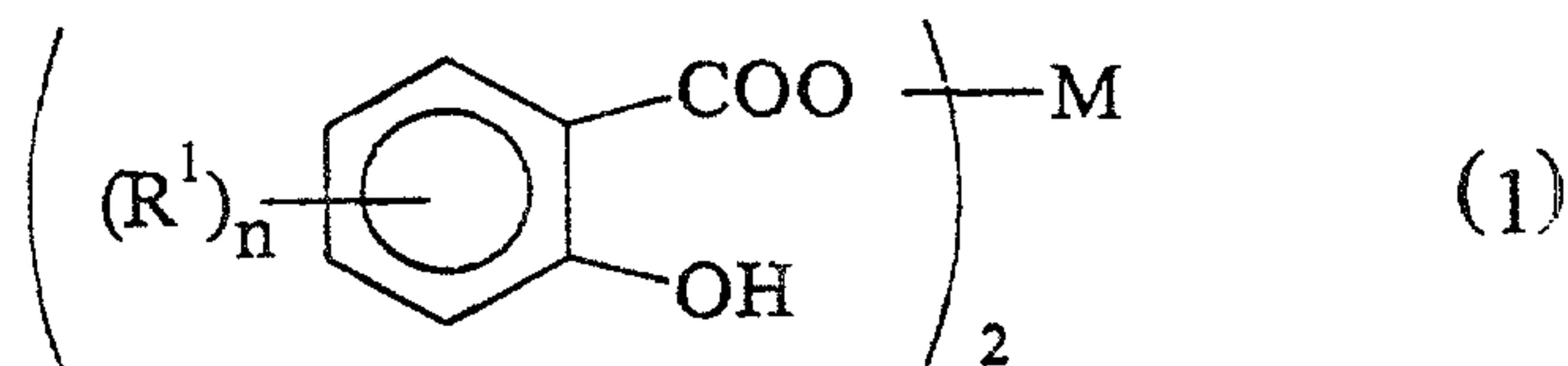
Various sulfur compounds can be used to improve brightness of the object to be treated, including compounds of sulfides, disulfides, polysulfides, mercaptans and thiophenes. More specifically, sulfides include diethylsulfide, di-n-propylsulfide, di-n-butylsulfide, di-iso-butylsulfide, di-tert-butylsulfide, di-n-hexylsulfide, diphenylsulfide, dibenzylsulfide and the like. Disulfides include diethyldisulfide, di-n-propyldisulfide, di-n-butyldisulfide, di-iso-butyldisulfide, di-sec-butyldisulfide, di-tert-butyldisulfide, di-n-heptyldisulfide, di-tert-heptyldisulfide, di-tert-lauryldisulfide, diphenyldisulfide, dibenzylsulfide and the like. Polysulfides include dibenzylpolysulfide. Mercaptans include n-butylmercaptan, n-hexylmercaptan, tert-dodecylmercaptan, n-tetradecylmercaptan, n-cetylmercaptan, thiophenol, p-thiocresol and the like. Further, thiophenes include thiophene, dibenzothiophene and the like. Besides, there can be mentioned sulfurized alkylphenate of an alkaline earth metal, a dithiophosphoric acid metal (Zn-DTP and the like), a mineral oil having a sulfur content of not more than 2.0%, a sulfurized mineral oil, olefin sulfide, a sulfurized fat and the like. It is preferable that this mineral oil having

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the sulfur content of not more than 2.0% has particularly a nitrogen content of not more than 400ppm as well.

However, among the sulfur compounds, for example sulfoxide or sulfonic acid or its salts practically cannot improve brightness or reduce the quenching distortion in the object to be treated.

The alkaline earth metal salt of salicylic acid as the (B) component of the present invention is incorporated into (I) the base oil consisting of the (A) component singly or the (A) component and the (C) component in combination. Examples of this alkaline earth metal salt of salicylic acid include various compounds, and most suitable is a salicylate compound represented by the following general formula (1):



wherein the R^1 is a hydrogen atom or an alkyl group having from 8 to 20 carbon atoms, n is an integer of from 1 to 4 and M is Ca, Ba or Mg.

