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METHOD OF INHIBITING EVOLUTION OF HYDROGEN SULFIDE FROM SULFURIZED OIL LUBRICANTS

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In the manufacture of extreme pressure lubricants for various purposes it is common practice to sulfurize the mineral oil stock or to blend mineral oil with a sulfurized oil or fat such as lard oil, sperm oil, hydrogenated fats, etc.

In the step of sulfurization, which is a direct addition of sulfur to the heated oil, more or less hydrogen sulfide is evolved. This is customarily removed by air blowing; so that the finished product is free from objectionable odor.

Unfortunately, however, the reaction by which hydrogen sulfide is produced is often not completed during the manufacture of the oil, but continues during the storage of the product. The odor thus generated is not particularly detrimental if the oil is used in a closed shell, as for example a gear case, but where the product is used for metal cutting, grinding or forming, the fetid odor of hydrogen sulfide is highly objectionable to the operator and is the source of many complaints.

I have discovered that when an oil-soluble soap of a water-insoluble, heavy metal which forms a stable sulfide is added to the sulfurized product, preferably as a final step in its manufacture and after all free hydrogen sulfide has been blown off, the further formation of hydrogen sulfide is inhibited over extended storage periods. Apparently the inhibiting action is common to a long list of heavy metals, including cadmium, copper, cobalt, iron, lead, manganese, mercury, nickel, silver, tin, and zinc, and is indifferent to the nature of the soap-forming organic acid with which the metal is combined, so long as the soap is readily oil-soluble. For reasons of economy, however, and also because of their somewhat greater effectiveness, I prefer to use the lead, copper, and cadmium soaps, and particularly the naphthenates and the oleates of these metals.

The effectiveness of these agents in inhibiting the release of free hydrogen sulfide, with its production of an unpleasant odor, was demonstrated by a series of experiments in which lead naphthenate, lead oleate, copper naphthenate, copper oleate, zinc naphthenate, and the naphthenates of chromium, nickel, manganese, cadmium, iron, and cobalt were used as inhibiting agents; and (A) copper sulfate, (B) cadmium chloride, and (C) mercuric chloride as indicators.

In making the tests the sulfurized compounded oils were heated and blown until free from odor and were then divided into the requisite number of portions and the additives mixed in. The samples were then stored for various periods, at the end of which paper strips spotted with solutions of the three indicators were introduced into the vapor space above the oil and allowed to remain for five minutes (in the case of Test

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3 for 40 hours). The varying sensitivities of these indicators is shown by the following table:

TABLE I

Sensitivity of indicators

Reactions	Classification by Sense of Smell	Vol. Per cent H_2S in Vapor
A-B-C positive	Strong	More than 0.002%.
A-B positive, C negative	Medium	0.001 to 0.002%.
A positive, B-C negative	Slight	Less than 0.001%.
A-B-C negative	None	Undetermined.

TABLE II

Mineral oil with 50% sulfurized lard oil (15% S)

[Lead naphthenate inhibitor]

Percent Lead added	Storage Period				
	49 Days	76 Days	203 Days	329 Days	522 Days
None	Strong				
0.06	do				
0.14	None	None	Medium	Slight	Slight.
0.28	do	do	Slight	do	
0.56	do	do	None	None	None.
1.01	do	do	do		
1.40	do	do	do		

TABLE III

Sulfurized mineral oil (0.7% added S) with 6.4% sulfurized lard oil (15% S)

[Lead naphthenate inhibitor]

Percent Lead Added	Storage Period		
	3 Days	148 Days	274 Days
None	Strong		
0.06	None	None	None.
0.11	do	do	Do.
0.17	do	do	Do.

TABLE IV

Mineral oil with 70% of sulfurized mineral oil (8% added S)

[Lead naphthenate inhibitor]

Percent Lead Added	Storage Period	
	84 Days	201 Days
None	Strong	Strong.
0.08	None	Medium.
0.11	do	Slight.
0.17	do	None.
0.28	do	Do.

TABLE V

Mineral oil with 50% sulfurized lard oil (15% S)

Inhibitor	Per cent Metal Added	Storage Period		
		95 days	213 days	406 days
Lead Naphthenate	0.056 Pb	Slight	Medium	Strong.
Do	0.11 Pb	do	Slight	Medium.
Do	0.17 Pb	None	None	Slight.
Lead Oleate	0.026 Pb	Medium	Strong	
Do	0.05 Pb	Slight	Medium	
Do	0.08 Pb	do	do	Strong.
Copper Naphthenate	0.016 Cu	do	Strong	
Do	0.03 Cu	do	do	
Do	0.05 Cu	None	Medium	Strong.
Copper Oleate	0.017 Cu	Strong	Strong	
Do	0.03 Cu	Slight	Medium	
Do	0.05 Cu	None	Slight	Strong.
Zinc Naphthenate	0.016 Zn	Strong	Strong	
Do	0.03 Zn	Medium	do	
Do	0.05 Zn	do	Medium	Strong.

