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CHLOR BENZYL XANTHATES

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6 Claims. (Cl. 260—455)

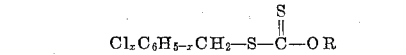
This invention relates to lubricating compositions and to methods of preparing the same and more particularly to lubricating compositions adapted for use under extreme pressure conditions.

Various types of modern machinery such as the hypoid gears in motor vehicles develop enormous pressures between engaged surfaces. The ordinary type of hydrocarbon lubricant composed only of a petroleum fraction is incapable of satisfying the severe requirements demanded in the proper lubrication of hypoid gears, bearing surfaces, metal cutting tools and the like, subjected to unusually heavy loads per unit area of surface. This fact has led to the development of the so-called extreme pressure lubricant which is composed of a suitable carrying agent, such as mineral oil, and another ingredient which imparts to the lubricating composition the property of maintaining between the engaged surfaces a lubricating film under the high pressures encountered.

Among the various E. P. bases which have been proposed and which have met with varying degrees of success are organic materials which contain sulfur or both sulfur and chlorine. The present invention relates to the general type of organic materials which contain both sulfur and chlorine. The presence of chlorine frequently increases the effectiveness of organic sulfur compounds but this increased effectiveness is accompanied by increased corrosiveness and decreased stability. However, the new adjuvants while considerably more effective than the corresponding chlorine free sulfur compounds, actually appear to be more stable and are not corrosive.

A primary object of this invention is to provide a new and novel sulfur-and-chlorine-containing material capable of imparting extreme pressure lubricant properties to a lubricating oil composition otherwise incapable of withstanding extreme pressure conditions. A further object is to provide a mineral oil adjuvant which is not corrosive and yet is a very effective extreme pressure addition agent. Still further objects are to provide extreme pressure addition agents which are cheap and easily prepared.

In accordance with this invention it has been discovered that chlorbenzyl esters of xanthic acids are very effective extreme pressure lubricant agents. The chlorbenzyl xanthates possess the structure



where R is an alkyl radical and x is an integer. As is well known chlorine linked to an aryl group is much more tightly bound than chlorine linked to an alkyl group. As a general rule aromatic chlorine while much less corrosive to the metal surface does not materially enhance the load carrying capacity of organic sulfur compounds. However, chlorbenzyl xanthates are an exception to this general rule. They are markedly more effective than the chlorine free benzyl xanthates and yet do not tend to corrode metal surfaces nor form gum nor separate into their constituent parts in long continued use.

The amounts of chlorbenzyl esters required to be added to hydrocarbon or fatty lubricating oils for the preparation of compositions of this invention vary somewhat, depending upon the character of the lubricating stock used as a base, and the severity of the service for which they are designed; however, the active agent is always present in minor amounts with respect to the oil base and in general varies between about 1% and about 10% of the oil base by weight although amounts outside of this range can be used where convenient or desirable. Since chlorbenzyl xanthates are freely soluble in lubricating oils, a wide range of homogeneous compositions can be prepared. Where desired concentrates can be prepared containing relatively large amounts, as for example 50%, of chlorbenzyl xanthate. Such concentrates may be stored or transported in this form and diluted to the desired concentration before actual use.

Typical examples of chlorbenzyl xanthates which may be used in the practice of the invention comprise trichlorbenzyl sec-butyl xanthate, dichlorbenzyl sec-butyl xanthate, o-chlorbenzyl sec-butyl xanthate, trichlorbenzyl tert. butyl xanthate, dichlorbenzyl tert. butyl xanthate, o-chlorbenzyl tert. butyl xanthate, trichlorbenzyl isopropyl xanthate, tetrachlorbenzyl isopropyl xanthate, o-chlorbenzyl isopropyl xanthate, trichlorbenzyl heptadecyl xanthate, trichlorbenzyl octadecyl xanthate, trichlorbenzyl dodecyl xanthate, trichlorbenzyl tetradecyl xanthate, trichlorbenzyl hexyl xanthate, trichlorbenzyl heptyl xanthate, trichlorbenzyl decyl xanthate, trichlorbenzyl octyl xanthate, monochlorbenzyl methyl xanthate, methyl monochlorbenzyl methyl xanthate, methyl dichlorbenzyl ethyl xanthate, dichlorbenzyl ethyl xanthate and dichlorbenzyl amyl xanthate.

There are a variety of procedures suitable for the preparation of the new adjuvants and in general any of the methods suitable for the preparation of esters of xanthic acids can be used. A

particularly convenient synthesis which has been found to give excellent yields is to react a chlorbenzyl chloride with an alkali metal xanthate and separate the alkali metal chloride formed as a by-product. It is not at all necessary to use pure materials. Products obtained by reacting mixtures of various chlorbenzyl chlorides are satisfactory. The following examples describe in detail the synthesis of typical chlorbenzyl xanthates but it is to be understood that the invention is not limited thereto.