The salicylate compound having a total base number (TBN) of not more than 500mgKOH/g, preferably 100 to 400mgKOH/g is effective in improving brightness of the object to be treated. Particularly, calcium salicylate and magnesium salicylate are most suitable.

Of these alkaline earth metal salts of salicylic acid, not only one member alone can be used singly but also two or more in their discretionary combination. The mixing amount thereof is not particularly limited and is variable depending upon

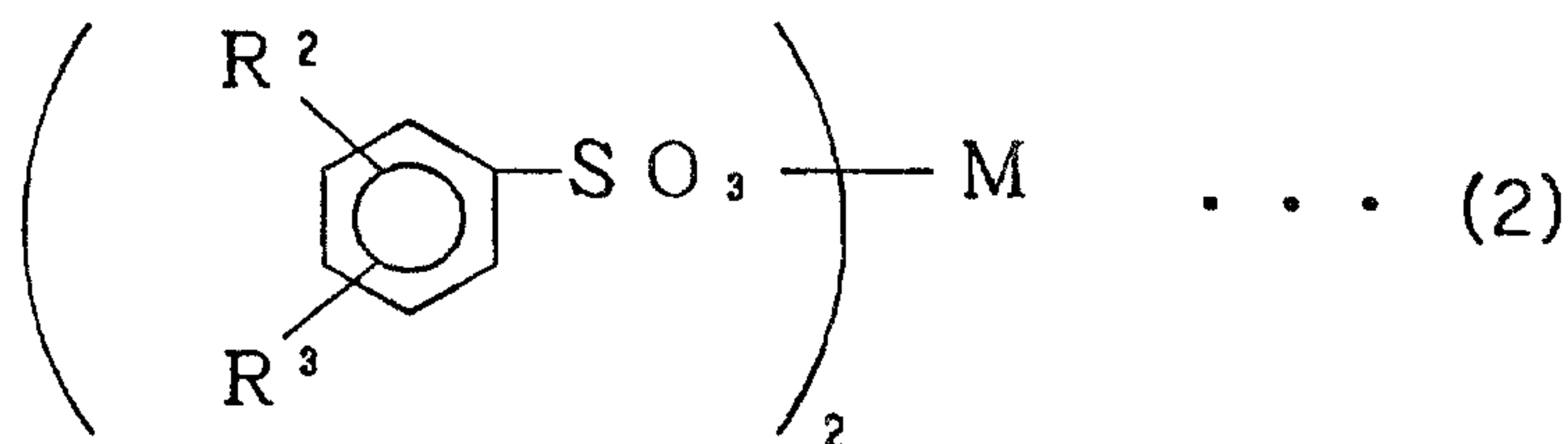
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circumstances but ordinarily 0.1 to 50% by weight, preferably 1 to 30% by weight of a compound is mixed in the composition as a whole. When the mixing amount is less than 0.1% by weight, the effect aimed by the present invention often cannot be obtained. On the other hand, when the mixing amount is more than 50% by weight, the effect is not improved in proportion thereto to an economical disadvantage.

Alkaline earth metal salts of sulfonic acid and phenol as the (D) component of the present invention are used in the same way as the alkaline earth metal salt of salicylic acid of the (B) component, but it is necessary that the (D) component should be incorporated into the base oil consisting of the (A) component and the (C) component in combination. Even if the (D) component is incorporated into the base oil consisting of the (A) component singly, the effect aimed by the present invention often cannot be obtained.

The various alkaline earth metal salts of sulfonic acid and phenol can be used in the present invention.

