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XANTHIC FORMATES

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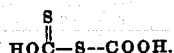
This invention relates to new compositions of matter, and more particularly to high molecular weight polysulfur compounds, and still more particularly to xanthic formic esters and their ammonolytic derivatives.

Lower aliphatic xanthates, their esters and anhydrides have been prepared and these have been proposed for insecticides, flotation agents, and rubber accelerators. However, they have the disadvantage of having an undesirable odor, a high volatility, and poor stability in water.

The object of this invention is to prepare high molecular weight water insoluble derivatives of xanthic formic acid. A further object is to prepare these compounds for use as insecticides, flotation agents, and rubber accelerators. A still further object is to prepare the esters and ester-amides of xanthic formic acid, said compounds containing at least one long-chain radical. These objects are accomplished by the following invention.

Water-insoluble derivatives of carbon bisulfide are prepared by the introduction of long aliphatic chains into the compounds. Particularly suitable are those compounds made from octyl and higher alcohols, especially those obtainable from the catalytic hydrogenation of the carboxyl group in coconut oils.

Chemically speaking, the applicant's invention involves the derivatives of xanthic formic acid,



Xanthic formic acid is a dibasic acid and this invention relates to the mono esters of xanthic formic acid, such as $\text{ROCSS}-\text{COOH}$, in which "R" is an aliphatic hydrocarbon radical of at least eight carbon atoms; to the diesters of xanthic formic acid, such as $\text{ROCSS}-\text{COOR}'$, in which "R" and "R'" are aliphatic hydrocarbon radicals and at least one of the radicals contains at least eight carbon atoms; to the xanthic esters of xanthic formic acid, such as



in which "R" and "R'" are aliphatic hydrocarbon radicals and at least one of the radicals contains at least eight carbon atoms; and to the ammonolytic derivatives, otherwise known as amide esters such as



in which "R" is an aliphatic hydrocarbon radical, "R'" is a hydrogen or an aliphatic hydrocarbon radical, and "R'' is hydrogen, an aliphatic hydrocarbon radical, or an aryl group, and at least one of the aliphatic hydrocarbon radicals contains at least eight carbon atoms.

While various related groupings come within the scope of this invention, all of the compounds obtained have common physical properties; namely, high boiling, low melting, low in odor,

organic soluble, and water insoluble. The compounds having an aliphatic hydrocarbon group containing eight or more carbon atoms are markedly superior in these characteristics.

The method of preparation of the various compounds is relatively simple. It involves the reaction of carbon bisulfide on an alcohol in the presence of a caustic alkali and then condensing the intermediate xanthate salt with phosgene or a phosgene derivative, such as an alkyl chlorocarbonate or an amido chlorocarbonate. The various methods of forming these compounds may be outlined as follows:

(1) To make an aliphatic xanthic formic acid chloride, react an alkali aliphatic xanthate with phosgene; for example, potassium dodecyl xanthate will react with phosgene to form dodecyl xanthic formic acid chloride.

(2) To make a xanthic ester of an aliphatic xanthic formic acid, react an aliphatic xanthic formic acid chloride with an alkali xanthate; for example, potassium dodecyl xanthate will react with dodecyl xanthic formic acid chloride to yield the dodecyl xanthic ester of dodecyl xanthic formic acid.

(3) To make an alkyl ester of an aliphatic xanthic formic acid, react dodecyl xanthic formic acid chloride with an aliphatic alcohol; for example, dodecyl xanthic formic acid chloride will react with ethyl alcohol to form the ethyl ester of dodecyl xanthic formic acid. It is preferred, however, in making an alkyl ester of an aliphatic xanthic formic acid to react an alkali aliphatic xanthate with an alkyl chlorocarbonate; for example, potassium dodecyl xanthate with dodecyl chlorocarbonate yields the dodecyl ester of dodecyl xanthic formic acid.

(4) To make an amide of an aliphatic xanthic formic acid, react an aliphatic xanthic formic acid chloride with an amine; for example, dodecyl xanthic formic acid chloride reacts with aniline to yield the anilide of dodecyl xanthic formic acid.