Preparation of trichlorbenzyl chloride

Substantially 1500 parts by weight of dry toluene were charged into a chlorinator of suitable capacity. Substantially 15 parts by weight of iron filings were added as catalyst carrier for ring chlorination and chlorine introduced at about 20° C. During the last part of the run the temperature was increased to about 70° C. in order to keep the reaction mixture fluid and the flow of chlorine continued until the increase in weight corresponded to that calculated for trichlor toluene. Thus, when the product analyzed 54.8% chlorine, the flow of chlorine was interrupted and the trichlor toluene given a 10% caustic wash and filtered through a bed of clay in order to remove the iron. The product was then chlorinated at 160° C. in the presence of ultra violet light until the gain in weight was that calculated for trichlorbenzyl chloride. Analysis of the product for chlorine at this point gave 61.8%.

EXAMPLE I

Trichlor benzyl ethyl xanthate

Substantially 460 parts by weight of trichlorbenzyl chloride (substantially 2.0 molecular proportions) was added in a slow stream to sodium ethyl xanthate prepared by reacting 190 parts by weight (substantially 2.5 molecular proportions) of carbon disulfide, 91.5 parts by weight of 96.5% caustic soda (substantially 2.2 molecular proportions) and substantially 808 parts by weight of ethyl alcohol. When the temperature of the reaction mixture reached 50° C. cooling was applied so as to keep the temperature at 50–55° C. during the addition of the remainder of the chloride. The mass was slowly heated to refluxing temperature and then heated under reflux for about an hour. The excess alcohol was stripped out by heating under a vacuum and the residue washed with water and dried. A brown oily liquid was obtained in good yield which was freely soluble in mineral hydrocarbon lubricating oils.

EXAMPLE II

Trichlorbenzyl amyl xanthate

Substantially 98.8 parts by weight of dry 90% potassium amyl xanthate (substantially 0.44 molecular proportions) was added to substantially 350 parts by weight of ethyl alcohol and then 92.0 parts by weight (substantially 0.4 molecular proportions) of trichlorbenzyl chloride was added in a slow stream. The temperature rose slightly during the addition of the chloride but not enough to require external cooling. The mixture was heated to refluxing temperature for about 90 minutes and the alcohol removed by distillation, the last traces being stripped out under vacuum. The residue was washed with water, filtered through a bed of clay and dried. A good yield of a deep colored watery liquid freely soluble in mineral hydrocarbon oils was obtained.

The effectiveness of the chlorbenzyl esters of thio acids is demonstrated by the conventional tests on compositions comprised of these ingredients and a lubricating oil carrying agent. More specifically a minor amount of chlorbenzyl xanthate was added to a high viscosity hydrocarbon lubricating oil (Saybolt Universal viscosity of 101 seconds at 210° F.) and samples of the blended lubricant subjected to the Almen Pin test described by Wolf and Mougey, Proc. A. P. I., 1932, pages 118–130 and the S. A. E. test described in S. A. E. Journal 39, 23–4 (1936). These two tests are commonly accepted in the art as standards to determine the extreme pressure characteristics of a lubricant.

	Percent in oil	Extreme pressure tests, lbs. failed	
		S. A. E. (1,000 R. P. M.; 14:6:1 rubbing ratio; 77–79 lbs./sec. loading rate	Almen
Benzyl ethyl xanthate	7.0	220	8
Trichlorbenzyl ethyl xanthate	7.0	300	30
Trichlorbenzyl amyl xanthate	7.0	326	40
Trichlorbenzyl methyl xanthate	7.0	326	40

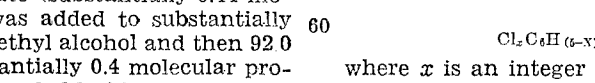
The above data show that the chlorbenzyl xanthates are remarkably efficient E. P. lubricants and much superior to the chlorine free benzyl xanthates.

Again, the foregoing examples are to be taken as illustrative of the invention and not limitative thereof. While the character of the invention has been described in considerable detail and numerous examples furnished of the preparation of the new additives and of the preparation and properties of the new oil compositions, it will be obvious to one skilled in the art that numerous modifications and changes can be made. For example, the carrying agent for the extreme pressure agent can be varied widely. The invention includes broadly the chlorbenzyl esters of xanthic acids dissolved, dispersed or emulsified in any suitable carrying agent such as kerosene or other light petroleum hydrocarbon, benzene and other related hydrocarbons, alcohols, esters, ethers, fatty vegetable and animal oils as well as mineral hydrocarbon lubricating oils. This invention is limited solely by the claims attached hereto as part of the present specification. The present application is a division of co-pending application Serial No. 540,890 filed June 17, 1944.

What is claimed is:

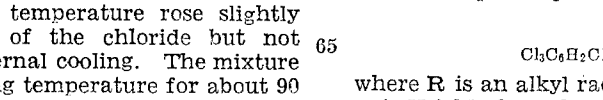
1. The composition comprising a chlorbenzyl ester of a xanthic acid.

2. A compound possessing the structure



where x is an integer and R is an alkyl radical.

3. A compound possessing the structure



where R is an alkyl radical.

4. Trichlorbenzyl methyl xanthate.

5. Trichlorbenzyl ethyl xanthate.

6. Trichlorbenzyl amyl xanthate.

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