Most suitable among the alkaline earth metal salts of sulfonic acid is, for example a sulfonate compound represented by the following general formula (2):

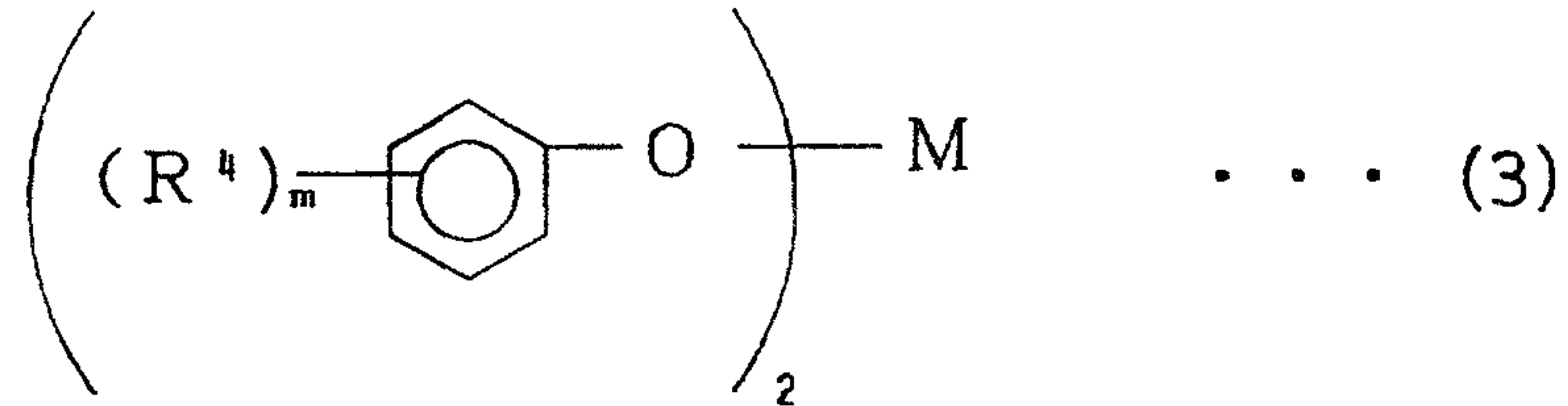


wherein R² and R³ each are a hydrogen atom or an alkyl group having from 12 to 24 carbon atoms, provided that R² and R³ are

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not the hydrogen atom at the same time; and M is same as defined above.

Most suitable among the alkaline earth metal salts of phenol is a phenate compound of the general formula (3):



wherein R^4 is an alkyl group having from 9 to 24 carbon atoms, m is an integer of from 1 to 4 and M is same as defined above.

Of these alkaline earth metal salts of sulfonic acid and phenol, not only one member alone can be used singly but also two or more in their discretionary combination. Furthermore, they can be combined with the (B) component. Meanwhile, conditions of their total base number (TBN) and mixing amount are same as those of the alkaline earth metal salt of salicylic acid as the (B) component.

Basically, the composition of the present invention is prepared by incorporating (II) the additives such as (B) component and (D) component into (I) the base oil consisting of the (A) component singly or the (A) component and (C) component in combination and, when desired, (E) a barium compound, (F) an antioxidant and various other additives may as well be further mixed therein.

Various barium compounds can be used as the (E) component, but barium sulfonate and barium naphthenate are most effective. Of them, the barium sulfonate to be used herein is a neutral or

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basic barium sulfonate having a total base number (TBN) of 0 to 500mgKOH/g.

The mixing amount of the barium compounds is not particularly limited and is variable depending upon the kind of each of (A) to (D) components, the kind of the object to be treated, the quenching conditions and further the property desired for the object to be treated and the like. But ordinarily 50 to 25,000ppm (in terms of barium) of a barium compound is mixed with the composition as the whole. When these barium compounds are mixed, brightness is further improved and decreasing of the quenching distortion is expedited in the object to be treated particularly in the initial phases of quenching (with a new oil).

Ordinarily, the antioxidant of the (F) component is effective when 0.05 to 10% by weight thereof is mixed with the composition as the whole. Examples of this antioxidant include a hindered phenol antioxidant (for example, 2,6-di-tert-butylparacresol and the like), an amine antioxidant (for example, α -naphthylamine, phenyl-naphthylamine, diphenylamine and the like) or a phosphoric antioxidant or the like.

Examples of the other additive include an cooling capacity improver (for example, polybutene, polymethacrylate and the like) and a brightness agent (for example, succinic acid, sorbitan ester, succinimide and the like).

