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RUST PREVENTIVE COMPOSITIONS

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The present invention relates to rust preventive compositions and particularly to compositions which are useful in lubricating oils, especially mineral base lubricating oils and the like, to enhance their rust preventive characteristics. The invention is concerned also with an inhibited oil as a new composition of matter.

Under certain conditions, particularly conditions of elevated temperature and high humidity, the problem of preventing rust, particularly of polished steel surfaces or highly machined surfaces, is a very serious one. Numerous compositions have been prepared in recent years in attempts to meet this problem and to provide slushing oils, lubricating oils, and the like, which give good protection against rust to steel and iron surfaces. Some of these have met with fairly good success but further improvements still appear to be in urgent need.

The present invention is based upon the discovery that certain esters, especially those esters which are predominantly mono-esters of polyglycerol have unusual and unexpected rust inhibiting properties, especially when used in liquid lubricating oils, slushing oils and the like. It has been suggested in the United States patent to Hodson, No. 2,345,199 that certain esters of glycerol may be used in lubricating compositions. The present invention is based on the discovery of a very material and striking improvement in the rust inhibiting qualities of the polyglycerol esters as distinguished from the simple monoglycerol esters.

In addition to rust preventing characteristics, the present invention is concerned with the improvement of extreme pressure or load carrying characteristics of mineral lubricating oils. The partial esters involved in the present invention impart outstanding rust preventive properties and at the same time improve materially the load carrying properties of mineral lubricating oils even in very low percentages, for example in proportions of as little as 0.1% and up to 10% by weight, based on the total lubricant. These materials may be used in transformer oils, in ordinary lubricating oils, in slushing compounds which also may, if desired, contain other additives such as petroleum sulfonates, degras and the like, and also in greases. They may also be reacted with compounds which incorporate therein sulfur, phosphorus or other load carrying agents to provide extreme pressure lubricants. The phosphorized or sulfurized compounds, as well as the simple polyglycerol esters, may be used in lubricating greases as well as in slushing oils and liquid lubricants.

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A typical starting material for carrying out the present invention consists of polyglycerol prepared by heating glycerin with or without a catalyst. Catalysts such as iodine, hydrochloric acid, or potassium hydroxide may be employed for more rapid polymerization if desired, but are not absolutely necessary. By heating the glycerin, with or without a catalyst, to a temperature of 225°–250° F. for a suitable period, an appreciable increase in molecular weight results. The heating time may vary considerably depending upon the catalyst used, etc. It has been found that a heating period of 15 to 48 hours may ordinarily be required. Under such conditions, the viscosity of the treated glycerin increases from an initial value of 550 S. S. U. at 100° F. to about 1070 S. S. U. at the same temperature. The product having a viscosity of 1070 S. S. U. appears to be predominantly the dimer of glycerin although higher polymers are probably present in minor quantities.

A polyglycerol, prepared as indicated above, was esterified to produce a product consisting predominantly of the mono-ester by reacting the polymer with the calculated amount of oleic acid for a period of about 4 hours at 380° F. As a catalyst 0.2% by weight, based on the reactant materials, of tin tetra chloride ($SnCl_4$) was used. The esterified product was finished by filtering it through a thin layer of oil-filtering clay. It might also be purified by water washing if desired. The product prepared as above described had a neutralization number of 1.4 and a saponification number of 171.

To determine the rust inhibiting properties of these polymers, steel panels were immersed in the oil blends described below and then suspended in a standard AN–H–31 humidity cabinet at a temperature of 120° F.

Under these conditions, panels coated with a transformer oil having a viscosity of 58 S. S. U. at 100° F. had a humidity cabinet life (hours to incipient rusting) of approximately one-half hour. The addition of 3% by weight of the

simple glycerol mono-oleate to the same oil resulted in a humidity cabinet life of 24 hours. However, when 3% by weight of polyglycerol mono-oleate was added to the transformer oil, the humidity cabinet life was increased to 240 hours.

Similarly, panels coated with an aviation oil having a viscosity of 120 S. S. U. at 210° F. had a humidity cabinet life of approximately one hour, but on the addition of 3% by weight of polyglycerol mono-oleate the humidity cabinet life was extended to 280 hours.