This invention will be more readily understood by reference to the following examples, but it is not intended that these examples should limit the scope of the invention:

Example 1

Dodecyl xanthic ester of dodecyl xanthic formic acid was prepared by the following process: Twelve parts by weight of potassium dodecyl xanthate was suspended in about 10 cc. of toluene, and 12 parts by weight of a toluene solution containing 3 parts by weight of phosgene was mixed together in a flask and warmed to about 40° C. A white solid separated. The toluene solution was washed thoroughly with water and the toluene evaporated on a steam bath. The product was a yellow liquid which an-

alyzed 22.5% sulfur, calculated 23.2% sulfur. The oil was insoluble in water but soluble in alcohol, ether, benzene, kerosene, and toluene.

Example 2

Dodecyl xanthic formic acid chloride was prepared by the following process: 40 parts by weight of a 10% solution of potassium dodecyl xanthate in toluene was mixed with 4 parts by weight of a 25% solution of phosgene in toluene. The solution became warm and a solid separated. The solution was filtered and blown with air for an hour to remove hydrogen chloride. The product was a toluene solution of dodecyl xanthic formic acid chloride. The chloride may be isolated by evaporating the toluene and by treatment with water may be converted to dodecyl xanthic formic acid.

Example 3

Dibutyl amide of dodecyl xanthic formic acid was prepared by the following process: Dibutylamine was added to a solution of dodecyl xanthic formic acid chloride in toluene. Dibutylamine hydrochloride separated and was filtered off. The product was a toluene solution of the dibutyl amide of dodecyl xanthic formic acid.

Example 4

Anilide of dodecyl xanthic formic acid was prepared by the following process: Aniline was added to a cold toluene solution of dodecyl xanthic formic acid chloride. Aniline hydrochloride precipitated at once and was filtered off. The water insoluble anilide of dodecyl xanthic formic acid may be isolated by evaporating the toluene at reduced pressure.

Example 5

Dodecyl ester of dodecyl xanthic formic acid was prepared by the following process: Dodecyl chlorocarbonate was dissolved in cold ethyl alcohol and mixed immediately with a cold ethyl alcohol solution of potassium dodecyl xanthate. A white precipitate which formed at once was filtered off. The white precipitate was soluble in water. The product was an alcohol solution of the dodecyl ester of dodecyl xanthic formic acid.

Example 6

Dodecyl xanthic formyl pyridinium chloride was prepared by the following process: Pyridine was added to a cold toluene solution of dodecyl xanthic formic acid chloride. The solution became slightly cloudy but no precipitate formed. The product was a toluene solution of dodecyl xanthic formyl pyridinium chloride.

Dodecyl xanthic ester of dodecyl xanthic formic acid may be used in the following manner as a flotation agent.

A Denver Sub-A flotation cell of 1000 g. capacity was charged with 800 g. of a copper sulfide ore, .08 g. pine oil, 1.2 g. sodium carbonate and .05 g. of the dodecyl xanthic ester of dodecyl xanthic formic acid. An analysis for copper in the heads indicated a 74% recovery in the concentrate. Under similar conditions potassium ethyl xanthate resulted in a 32% recovery of copper in the concentrate.

By an ester of a xanthic formic acid it is meant to include: (a) the mono esters of xanthic formic acid, such as octyl xanthic formic acid, $C_8H_{17}OCSSCOOH$, and its homologues; (b) the diesters of xanthic formic acid, such as the octyl ester of methyl xanthic formic acid,

$CH_3OCSSCOOC_8H_{17}$ and its homologues; (c) the xanthic esters of xanthic formic acid such as tetradecyl xanthic ester of methyl xanthic formic acid, $CH_3OCSSCOSSCOC_{14}H_{29}$, and its homologues; and (d) the ester amides of xanthic formic acid, such as N-dodecyl amide of methyl xanthic formic acid, $CH_3OCSSCONHC_{12}H_{25}$, and its homologues.

In the preparation of esters and ester amides of methyl xanthic formic acid and its homologues, the "coconut alcohols" obtainable from the catalytic hydrogenation of the carboxyl group in coconut oil, coconut oil acids or palm kernel oil, or mixtures of these alcohols are particularly suitable. In place of the coconut alcohols the naphthenyl alcohols obtainable by the carboxylic hydrogenation of naphthenic acids may be employed.

