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SULFURIZED OIL-SOLUBLE ESTERS OF CHLORENDIC ACID

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3 Claims. (Cl. 260—125)

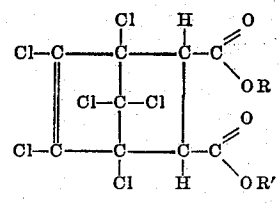
This invention relates to sulfurized esters of chlorendic acid, and particularly to the use of such esters in mineral oils to provide extreme pressure lubricants and metal-working oils having improved properties. This invention also relates to extreme pressure lubricants of improved load carrying ability which satisfy the requirements demanded in the lubrication of bearings, 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 the addition of oil-soluble sulfurized unsaturated esters of chlorendic acid to mineral lubricating oils affords extreme pressure lubricating compositions of improved load carrying ability under conditions of high mechanical loading. As metal working fluids the lubricating compositions of this invention are advantageous inasmuch as they are capable of reducing the surface roughness of machined parts.

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



in which R is an unsaturated aliphatic, including cycloaliphatic, or aromatic 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, aryl and aralkenyl groups such as allyl, oleyl, cyclohexenyl, phenyl, and naphthyl ester groups from unsaturated alcohols derived from acids such as phenyl acrylic, linoleic, myristoleic, cinnamic, angelic and the like, which unsaturated members can, if desired, be substituted as with chlorine for instance. 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 reaction can be carried out in the presence of an esterification catalyst such as p-toluene sulfonic acid until the theoretical amount of water has been removed. If desired, the same method of preparation is applicable when using chlorendic acid instead of the anhydride. In this method two moles of water are evolved for each mole of chlorendic diester formed and the water of reaction may be removed azeotropically by distillation with a solvent such as benzene or toluene.

In carrying out the sulfurization of the chlorendic acid ester about one-half to four gram-atoms of elemental sulfur are reacted with each mole of chlorendate ester at a temperature of from about 300° to 450° F. Preferably, however, the sulfurization is accomplished by reacting each mole of ester with about one-half to two gram-atoms of sulfur at a temperature of about 320° to 375° F. At temperatures below 320° F. the sulfurization reaction is slow, whereas at higher temperatures, i.e. above 375° F., large amounts of sulfur are lost in the form of hydrogen sulfide.

The amount of the sulfurized esters of chlorendic acid added to the mineral oil for the preparation of the compositions is sufficient to impart increased load carrying capacity to the base oil and may vary, depending upon the service application for which the composition is designed. In general, for metal working fluids used as cutting oils, and depending upon the smoothness of the work piece desired, the amount of sulfurized ester required to be added will depend upon the particular ester and will usually vary between about 5 to 35% by weight of the oil base. The compounding of oils for use as extreme pressure lubricants, as distinguished from cutting oils, requires about 0.5 to 10% by weight of the sulfurized ester material.

The following examples, which are not to be considered limiting, illustrate the preparation of sulfurized chlorendic acid esters and the compounding of mineral lubricating oils containing the same for use as extreme pressure lubricants.

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 as a catalyst. The mixture was heated to reflux for 10 hours until 44 cc. of water had been collected in a Dean-Stark 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

Sulfurization of oleyl chlorendate diester

A 436-gram portion of dioleyl chlorendate containing 19.4% chlorine, with a saponification number of 99.6 and an iodine number of 47.9, was reacted with 26.5 grams of sulfur for 6 hours at temperatures starting at 320° F. and gradually increasing to 370° F. The mixture was then blown with air for 4 hours and the temperature was allowed to drop to 75° F. The product was a dark, viscous material containing 6.12% sulfur and 17.2% chlorine.

EXAMPLE IV

Sulfurization of allyl chlorendate diester

A mixture of 512 grams of diallyl chlorendate and 60 grams of sulfur was heated in the temperature range 300°–360° F. for 6 hours. When the reaction mixture cooled to room temperature it solidified to a black, brittle material which melted to a fluid at 280°–320° F. The product contained 11.1% sulfur and 40.5% chlorine. It was not a homogeneous substance since it was only partly soluble in an acid-refined Coastal oil. The insoluble residue was a tar.

EXAMPLE V

Compounded oils containing sulfurized oleyl chlorendate diester

Compounded oils were prepared with sulfurized dioleyl chlorendate by blending the additive into acid refined Coastal naphthenic oils at 150° 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	2.10	5.30	148
2	10	0.74	2.03	181
3	10	0.99	2.16	153
4	5	0.54	1.09	159

Mineral oil compositions of this invention are also prepared by adding at 175° F. 5, 10 and 25 percent of the sulfurized diester of Example IV to a Coastal naphthenic oil of 150 SUS at 100° F. viscosity.

The advantages obtained by employing the lubricating compositions of the present invention as cutting oils became particularly apparent in cases where the surface finish requirements for the work piece are unusually stringent. The effect of oil blends containing sulfurized dioleyl chlorendate as a cutting oil was demonstrated by means of an orthogonally cutting planer operation. As shown below various oil blends prepared in accordance with Example V 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 Blend of Ex. 5	Surface Roughness, microinches			
	AISI 1045 Steel	AISI 4150 Steel	AMS 6260 Steel	AISI 8620 Steel
1	76	56	50	55
2		95	80	73
Base Oil	173	98	131	85

Oil blends 3 and 4 of Example 5 which contained 10% and 5% by weight of sulfurized dioleyl chlorendate, respectively, were tested for extreme pressure load carrying ability in the Falex lubricant testing apparatus. A similar oil blend containing 26% of the unsulfurized diester was also tested. In this test an uncompounded mineral oil does not permit the test to run for the three minute break-in period at 300 pounds without failure. As shown below, oil blends containing sulfurized oleyl chlorendate diester provide extreme pressure lubricants of improved load carrying ability.

Oil Blend of Example 5	Additive, Wt. Percent	Failure Load, lbs.
3	10	2,750
4	5	2,750
5 (contained unsulfurized diester)	26	1,250

The present application is a division of Serial No. 602,062, filed August 3, 1956, now Patent No. 2,969,326.

I claim:

1. A sulfurized oil-soluble ester of chlorendic acid produced by reacting sulfur and an oil-soluble chlorendic acid ester in a ratio of about one-half to four gram-atoms of sulfur to one mole of chlorendic acid ester in which said ester group is an unsaturated hydrocarbon radical containing from 3 to 20 carbon atoms.

2. The product of claim 1 wherein the ester of chlorendic acid is a diester in which each ester group is an aliphatic unsaturated hydrocarbon radical containing from 3 to 20 carbon atoms.

3. The product of claim 2 wherein the chlorendic acid diester is dioleyl chlorendate.

No references cited.