TABLE VI

Mineral oil with 50% sulfurized lard oil (15% S)

Inhibitor	Per Cent Metal Added	Storage 141 Days
Chromium Naphthenate	0.014 Cr	Strong.
Do	0.028 Cr	Do.
Do	0.042 Cr	Medium.
Nickel Naphthenate	0.016 Ni	Strong.
Do	0.032 Ni	Do.
Do	0.048 Ni	Medium.
Manganese Naphthenate	0.015 Mn	Strong.
Do	0.030 Mn	Do.
Do	0.044 Mn	Medium.
Cadmium Naphthenate	0.030 Cd	Do.
Do	0.060 Cd	Slight.
Do	0.091 Cd	None.
Iron Naphthenate	0.015 Fe	Strong.
Do	0.030 Fe	Do.
Do	0.045 Fe	Medium.
Cobalt Naphthenate	0.014 Co	Strong.
Do	0.028 Co	Medium.
Do	0.042 Co	Do.

TABLE VII

Mineral oil with 5% and 10% of a phosphorized and sulfurized oil

[Lead naphthenate inhibitor]

Percent Lead Added	With 5% Phosphorized and Sulfurized Oil 15 Days' Storage	With 10% Phosphorized and Sulfurized Oil 15 Days' Storage
None	Strong	Strong.
0.28	None	None.
0.56	do	Do.

The effect of these minute additions of heavy metal soaps on the extreme pressure characteristics of the lubricant is immaterial. The lead soaps, when used in greater quantity, impart extreme pressure resistance, while the effects of the other heavy metal soaps are either favorable or neutral.

The tests summarized in Tables II–VI, inclusive, show that as regards the development of free hydrogen sulfide, the lead soaps and copper and cadmium naphthenate are substantially on a parity when the dosage is proportionate to the molecular weight of the metal, being notably effective as deodorizers. Copper oleate and the naphthenates of other heavy metals, for example, chromium, nickel, manganese, cadmium, iron, and cobalt are seen to be also effective, though the reactions are somewhat less marked. All may be useful under given circumstances. It is additionally apparent that the particular organic acid with which any of the metals is combined appears to affect only the solubility of the soap in mineral oil, a characteristic which is prerequisite to functionality.

The tests shown in Table VII indicate that lead as lead naphthenate effectively deodorizes a phosphorized and sulfurized oil, and it is believed that other heavy metal soaps will serve similarly.

While the above tests show that a very minute quantity of the heavy metal soap suffices to inhibit the evolution of hydrogen sulfide in storage, it will be understood that much larger quantities of the soap may be used if desired, up to the point, if any, at which the soap begins to exercise a deleterious effect on the extreme pressure-resisting properties of the lubricant.

It is further understood that I do not intend to be restricted either as to nominal dosage quantities of the heavy metal soaps hereinabove mentioned, or as to the particular solutions thereof, but rather intend to include all such usage within the spirit of my invention and the scope of the appended claims.

I claim as my invention:

1. The method of inhibiting the evolution in storage of hydrogen sulfide from lubricants compounded with sulfurized oils which consists in adding to the compounded lubricant, after removal therefrom of free hydrogen sulfide, an oil-soluble soap of a metal selected from the group consisting of lead, cadmium, copper, zinc, chromium, manganese, iron, nickel, and cobalt, in proportions of about 4 to 75 parts by weight of said metal per thousand parts by weight of sulfur.

2. The method of inhibiting the evolution in storage of hydrogen sulfide from lubricants compounded with sulfurized oils which consists in adding to the compounded lubricant, after removal therefrom of free hydrogen sulfide, an oil-soluble soap of lead in proportions of about 4 to 75 parts by weight of lead per thousand parts by weight of sulfur.

3. The method of inhibiting the evolution in storage of hydrogen sulfide from lubricants compounded with sulfurized oils which consists in adding to the compounded lubricant, after removal therefrom of free hydrogen sulfide, an oil-soluble soap of copper in proportions of about 4 to 75 parts by weight of copper per thousand parts by weight of sulfur.

4. The method of inhibiting the evolution in storage of hydrogen sulfide from lubricants compounded with sulfurized oils which consists in adding to the compounded lubricant, after removal therefrom of free hydrogen sulfide, an oil-soluble soap of cadmium in proportions of about 4 to 75 parts by weight of cadmium per thousand parts by weight of sulfur.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
604,515	Bragg	May 24, 1898
2,242,624	Schulz	May 20, 1941
2,246,281	Zimmer	June 17, 1941

OTHER REFERENCES

"The Alkaline Earth and Heavy Metal Soaps," Elliott (1946), pages 144, 169, 201, 213, 214, 219 and 220.