Patented May 17, 1949 2,470,276

UNITED STATES PATENT OFFICE

2,470,276

OIL ADDEND

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No Drawing. Application November 29, 1945, Serial No. 631,771

2 Claims. (Cl. 252—52)

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This invention relates to a method for inhibiting the sulfiding of metallic copper by elemental sulfur present in petroleum oils and embraces compositions comprising petroleum oils and the inhibitors employed in the practice of the method.

Because of its corrosive action, particularly with respect to copper, the presence of even very small amounts of elemental sulfur in petroleum oils, including insecticide base kerosene, naphtha, gasoline, hydraulic oils, medicinal oils, lubricating oils etc., is sometimes highly objectionable. While a number of processes are available for the removal of sulfur from such oils, these processes are only partially effective in many cases, supplemental treatment being frequently required to meet product specifications.

I have discovered that a small amount of a hydrocarbon hydroperoxide when added to a petroleum oil containing elemental sulfur inactivates the sulfur so that it will not react with copper metal. Of the hydrocarbon hydroperoxides I particularly prefer tertiary-butyl hydroperoxide. As little as 0.006 per cent of this hydroperoxide on a volume basis is sufficient in most cases. Apparently inhibiting or inactivating action of the tertiary-butyl hydroperoxide is not due to reaction between it and the sulfur since the hydroperoxide is effective immediately upon addition to the oil and since agitating the oil under condtions which would remove uncombined peroxide by evaporation results in immediate restoration of the corrosive property of the oil.

The tertiary-butyl hydroperoxide is quite permanent in its action. Thus, samples of this hydroperoxide in kerosene containing elemental sulfur as an impurity, after storage at room temperature for nearly six months did not corrode copper strips kept suspended in the samples for three hours at 212° F.

For a peroxide, tertiary-butyl hydroperoxide is unusually stable as shown by the fact that it can be distilled under reduced pressure without decomposition. It is readily available commercially, at reasonable cost considering the low concentrations in which it is effective, and is comparatively safe to work with and to keep in storage.

Table I below illustrates the relative effectiveness of hydrocarbon hydroperoxides and ordinary hydrocarbon peroxides in preventing the corrosion of copper by sulfur in petroleum oil. In each case the base oil was an oleum-treated grade A South Texas distillate of the following characteristics:

Gravity, °API	31.0
Flash point, °F.	300

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Fire point, °F.	345
Viscosity @ —40° F. Cs.	4867.6
Viscosity @ 100° F. Cs.	12.0
Viscosity @ 210° F. Cs.	2.95
Cloud point, °F.	Below —70
Pour point, °F.	Below —70
Acid No.	0.00
Saponification No.	0.29
Aniline point, °F	191.5
Sulfur	0.03
Corrosion copper strip	Negative

From the table, in which the percentage sulfur is by weight and the percentage inhibitor by volume, it will be seen that while tertiary-butyl hydroperoxide gives protection in lower concentration than para-cymene hydroperoxide, the latter compound is effective at 0.02% concentration which is not true of acetyl peroxide, tertiary-butyl perbenzoate, lauroyl peroxide, and benzoyl peroxide.

Table I

	Copper Strip Corrosion—Federal Specification VV-L-791, Method 530.31
Base Oil+0.004% Elementary Sulfur	Positive.
Base Oil+0.004% Elementary Sulfur+0.02% Tertiarybutylhydroperoxide.	Negative.
Base Oil+0.004% Elementary Sulfur+0.01% Tertiarybutylhydroperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.006% Tertiarybutylhydroperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.004% Tertiarybutylhydroperoxide.	Positive.
Base Oil+0.004% Elementary Sulfur+0.020% Para-cymenehydroperoxide.	Negative.
Base Oil+0.004% Elementary Sulfur+0.010% Para-cymenehydroperoxide.	Positive.
Base Oil+0.004% Elementary Sulfur+0.006% Para-cymenehydroperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.020% Acetylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.010% Acetylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.006% Acetylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.020% Tertiarybutylperbenzoate.	Do.
Base Oil+0.004% Elementary Sulfur+0.010% Tertiarybutylperbenzoate.	Do.
Base Oil+0.004% Elementary Sulfur+0.006% Tertiarybutylperbenzoate.	Do.
Base Oil+0.004% Elementary Sulfur+0.02% Lauroylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.01% Lauroylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.006% Lauroylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.02% Benzoylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.01% Benzoylperoxide.	Do.
Base Oil+0.004% Elementary Sulfur+0.006% Benzoylperoxide.	Do.

