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3,422,166

TRIETHANOLAMINE SALTS OF MONO- AND DI-NONYL PHENOL (ETHOXYLATE) PHOSPHATE ACID ESTERS

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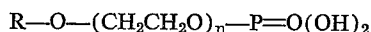
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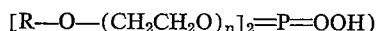
1 Claim

ABSTRACT OF THE DISCLOSURE

Compositions, suitable for use as corrosion-inhibitors, are provided comprising the reaction product of triethanolamine and an ester selected from the group consisting of mono-esters having the formula



and di-esters having the formula



wherein R is a hydrocarbon group having at least 9 aliphatic carbon atoms and n is an integer from about 3 to about 30; the proportions of triethanolamine and ester being such that a neutral product is produced.

This application is a division of my application, Ser. No. 353,612, filed Mar. 20, 1964, now U.S. Patent No. 3,310,489, issued Mar. 21, 1967, and the invention herein relates to new and useful lubricant compositions for use in metal-working operations. More specifically, in this aspect, the invention relates to new and useful lubricant compositions suitable for metal-working operations, of such metals as aluminum, magnesium, iron, steel and various other metals and alloys.

The rolling of metals, comprising one of the metal-working operations, to which this invention has particular applicability, involves the generally known method of passing a billet of the metal through the bit of a pair of rolls, for a sufficient number of times to reduce the billet to a sheet of the desired thickness. The degree of reduction, in each pass, is dependent upon several factors, which include the particular composition of the metal being rolled, the temperature employed during the rolling operation, the necessity for intermediate annealing, and other factors. During the rolling operation, it is necessary to lubricate and cool one or more of the working rolls, employing suitable lubricant and coolant compositions. These compositions are usually applied to the working rolls, in the form of a plurality of liquid streams or sprays, in sufficient quantity to prevent them from being damaged by the heat developed during metal deformation and to keep the friction between the rolls and the metal being rolled to a minimum, and also to prevent metallic "pick-up" on the rolls. Examples of typical rolling mills and their operation are illustrated and described in "Metal-working Lubricants," E.L.H. Bastian, 1951, McGraw-Hill, New York.

Various lubricants have heretofore been proposed for use in metal-working operations; however, these lubricants have generally fallen short of the expected performance necessitated by present-day industrial practices. This is particularly apparent with respect to modern techniques for cold-rolling and hot-rolling of such metals, as aluminum. In this instance, corrosion or staining of the alumi-

num, particularly by lubricants containing polyphosphates, is a serious problem in both cold and hot-rolling operations, where it is highly desirable to obtain a bright clean surface after the metal has been reduced in size. Hence, prior to the present invention there has long been a need for a satisfactory lubricant composition for metal-working operations, free from the disadvantages encountered with lubricant compositions heretofore employed for this purpose.

It is, therefore, an object of the present invention to provide a lubricating composition having improved lubricating and corrosion-inhibiting properties.

Another object of the invention is to provide a lubricant composition having particular utility in the cold and hot-rolling of such metals as aluminum, magnesium, iron or steel.

Other objects and advantages inherent in the invention will become apparent from the following more detailed description.

The foregoing objectives of the present invention, as more fully hereinafter described, are, in general, realized by the development of new and useful lubricant compositions containing, as a corrosion-inhibitor, the reaction product of an amine and a phosphate ester selected from the group consisting of mono-esters having the formula $R-O-(CH_2CH_2O)_n-P=O(OH)_2$, and di-esters having the formula $[R-O-(CH_2CH_2O)_n]_2P=OOH$, in which R is an organyl group, viz, an alkyl, aryl or heterocyclic group, having at least 9 carbon atoms, and n is an integer from about 3 to about 30. In this respect, it has now been found that the incorporation of the aforementioned reaction product of an amine and a specific type of phosphate ester in a lubricating vehicle, results in obtaining lubricating compositions which possess effective corrosion-inhibiting and stain-resisting properties in the cold or hot-rolling of metallic materials, such as those previously described. On a comparative basis, as more fully hereinafter discussed, such corrosion inhibiting and stain-resisting properties, are not achieved in commercially available lubricants, or even in such lubricants which contain phosphate esters of a general type, but which are not specifically limited to those to which the present invention is restricted and having the above-described formulation, and which do not contain the amine reactant, to produce the novel additive product for incorporation into the lubricant vehicle.

The amine employed as a reactant with the phosphate-ester in producing the novel reaction product, may be of any type and of any molecular weight. These amines may, therefore, comprise primary, secondary or tertiary amines, and of either the alkyl or aryl structure. Of particular utility are the alkanolamines, with the lower molecular weight compounds being generally preferred. For this purpose, it has been found that such alkanolamines as mono-, di-, or triethanolamine are most effective. The alkanolamine may be employed as either a specific compound or as a combination, of such compounds, if so desired.