A metal material such as steel material is subjected to a quenching treatment using a composition of the present invention by presetting a temperature of the composition as the

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heat treating oil preferably at an ordinary quenching temperature (around 60 to 150°C) and more preferably at a higher temperature of 170 to 250°C. When the metal material such as steel material is treated and quenched by using the composition of the present invention under the condition of such a high oil temperature, cooling unevenness is hard to occur, the object to be treated is provided with excellent and long surviving brightness and further the distortion of the object to be treated is decreased. Furthermore, the composition of the present invention has the excellent stability at high temperatures and thus can be used for a long period of time.

Furthermore, the heat treating oil composition of the present invention is as effective in the tempering treatment as in the quenching treatment.

As stated above, the heat treating oil composition of the present invention is excellent in the quenching treatment at high oil temperatures as compared with conventional methods and further the performance of the composition can be improved to a great extent by combining various components of the present invention.

Therefore, the heat treating oil composition of the present invention will find very high usefulness in the quenching treatment at high oil temperatures.

Particularly, it will be very highly useful in the field of quenching precision parts such as carburized gear and bearing wherein a CAFE (Cooperated Average Fuel Economy) measure and an

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anti-noise measure are critical.

Next, the present invention will be described in greater detail with reference to examples and comparative examples.

Table 1 shows the mixing ratio of the components in all examples and comparative examples.

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Table 1-1

Mixing Ratio (% by weight)		Examples			
		1	2	3	4
A	Mineral oil 1 S content (0.5wt%)	-	-	-	-
	Mineral oil 2 S content (300ppm)	-	-	-	-
	Mineral oil 3 S content (100ppm)	-	-	-	-
	Mineral oil 4 S content (3ppm >)	95	94.95	-	-
	Synthetic oil* ¹	-	-	94	95
B	Ca salicylate (TBN300)	5	5	5	5
C	Sulfurized Ca phenate	-	-	1	-
	Benzothiophene S content (17.4wt%)	-	0.05	-	-
D	Ca sulfonate (TBN300)	-	-	-	-
	Ca phenate (TBN200)	-	-	-	-
E	Ba sulfonate (TBN200)* ²	-	-	-	-
F	α - naphthylamine	-	-	-	-
Total sulfur content (ppm)		3 >	100	300	3 >

*1: A hydrogenated product of oligomer of olefin C₁₀

*2: Ba sulfonate is a (D) component as well

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Table 1-2

Mixing Ratio (% by weight)		Examples			
		5	6	7	8
A	Mineral oil 1 S content (0.5wt%)	-	-	-	-
	Mineral oil 2 S content (300ppm)	-	-	-	-
	Mineral oil 3 S content (100ppm)	-	-	-	-
	Mineral oil 4 S content (3ppm >)	95	94.95	-	94
	Synthetic oil* ¹	-	-	93.45	-
B	Ca salicylate (TBN300)	4	4	5	4
C	Sulfurized Ca phenate	1	-	-	1
	Benzothiophene S content (17.4wt%)	-	0.05	0.05	-
D	Ca sulfonate (TBN300)	-	-	-	-
	Ca phenate (TBN200)	-	-	-	-
E	Ba sulfonate (TBN200)* ²	-	1	1	1
F	α - naphthylamine	-	0.5	0.5	-
Total sulfur content (ppm)		300	100	100	300

*1: A hydrogenated product of oligomer of olefin C₁₀

*2: Ba sulfonate is a (D) component as well

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Table 1-3

Mixing Ratio (% by weight)		Examples			
		9	10	11	12
A	Mineral oil 1 S content (0.5wt%)	5	-	-	-
	Mineral oil 2 S content (300ppm)	-	-	-	-
	Mineral oil 3 S content (100ppm)	-	95	-	-
	Mineral oil 4 S content (3ppm >)	83.5	-	94.95	94.95
	Synthetic oil* ¹	-	-	-	-
B	Ca salicylate (TBN300)	10	5	-	-
C	Sulfurized Ca phenate	-	-	-	-
	Benzothiophene S content (17.4wt%)	-	-	0.05	0.05
D	Ca sulfonate (TBN300)	-	-	-	5
	Ca phenate (TBN200)	-	-	5	-
E	Ba sulfonate (TBN200)* ²	1	-	-	-
F	α - naphthylamine	0.5	-	-	-
Total sulfur content (ppm)		250	100	100	100