My invention is further illustrated by the following examples, showing the application of my preferred inhibitor to various petroleum stocks:

Example 1

The oil involved in this test was a hydraulic oil corrosive to copper, as shown by the Federal test identified in Table I, and having the other properties indicated below:

Gravity, °API	33.0
Flash point, °F	200
Fire point, °F	215
Viscosity @ 100° F. Cs	3.12
Viscosity @ 210° F. Cs	1.22
Pour point, °F	Below —70
Neutralization No	0.00
Aniline point, °F	154.8

After the addition of two drops of tertiary-butyl hydroperoxide to 100 cc. of the oil, it successfully passed the test.

Example 2

0.004% sulfur by weight was added to a second hydraulic oil which had tested non-corrosive to copper. The oil tested positive following addition of the sulfur but repassed the test when 0.006% by volume of tertiary-butyl hydroperoxide was added. The inspection on this oil was as follows:

Gravity, °API	31.2
Flash point, °F	305
Fire point, °F	340
Viscosity @ 100° F. Cs	11.39
Viscosity @ 210° F. Cs	2.63
Pour point, °F	—65
Neutralization No	0.00
Aniline point, °F	191.1

Example 3

The oil here involved was an insecticide base oil corrosive to copper and having the following other characteristics:

Gravity, °API	46.4
Initial B. P., °F	358
10%	380
50	416
90	455
End point	495

The oil was rendered non-corrosive by the addition of 0.006% by volume of tertiary-butyl hydroperoxide.

Example 4

0.004% sulfur by weight was added to lubricating oil stock which had tested non-corrosive to copper. The oil tested positive following addition of the sulfur but when 0.20% by volume of tertiary-butyl hydroperoxide was added it repassed the test. In the case of lubricating oils an amount of the inhibitor greater than 0.006% appears necessary for adequate protection. This particular lubricating oil stock showed the following inspection:

Gravity, °API	25.0
Flash point, °F	285
Fire point, °F	315
Viscosity @ 100° F. Cs	8.07
Viscosity @ 210° F. Cs	2.09

Pour point, °F	Below —70
Neutralization No	0.00
Aniline point, °F	140.0
Copper strip corrosion	Negative

Example 5

To a compounded hydraulic oil containing an isobutylene polymer (Paratone) as a viscosity index improver was added 0.004% by weight of sulfur. When subsequently subjected to the copper corrosion test the oil tested positive. The result upon re-testing after addition of 0.01 per cent tertiary-butyl hydroperoxide was negative. This test is significant as showing that viscosity index improvers of the type of Paratone do not adversely effect the action of the hydroperoxide.

Example 6

0.004% by weight of sulfur was added to a sample of re-run alkylate stock which had tested non-corrosive to copper. The sample tested positive following addition of the sulfur but when 0.04% of tertiary-butyl hydroperoxide was added it repassed the test. The inspection on the alkylate stock was as follows:

Gravity, °API	70.4
Initial B. P., °F	125
10%	170
50	221
90	288
End point	346

Example 7

To a sample of gasoline produced by fluid catalytic cracking was added sufficient sulfur by weight to give a positive corrosion test, 0.1% tertiary-butyl hydroperoxide was then added and the gasoline re-tested. The results were negative.

I claim:

1. A petroleum oil, normally corrosive to copper by reason of its content of sulfur, containing an amount of a hydroperoxide from the group tertiary-butyl hydroperoxide and para-cymene hydroperoxide sufficient to inhibit such corrosion.

2. A petroleum oil, normally corrosive to copper by reason of its content of sulfur, containing an amount of tertiary-butyl hydroperoxide sufficient to inhibit such corrosion.

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