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EXTREME PRESSURE LUBRICATING OIL CONTAINING SULFUR-CHLORINATED ESTERS OF CHLORENDIC ACID

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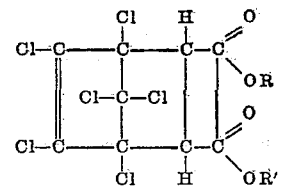
This invention relates to sulfur-chlorinated esters of chlorendic acid, and particularly to the use of such esters in mineral oils to provide extreme pressure lubricants and metal-working oils having improved properties. This invention further relates to extreme pressure lubricants of improved load carrying ability which satisfy the requirements demanded in the lubrication of bearing, gears, and the like, subjected to heavy loads per unit area of surface.

The present invention is particularly concerned with cutting oils used in broaching, gear cutting, hobbing, planing and similar operations in which metal is removed from the work piece at a comparatively low rate, e.g. at cutting speeds of 10 to 20 surface feet per minute. The metal chips removed vary in thickness from 0.005 to 0.0005 inch. A major objective of cutting operations of this type is the achievement of a good surface finish, and, therefore, one of the functions of a cutting oil used in such operations is to improve the surface finish obtained.

Certain short chain chlorinated compounds such as carbon tetrachloride, ethylene dichloride and diisobutylene dichloride are known to be especially effective as additives for broaching and gear cutting oils. Although an excellent surface finish can be obtained on work pieces by the inclusion of carbon tetrachloride in broaching and gear cutting oils, this compound is not suitable as a cutting oil additive for two reasons. First, due to its volatility carbon tetrachloride is rapidly lost by evaporation from the cutting oil during use thus necessitating close control of the concentration and frequent replenishment with fresh carbon tetrachloride. Second, carbon tetrachloride is a toxic substance which causes severe physiological damage when inhaled as a vapor or when absorbed through the skin by contact. Ethylene dichloride is also highly volatile. Diisobutylene dichloride, which might be used as a substitute for carbon tetrachloride due to its lack of toxicity, is objectionable because of its highly unpleasant odor which could not be tolerated for the length of an average working day. Therefore, a need exists for a non-toxic, non-volatile, substantially odorless, mineral oil-soluble additive which imparts extreme pressure properties to a cutting oil composition.

In accordance with the present invention I have discovered that valuable extreme pressure additives can be prepared by sulfur-chlorinating unsaturated esters of chlorendic acid and that the addition of such additives to mineral lubricating oils provides extreme pressure lubricating compositions of improved load carrying ability under conditions of high mechanical loading. As cutting oils or metal working fluids, mineral oils which contain sulfur-chlorinated esters of chlorendic acid are useful in reducing the surface roughness of machined parts.

The oil-soluble sulfur-chlorinated esters added to mineral lubricating oils in preparing lubricating compositions of this invention can be obtained by sulfur-chlorinating an oil-soluble ester of chlorendic acid of the following formula:



in which R is an unsaturated aliphatic, including cycloaliphatic, hydrocarbon group containing 3 to 20 carbon atoms and R' is hydrogen or the identical or non-identical member selected from the same group as R. More specifically, the unsaturated members include alkenyl groups such as allyl, oleyl, cyclohexenyl and ester groups from unsaturated alcohols derived from acids such as linoleic, myristoleic, cinnamic, angelic and the like, which unsaturated members can, if desired, be substituted as with chlorine for instance. Although the monoesters can be employed, the preferred esters of chlorendic acid are diesters and particularly those in which the ester groups are mono-olefinic and contain from 16 to 18 carbon atoms. A preferred diester can be obtained from the unsaturated alcohols derived from sperm oil. The esters can be prepared by any suitable method as, for example, by reacting chlorendic anhydride with an excess of the appropriate unsaturated alcohol. The esterification reaction can be carried out in the presence of a catalyst such as p-toluene sulfonic acid until the theoretical amount of water has been removed. Alternatively, chlorendic acid may be used instead of the anhydride and in this method two moles of water are evolved for each mole of chlorendic diester formed. The water of reaction may be removed azeotropically by distillation with a solvent such as benzene or toluene.