*1: A hydrogenated product of oligomer of olefin C₁₀

*2: Ba sulfonate is a (D) component as well

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Table 1-4

Mixing Ratio (% by weight)		Comparative Examples		
		1	2	3
A	Mineral oil 1 S content (0.5wt%)	94.5	94.5	25
	Mineral oil 2 S content (300ppm)	-	-	-
	Mineral oil 3 S content (100ppm)	-	-	-
	Mineral oil 4 S content (3ppm or less)	-	-	70
	Synthetic oil*1	-	-	-
B	Ca salicylate (TBN300)	-	-	5
C	Sulfurized Ca phenate	-	5	-
	Benzothiophene S content (17.4wt%)	-	-	-
D	Ca sulfonate (TBN300)	5	-	-
	Ca phenate (TBN200)	-	-	-
E	Ba sulfonate (TBN200)*2	-	-	-
F	α - naphthylamine	0.5	0.5	-
Total sulfur content (ppm)		4730	6230	1250

*1: A hydrogenated product of oligomer of olefin C₁₀

*2: Ba sulfonate is a (D) component as well

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Table 1-5

Mixing Ratio (% by weight)		Comparative Examples	
		4	5
A	Mineral oil 1 S content (0.5wt%)	-	-
	Mineral oil 2 S content (300ppm)	-	-
	Mineral oil 3 S content (100ppm)	-	-
	Mineral oil 4 S content (3ppm or less)	99.45	97.0
	Synthetic oil* ¹	-	-
B	Ca salicylate (TBN300)	-	-
C	Sulfurized Ca phenate	-	2.5
	Benzothiophene S content (17.4wt%)	0.05	-
D	Ca sulfonate (TBN300)	-	-
	Ca phenate (TBN200)	-	-
E	Ba sulfonate (TBN200)* ²	-	-
F	α - naphthylamine	0.5	0.5
Total sulfur content (ppm)		100	750

*1: A hydrogenated product of oligomer of olefin C₁₀

*2: Ba sulfonate is a (D) component as well

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Examples 1 to 12 and Comparative Examples 1 to 5:

These examples and comparative examples were carried out, as follows:

The test piece was a steel material S45C (a diameter of 10mm x a length of 40mm; a hardness of $H_{RC}16$). The test piece was fed into various quenching oils prepared according to the compositions shown in Table 1, treated and quenched. Quenching was carried out under the condition of an oil temperature of 200°C. The used mineral oil was a paraffinic mineral oil having a kinematic viscosity of 10cSt at 100°C.

The performance of the heat treating oil was evaluated by measurement with the changes of brightness after the test piece was treated and quenched with a new oil and an oil deteriorated by force.

Meanwhile, forced deterioration was conducted according to the Indiana Oxidation Test Method (IOT).

Manufacturing Conditions of Deteriorated Oil

Oil temperature	170°C
Air	10litre/minute
Catalyst	Fe, Cu

Determination of brightness performance (surface outlook)

◎: very good . . .No discolored parts in metallic lustre all over the surface.

○: good . . .Metallic lustre slightly reduced, with grayish parts.

△: fairly good . . .Partly turned black or brown.

×: no good . . .Black and brown all over, with no metallic lustre.

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The results of evaluating the performance are shown in Table 2. Furthermore, in Examples 1 and 7, the objects to be treated were subjected to a quenching treatment using an deteriorated oil for 24 hours, resulting in a finding that all of them had a hardness of approximately HR_{Rc}45.