Compounds of the formula $ROCSSCOX$, where "R" is an aliphatic hydrocarbon group and where "X" may be either OH, OR', halogen, NR''R''', or R'OCSS—, where "R" is an aliphatic hydrocarbon group, "R'" is hydrogen or an aliphatic hydrocarbon group, and "R'''" is hydrogen, an aliphatic hydrocarbon group or an aryl group, and where at least one of the aliphatic hydrocarbon groups contains at least eight carbon atoms, are the compounds that are included within the scope of this invention. These compounds include the methyl ester of octyl xanthic formic acid $C_8H_{17}OCSSCOOCH_3$; octyl ester of methyl xanthic formic acid, $CH_3OCSSCOOC_8H_{17}$; dodecyl xanthic formic acid chloride, $C_{12}H_{25}OCSSCOCl$; dodecyl xanthic formic acid, $C_{12}H_{25}OCSSCOOH$; cetyl xanthic ester of cetyl xanthic formic acid, $(C_{16}H_{33}OCSS)_2CO$; tetradecyl xanthic ester of octyl xanthic formic acid, $C_8H_{17}OCSSCOSSCOC_{14}H_{29}$; amide of decyl xanthic formic acid, $C_{10}H_{21}OCSSCONH_2$; N-methyl N-ethyl amide of dodecyl xanthic formic acid, $C_{12}H_{25}OCSSCONCH_3(C_2H_5)$; N-dodecyl amide of methyl xanthic formic acid,

$CH_3OCSSCONHC_{12}H_{25}$;
anilide of eicosyl xanthic formic acid,

$C_{20}H_{41}OCSSCONHC_6H_5$;
dodecyl xanthic ester of 9,10-octadecenyl xanthic formic acid, $C_{18}H_{35}OCSSCOSSCOC_{12}H_{25}$, mixed coconut alcohol esters of mixed alkyl (as present in coconut alcohols) xanthic formic acid; tetradecyl xanthic ester of naphthenyl xanthic formic acid.

The compounds falling within the scope of my invention may be used as insecticides, flotation agents and rubber accelerators; for example, the dodecyl xanthic ester of dodecyl xanthic formic acid is a very good parasiticide, a good flotation agent, and a rubber accelerator, and may be used as a dispersing agent for carbon black in rubber.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended patent claims.

I claim:

1. An aliphatic ester of a xanthic formic acid, said ester containing at least one aliphatic hydrocarbon radical having at least eight carbon atoms.

2. An aliphatic ester of a xanthic formic acid, said ester containing at least one alkyl radical obtainable from the alcohols obtained by the carboxyl hydrogenation of coconut oil.

3. An aliphatic ester of a xanthic formic acid, said ester containing at least one dodecyl radical.

4. An ester of xanthic formic acid with an aliphatic alcohol, said ester containing at least one aliphatic hydrocarbon radical having at least eight carbon atoms.
- 5 5. An ester of xanthic formic acid with an aliphatic alcohol, said ester containing at least one alkyl radical obtainable from the alcohols obtained by the carboxyl hydrogenation of coconut oil.
- 10 6. An ester of xanthic formic acid with an aliphatic alcohol, said ester containing at least one dodecyl radical.
- 15 7. A xanthic ester of a xanthic formic acid, said ester containing at least one aliphatic hydrocarbon radical having at least eight carbon atoms.
8. An xanthic ester of a xanthic formic acid, said ester containing at least one alkyl radical obtainable from the alcohols obtained by the carboxyl hydrogenation of coconut oil.
9. A xanthic ester of a xanthic formic acid, said ester containing at least one dodecyl radical.
10. An amide ester of a xanthic formic acid, 5 said ester containing at least one aliphatic hydrocarbon radical having at least eight carbon atoms.
11. An amide ester of a xanthic formic acid, said ester containing at least one alkyl radical obtainable from the alcohols obtained by the carboxyl hydrogenation of coconut oil. 10
12. An amide ester of a xanthic formic acid, said ester containing at least one dodecyl radical.
13. A dodecyl xanthic ester of dodecyl xanthic 15 formic acid.
14. A dibutyl amide ester of dodecyl xanthic formic acid.

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