The sulfur-chlorination of the chlorendic acid ester is accomplished by reacting each mole of chlorendate ester with about .5 to 2 moles of a sulfur chloride such as sulfur monochloride or sulfur dichloride at a temperature in the range of about 120° to 300° F. Frequently, the exothermic heat of reaction will maintain the reaction mixture within the desired temperature range although in large scale preparations it may be necessary to use external cooling means.

In oil blends which are used as metal working fluids in operations such as planing, broaching, gear cutting and the like, the amount of additive employed can depend upon the particular ester in the additive. For esters of high molecular weight, for example, sulfur-chlorinated oleyl chlorendate diester, the amount employed will usually be about 9 to 35% by weight whereas for the lower molecular weight esters, such as sulfur-chlorinated diallyl chlorendate, the amount used in general will range from 5 to 30% by weight. The compounding of oils for extreme pressure lubricants frequently requires about 0.5 to 10% of the sulfur-chlorinated chlorendate ester. These percentages are based on the weight of the mineral oil present. The manner in which the sulfur-chlorinated esesters of chlorendic acid are prepared and the properties of lubricating oils containing the esters are illustrated in the following examples which are not to be considered as limiting.

EXAMPLE I

Preparation of oleyl chlorendate diester

A mixture of 705 grams of chlorendic anhydride and 1000 grams of commercial oleyl alcohol (hydroxyl number 214, iodine number 83) was dissolved in 1000 cc. of xylene and 10 grams of p-toluene sulfonic acid were added added as a catalyst. The mixture was heated to reflux for 10 hours until 44 cc. of water had been collected in a Dean-Start trap attached to the esterification apparatus. The reaction mixture was then washed once

with 0.25 N KOH in 1:1 alcohol-water and twice with 1:1 alcohol-water. After clarification by filtration, the reaction mixture was freed of xylene by distillation and the last traces of solvent were removed under vacuum at a pot temperature of 300° F. The reaction product was a dark oily liquid with the characteristics listed below.

Percent chlorine	24.0
Acid number	0.28
Saponification number	127.9
Iodine number	50.1

EXAMPLE II

Preparation of allyl chlorendate diester

A mixture of 1500 grams chlorendic anhydride dissolved in 2000 cc. of allyl alcohol with 10 grams of p-toluene sulfonic acid as a catalyst was refluxed for 32 hours and the excess allyl alcohol was removed by distillation. The residue was taken up in a mixture of pentane and benzene and was washed first with aqueous KOH and then with water. The solvent was distilled off, first at atmospheric pressure and finally at 2–3 mm. pressure. The product was a dark viscous liquid having the following characteristics.

Percent chlorine	44.8
Acid number	0.10
Saponification number	236.8
Iodine number	107.1

EXAMPLE III

Sulfur-chlorination of oleyl chlorendate diester

A portion of oleyl chlorendate diester containing 22.6% chlorine, with a saponification number of 119.4 and an iodine number of 50.0, was reacted with sulfur monochloride. To 1541 grams of the di-oleyl chlorendate, 208 grams of sulfur monochloride were added at 140–167° F. and the reaction mixture was stirred for 6 hours at 158° F. The reaction mixture was then blown with air at 140° F. to purge it of free hydrogen chloride, and the further evolution of hydrogen chloride was inhibited by the addition of 0.2% of propylene oxide. The product, a thick, sticky, dark brown substance at room temperature, contained 5.85% sulfur and 25.8% chlorine.

EXAMPLE IV

Sulfur-chlorination of allyl chlorendate diester

To 600 grams of allyl chlorendate diester, 115 grams of sulfur monochloride were gradually added at a temperature of 195–210° F. The reaction mixture thickened progressively and eventually became so viscous that further stirring was impossible. This tacky, semi-solid material contained 7.18% sulfur and 44.7% chlorine.