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Table 2-1

I O T deteriorating time (hr)	Brightness			
	Examples			
	1	2	3	4
0	△	○	○	△
24	⊙	⊙	⊙	⊙
48	⊙	⊙	⊙	⊙
72	⊙	⊙	⊙	⊙
96	⊙	⊙	⊙	⊙
120	⊙	⊙	⊙	⊙
144	⊙	⊙	⊙	⊙
168	⊙	⊙	⊙	⊙
192	△	△	△	△

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Table 2-2

I O T deteriorating time (hr)	Brightness			
	Examples			
	5	6	7	8
0	○	⊙	⊙	⊙
24	⊙	⊙	⊙	⊙
48	⊙	⊙	⊙	⊙
72	⊙	⊙	⊙	⊙
96	⊙	⊙	⊙	⊙
120	⊙	⊙	⊙	⊙
144	⊙	⊙	⊙	⊙
168	⊙	⊙	⊙	⊙
192	△	○	○	△

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Table 2-3

I O T deteriorating time (hr)	Brightness			
	Examples			
	9	10	11	12
0	⊙	△	○	○
24	⊙	⊙	⊙	⊙
48	⊙	⊙	⊙	⊙
72	⊙	⊙	⊙	○
96	⊙	⊙	⊙	○
120	⊙	⊙	×	×
144	⊙	⊙	×	×
168	⊙	○	×	×
192	⊙	△	×	×

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Table 2-4

I O T deteriorating time (hr)	Brightness				
	Comparative Examples				
	1	2	3	4	5
0	△	△	×	○	○
24	○	○	⊙	○	○
48	⊙	⊙	⊙	○	○
72	×	×	×	○	○
96	×	×	×	△	△
120	×	×	×	×	×
144	×	×			
168	×	×			
192	×	×			

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As evident from Table 2, in all examples of the present invention the evaluation resulted in a far better outcome than in the comparative examples. It is observed that the base oil consisting of the (A) component and (B) component was effective by comparing the Examples 1, 4 and 10 with Comparative Example 3. It also is observed that the more excellent results were obtained by incorporating the (B) component into the base oil consisting of the (A) component and the (C) component in combination (see Examples 2, 3 and 7). The comparison of Examples 11 and 12 with Comparative Examples 2, 4 and 5 shows that the base oil consisting of the (A) component and the (C) component in combination and incorporating the the (D) component was effective. Moreover, there is a finding that the marked effect was obtained by the base oil incorporating the additional additives of (E) component and the (F) component (see Examples 6 to 9).

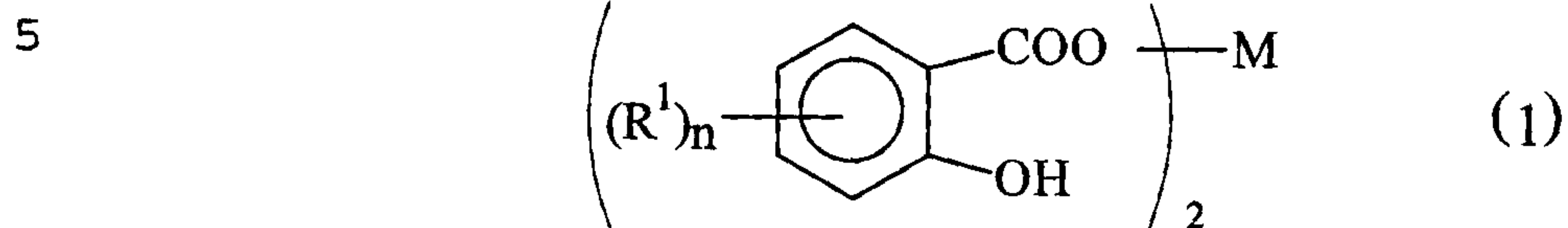
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CLAIMS:

1. A heat treating oil composition which comprises:
 - (I) a base oil having a sulfur content of 3 to 1,000 ppm and consisting of:
 - 5 (A) at least one member 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 sulfur and a sulfur compound, provided that the sulfur compound is
10 other than a sulfoxide, a sulfonic acid and a salt thereof; and
 - (II) an additive for quenching.
2. The heat treating oil composition according to claim 1, wherein the additive is (B) an alkaline earth metal
15 salt of salicylic acid.
3. The heat treating oil composition according to claim 1, wherein the additive is at least one member selected from an alkaline earth metal salt of sulfonic acid and an alkaline earth metal salt of phenol.
- 20 4. A heat treating oil composition for quenching and hardening a metal, which comprises:
 - (I) a base oil having a total sulfur content of 3 to 1,000 ppm and consisting essentially of (A) at least one member which is selected from a mineral oil and a synthetic
25 oil, each of which has a sulfur content of not more than 300 ppm and a kinematic viscosity of 2 to 100 cSt at 100°C, alone or in combination with (C) at least one member selected from sulfur and a sulfur compound; and