TABLE 1

AN–H–31 humidity cabinet results

Mineral Oil	Rust Preventive	Hours for Rust To Develop
Transformer Oil	None	½
Do	3% Glycerol Mono-oleate	24
Do	3% Polyglycerol Mono-oleate	240
Aviation Oil	None	1
Do	3% Polyglycerol Mono-oleate	280

A further investigation of the rust inhibiting properties of the polyglycerol partial esters was conducted using a combination internal combustion engine-humidity cabinet test as follows. A single cylinder air-cooled engine of 4.5 hp., operating at 2000 R. P. M. manufactured by the Wisconsin Motor Corporation, was operated on leaded gasoline and lubricated with the oil blend under investigation. Subsequent to being used in the engine with the oils described below, the cylinder-cylinder liner assemblies were stored in a humidity cabinet operating at a temperature varying between 70° and 90° F. during each 24 hour period and with relative humidity varying between 50% and 95% during the same period. After five days of storage in the cabinet under the conditions described, the amount of rusting of the cylinder liner in each case was noted in terms of the percentage of the entire surface which had become rusted. When an aviation oil of 120 S. S. U. viscosity at 210° F. was used as the lubricant in the above procedure, 30% rust was observed after 5 days of storage. However, the same base oil containing 1% by weight of polyglycerol mono-oleate resulted in only 6% of rust after 5 days of storage.

In addition to having excellent rust preventive properties the partial esters of polyglycerol are good oiliness agents and improve the load carrying properties of mineral base lubricating oil. A transformer oil subjected to the standard Almen extreme pressure test carried a weight of only 1 unit before failure. The same oil, including 2% by weight of polyglycerol mono-oleate, carried 6 weights before failure.

The prior art has shown that rust inhibiting compounds, such as slushing oils and the like, may be prepared by adding oil soluble petroleum sulfonates, degras and the like to mineral oils. For many uses such compounds are very satisfactory but under extreme conditions of temperature and humidity they show early failure. Tests have now demonstrated that by the addition to such compositions of small quantities of polyglycerol mono-oleate prepared as indicated above, the anti-rusting life was greatly extended. Table 2 shows the results of AN–H–31 humidity cabinet tests using a transformer oil base with various quantities of sulfonates and polyglycerol mono-oleate.

TABLE 2

AN–H–31 humidity cabinet results

Mineral Oil	Rust Preventive	Hours for Rust To Develop
Transformer Oil	None	½
Do	3.0% Polyglycerol Mono-oleate	240
Do	1.5% Sodium Sulfonates and 3.0% Polyglycerol Mono-oleate.	408
Do	2.0% Sodium Sulfonates and 2.0% Degras.	48
Do	2% Sodium Sulfonates, 2% Degras, 1% Polyglycerol Mono-oleate	400

The composition including about 3% of polyglycerol mono-oleate and a small amount of sodium sulfonate proved highly satisfactory. The same was true with a composition including only 1% of polyglycerol mono-oleate together with 2% sodium sulfonate and 2% degras. Oil including only the sulfonate and degras showed a shorter effective life as a rust preventative.

It has been found that other materials may be used in lieu of those listed in Table 1, for example, various metal salts of petroleum naphthenates may be used in conjunction with the partial esters of polyglycerol. Other conventional additives may also be included such as detergents, fatty oils, antioxidants, viscosity index improvers, pour point depressants and the like.

In lieu of partial esters of polyglycerol and oleic acid, partial esters of polyglycerol with other organic acids either singly or in combination may be employed. Thus partial or mixed esters of polyglycerol with stearic acid, lauric acid, naphthenic acids, tall oil and the like may be employed.

As indicated above, partial esters of the type described in the foregoing may be reacted with phosphorus compounds, phosphorus-sulfur compounds and/or free sulfur to improve the load carrying properties of lubricants which contain such esters. Thus the partial esters of polyglycerol may be reacted with PCl_3, $POCl_3$, P_2S_5, P_3S_4, sulfur and the like to introduce phosphorus, sulfur, chlorine or any two or more of these into the partial ester molecule. Esters so treated have the property of reacting with metal bearing surfaces at high temperatures to form therewith a highly effective load carrying film which prevents excessive wear. Chemical reactions referred to may be indicated as follows:

a.

$$3RCOOCH_2CHOHCH_2OCH_2CHOHCH_2OH + POCl_3 \longrightarrow$$

(Diglyceryl mono-oleate)

$$(RCOOCH_2CHOHCH_2OCH_2CHOHCH_2O)_3{-}P{=}O + 3HCl$$

b.

$$4RCOOCH_2CHOHCH_2OCH_2CHOHCH_2OH + P_2S_5 \longrightarrow$$

$$2(RCOOCH_2CHOHCH_2OCH_2CHOHCH_2O)_2{-}\overset{\overset{S}{\|}}{P}{-}SH + H_2S$$

R represents an aliphatic radical of a sufficient number of carbon atoms to give oil solubility.