EXAMPLE V

Compounded oils containing sulfur-chlorinated oleyl chlorendate diesters

Compounded oils were prepared with sulfur-chlorinated di-oleyl chlorendate, as prepared in Example III, by blending the additive into acid refined Coastal naphthenic oils at 150° F. to 210° F. The additive remained completely dissolved in the oil at room temperature. The following blends were made up in mineral oils of different viscosities.

Blend No.	Percent Additive	Percent S	Percent Cl	Viscosity, SUS at 100° F.
1	25	1.56	5.03	222
2	10	0.79	2.39	219
3	7	0.70	1.84	242
4	5	0.44	1.23	212
5	2	0.32	0.56	212

EXAMPLE VI

Compounded oils containing sulfur-chlorinated allyl chlorendate diester

Eighty parts of the sulfur-chlorinated diallyl chlorendate of Example IV were mixed with 20 parts of benzene to aid in blending the additive into oil. Seven hundred and eight-seven grams of this mixture were added to 5025 grams of an acid-refined Coastal oil of 175 seconds viscosity at 100° F. It was found necessary to add 1839 grams of benzene to keep the sulfur-chlorinated diallyl chlorendate completely dissolved in the oil at room temperature. The final blend, which had 8.25% of sulfur-chlorinated diallyl chlorendate incorporated therein, contained 0.79% sulfur and 3.28% chlorine; and had a viscosity of 96.6 SUS at 100° F.

EXAMPLE VII

Sulfur-chlorinated chlorendate esters as metal-working additives

The advantages obtained by employing the lubricating compositions of the present invention as cutting oils become particularly apparent in cases where the surface finish requirements for the work piece are unusually stringent. The effect of oil blends containing sulfur-chlorinated oleyl chlorendate diester as a cutting oil was demonstrated by means of an orthogonally cutting planer operation. As shown below, the various oil blends prepared in accordance with Examples V and VI were rated according to the surface roughness of the cut surface as determined by a profilometric measuring instrument. Results are shown in Table I below.

TABLE I

Oil Blends	Sulfur Chlorinated Diester	Surface Roughness, Microinches			
		AISI 1045 Steel	AISI 4150 Steel	AMS 6260 Steel	AISI 8620 Steel
1 [1]	Oleyl	77	78	80	80
3 [1]	Oleyl	123	97		
6 [2]	Allyl	124		65	37
Base Oil		173	98	131	85

[1] Blends prepared in Example V.
[2] Blend of Example VI.

Oil blends containing sulfur-chlorinated oleyl chlorendate diester were tested for extreme-pressure load carrying ability in the Falex lubricant testing apparatus. Also an oil blend containing 26% by weight of a non-sulfur-chlorinated oleyl chlorendate diester was tested. In this test an uncompounded mineral oil does not allow the test to run for the three-minute breakin period at 300 lbs. load without failure. As can be seen, the sulfur-chlorinated diesters provide extreme pressure lubricants of improved load carrying ability.

TABLE II

Oil Blend	Percent Additive	Failure Load, Lbs.
2 [1]	10	[3] >4,500
4 [1]	5	[3] >4,500
5 [1]	2	1,500
7 [2]	26	1,250

[1] Blends prepared as in Example V.
[2] 26% Oleyl chlorendate in oil.
[3] Did not fail at load limit of the apparatus.

I claim:

1. A new composition of matter consisting essentially of a mineral lubricating oil and an amount sufficient to increase the load carrying capacity of the oil of a sulfur-chlorinated oil-soluble ester of chlorendic acid produced by reacting a sulfur chloride and an oil-soluble chlorendic acid ester in a ratio of about .5 to 2 moles of sulfur chloride to 1 mole of said chlorendic acid ester wherein

said ester group is an unsaturated aliphatic hydrocarbon radical containing from 3 to 20 carbon atoms.

2. The composition of claim 1 in which the ester is about 5 to 35% of the mineral oil.

3. The composition of claim 1 in which the ester is about 0.5 to 10% of the mineral oil.

4. The composition of claim 2 in which the ester is a diester in which each ester group contains from 16 to 18 carbon atoms.

5. The composition of claim 4 in which the ester is a diester in which each ester group contains from 16 to 18 carbon atoms.

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