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(II) 0.1 to 50% by weight based on the heat treating oil of an additive for quenching that is at least one member of (B) an alkaline earth metal salt of a salicylate compound of the formula:



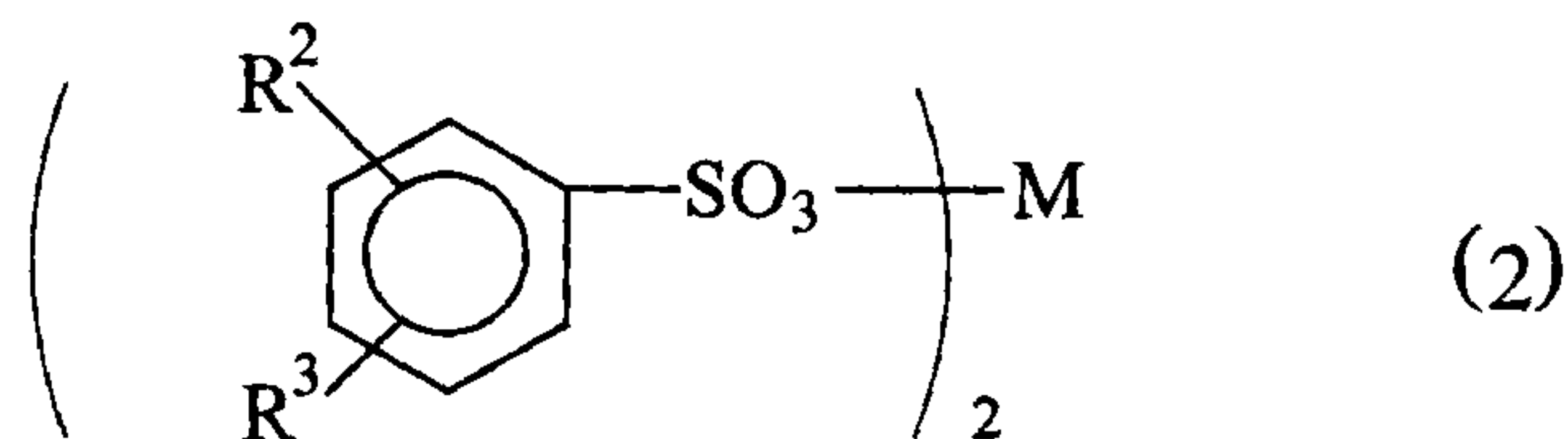
(wherein R^1 is a hydrogen atom or an alkyl group having 8 to 20 carbon atoms, n is an integer of from 1 to 4 and M is Ca, Ba or Mg), having a total base number of not more than 500mgKOH/g and (D) an alkaline earth metal salt of a sulfonic acid or phenol, provided that the additive for quenching (II) can be the alkaline earth metal salt of sulfonic acid or phenol (D) alone, only when the base oil (I) contains both the member (A) and the member (C) in combination.

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5. The heat treating oil composition according to claim 4, wherein the additive for quenching (II) comprises the alkaline earth metal salt of a sulfonic acid or phenol (D); the alkaline earth metal salt of a sulfonic acid is represented by the formula:

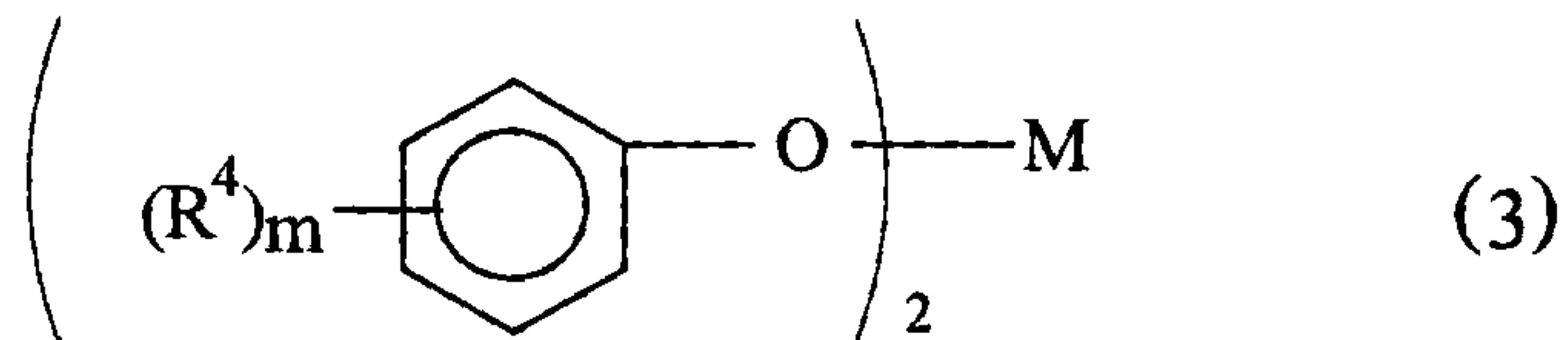
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(wherein R^2 and R^3 are each a hydrogen atom or an alkyl group having from 12 to 24 carbon atoms, provided that R^2 and R^3 are not a hydrogen atom at the same time; and M is Ca, Ba or Mg); and the alkaline earth metal salt of phenol is represented by the formula:

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(wherein R^4 is an alkyl group having from 9 to 24 carbon atoms, m is an integer of from 1 to 4 and M is Ca, Ba or Mg).

6. The heat treating oil composition according to claim 5, wherein the additive for quenching (II) comprises the alkaline earth metal salt of sulfonic acid.

7. The heat treating oil composition according to claim 5, wherein the additive for quenching (II) comprises the alkaline earth metal salt of phenol.

8. The heat treating oil composition according to claim 4, wherein the additive for quenching (II) is free of the alkaline earth metal salt of phenol.

9. The heat treating oil composition according to claim 4, wherein the additive for quenching (II) is free of the alkaline earth metal salt of a sulfonic acid or phenol.

10. The heat treating oil composition according to any one of claims 4 to 9, wherein the base oil (I) is free from sulfur and a sulfur compound (C).

11. The heat treating oil composition according to any one of claims 4 to 9, wherein the base oil (I) comprises at least one member selected from sulfur and a sulfur compound (C).

12. The heat treating oil composition according to claim 11, wherein the base oil (I) comprises a sulfur compound selected from sulfides, disulfides, polysulfides, mercaptans, thiophenes, sulfurized alkylphenates of alkaline

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earth metals, dithiophosphoric acid metals, mineral oils having a sulfur content of not more than 2%, sulfurized mineral oils, olefin sulfides and sulfurized fats.

13. The heat treating oil composition according to any one of claims 1 to 12, wherein the base oil (I) comprises an oligomer of an olefin having 8 to 12 carbon atoms or its hydrogenated product as the synthetic oil.

14. The heat treating oil composition according to any one of claims 1 to 12, wherein the base oil (I) comprises a paraffinic mineral oil as the mineral oil.

15. A method for treating a metal material, which comprises:

presetting a temperature of the heat treating oil composition as defined in any one of claims 1 to 14 to 170-250°C, and

quenching the metal material previously heated, in the heat treating oil composition.

16. The method according to claim 15, wherein the metal material is a steel material.

17. The heat treating oil composition according to any one of claims 1 to 3, which comprises, as the ingredient (C), a sulfur compound selected from the group consisting of sulfides, disulfides, polysulfides, mercaptans, thiophenes, sulfurized alkylphenates of alkaline earth metals, dithiophosphoric acid metals, mineral oils having a sulfur content of up to 2.0%, sulfurized mineral oils, olefine sulfides and sulfurized fats.

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18. The heat treating oil composition according to any one of claims 1 to 3, which comprises, as the ingredient (C), a sulfur compound selected from the group consisting of sulfides, disulfides, polysulfides, mercaptans, thiophenes, 5 sulfurized alkylphenates of alkaline earth metals, and dithiophosphoric acid metals.

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