The P_2S_5 reaction product can also be reacted with metal oxides to form detergent additives for oils.

From the foregoing it will be understood that a preferred composition is one which consists essentially of an oily base lubricant or lubricating type composition (oil or grease, etc.) containing a proper amount of a fatty acid ester of poly-

glycerol. For ordinary use, the proportions of ester to lubricant should be not less than 0.1 nor more than about 10% by weight of the ester based on the finished composition. It is desirable, however, for some purposes, to market the ester-containing material as a concentrate. Where this is done the composition may contain as little as 60% of the oil or lubricant and as much as 40% of the ester, with or without appropriate quantities of metal sulfonates, degras, and the like. Where used, these latter ingredients may consttiute 0.1 to 10% by weight of the composition. In concentrates the proportions may be higher. The sulfonates, such as sodium or other alkali or alkaline earth metal sulfonates may comprise as much as 20% or more by weight.

In the examples above, reference has been made specifically to mineral lubricating oil as the base material and such oil is ordinarily preferred. Its viscosity may be as low as about 35 and as high as 1000 S. S. U. at 210° F. It will be understood, however, that synthetic oils may also be used such as organic polymers and copolymers, esters and the like. Hence in the claims, reference to the base lubricant includes synthetic materials as well as petroleum base or hydrocarbon base oils and greases. By the expression "base" it is intended to include compositions which comprise soaps, thickeners, viscosity index improvers, extreme pressure additives, oiliness agents, anti-oxidants, corrosion inhibitors, and the like. Materials such as sulfonates, degras and the like which have been found suitable for use in slushing oils are also included.

The fatty acid which is used to esterify the polyglycerol may contain not less than 10 nor more than about 24 carbon atoms and may be saturated or unsaturated, preferably the latter. The preferred polyglycerol is the diglycerol as previously suggested, but higher polymers are also suitable.

For preparing the polyglycerol, monomeric glycerin is preferably heated to a temperature within the range of 200°–300° F. As indicated above, the reaction time required varies with temperature and when the specific preferred range of 225°–250° F. is employed the reaction time required is of the order of 15 to 48 hours. For esterifying, a higher temperature is ordinarily required, for example, 250°–400° F., although a lower temperature such as 210°–250° F. may be employed, especially if a water entraining agent such as toluene or naphtha is employed. As esterification catalyst, $SnCl_4$ is suitable, but other known catalysts such as sulfuric acid, toluene sulfonic acid, aluminum chloride, boron fluoride and the like may also be used.

As indicated above the ester may further be reacted with a material which will incorporate therein a load carrying agent such as phosphorus, sulfur or chlorine. Compounds including one or more of these elements are preferably reacted at a temperature of 50°–200° F., the reactions being exothermic in most cases. Material such as PCl_3, $POCl_3$, P_2S_5, P_2S_4, sulfur, SCl_2, S_2Cl_2, and the like are preferred materials, but others are not excluded.

Where the dimer of glycerin is used to form the ester, the finished material may have the following general formula:

$$RCOOCH_2CHOHCH_2OCH_2CHOHCH_2OX$$

where R is a radical having 10 to 24 carbon atoms and X is a radical containing active phosphorus.

It will be understood by those skilled in the art that various modifications may be made in proportions, temperatures of reaction, the use of catalysts, etc. as will be obvious.

What is claimed is:

1. A composition consisting essentially of hydrocarbon oil base lubricant containing 0.1 to 10% by weight of mono-oleate ester of polyglycerol which is predominantly diglycerol, said polyglycerol being prepared by heating glycerin to a temperature within the range of about 225° to 250° F. for a period of time sufficient to increase its viscosity substantially, 0.1 to 10% of metal sulfonate, and 0 to 10% of degras.

2. A rust preventive composition consisting essentially of a mineral base lubricating oil, about 1 to 3% by weight, based on the total composition, of the monooleate ester of a polyglycerol which is predominantly diglycerol produced by heating glycerin to a temperature within the range of 225° F. to 250° F. for a period of between 15 and 48 hours, and 1.5 to 2% of oil soluble sodium petroleum sulfonate.

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