The phosphate ester reactant, having the structural formulas previously illustrated, comprises a water-soluble or oil-soluble complex organic phosphate ester. This ester is, in general, prepared by reacting one mole of P_2O_5 with 2 to 4.5 moles of a nonionic surface active agent having the molecular configuration of a condensation product of at least one mole of ethylene oxide with one mole of a compound containing at least 6 carbon atoms and a reactive hydrogen atom, and selected from the group consisting of phenol, alkyl phenols, aliphatic alcohols, fatty acids, fatty amines, fatty amides, rosin amines, long chain sulfonamides, long chain-substituted aryl sulfonamides, and high molecular weight mercaptans under substantially

anhydrous conditions and at a temperature below about 110° C. down to about room temperature. This process does not require the use of an excess of the hydroxylic organic compound (in this instance, the defined nonionic surface active agent), in order to bring the P₂O₅ into solution. Substantially no tertiary phosphate ester is formed by the process and little or no P₂O₅ remains in the composition. Depending upon the particular ratio of P₂O₅ to the nonionic surface active agent employed, and the nature of such nonionic agent, the product may in some instances contain some unreacted nonionic surface active agent, which may, in some instances, actually be advantageous. If so desired, in order to produce an uncolored or lightly colored product, there may be first dissolved in the nonionic surface active agent a small amount of a phosphorus-containing compound selected from the group consisting of hypophosphorus acid, salts of hypophosphorus acid, phosphorus acid, and salts and esters of phosphorus acid. A more complete description for the preparation of these phosphate ester surfactants is contained in U.S. Patents 3,004,056 and 3,004,057, each issued on Oct. 10, 1961.

It will be noted that in the aforementioned indicated structural formula for the phosphate ester reactant, it is necessary that the organyl group R, have at least 9 carbon atoms. In this respect, as more fully hereinafter discussed, it is found that if this organyl group contains less than 9 carbon atoms, the desired corrosion-inhibiting or stain-resistant properties to be imparted to the lubricating vehicle by the novel reaction product, are not achieved. The lubricating vehicle employed in combination with the reaction product may be of any type, and may be aqueous or hydrocarbon in nature. Thus, the vehicle, for this purpose, may comprise water, or water-containing various additives, for example, organic acids, functioning as corrosion-inhibitors, water-containing suitable load-support agents, such as water-soluble polyoxyalkylene glycols; also, water-containing alkali metal nitrites, for example, sodium nitrite, as anti-rust agents, or the sodium salt of mercapto-benzothiazole (which is particularly useful where copper corrosion is sought to be avoided). Furthermore, as previously indicated, hydrocarbon vehicles may be employed in combination with the aforementioned amine-phosphate ester reaction product. These may include mineral oils, soluble oils containing soaps, and/or sulfonates, or amine salts of organic acids, as emulsifiers. In addition, soluble oil formulations may be employed, as the vehicle, containing nonionic emulsifiers, such as sorbitan, mono-oleate, or other esters or partial esters of polyvalent alcohols and fatty acids. Also, if so desired, the overall performance

properties of the lubricant composition containing the novel amine-phosphate ester reaction product may be enhanced by the addition of germicidal agents, particularly phenolic materials such as phenol, sodium salts of ortho-phenylphenol, chlorinated phenols, such as hexachlorophene, tetrachlorophenol and p-chloro-m-xenol, and also boric acid or oxides of boron. The amine-phosphate ester reaction product is employed in the lubricating vehicle in a minor proportion. Preferably, the lubricating vehicle may contain from about 0.001 to about 20 percent, by weight, of the reaction product.

The following examples and comparative data are intended to illustrate the novel amine-phosphate ester reaction product corrosion-inhibitors and lubricating compositions containing these inhibitors, of the present invention, and to demonstrate their effectiveness in improving the properties of lubricant compositions, particularly intended for use in metal-working operations. It will be understood, of course, that it is not intended the invention be limited to the particular compositions shown or to their method of preparation. Various other corrosion-inhibitors and lubricating vehicles, of the type disclosed can be utilized, as those skilled in the art will readily appreciate.

In the examples, a base formula was employed which contained, triethanolamine, in an amount of 23 percent, by weight, as the amine reactant; a phosphate ester, as shown, in an amount of 2 percent, by weight; and water, as the lubricating vehicle, in an amount of 75 percent, by weight. It will be noted that an excess of the triethanolamine was employed in order to assure complete reaction with the particular phosphate ester selected. In performing an evaluation test, with respect to determining the corrosion-inhibiting or stain-resistant properties of a particular lubricating composition, approximately ½ ounce of the lubricating solution to be evaluated, was placed in a 2 ounce jar, together with a 2" / 2" / 1/16" strip of aluminum, previously cleaned with a medium grade of emery cloth. Approximately one-half of this strip was immersed below the surface of the test solution, and the remaining portion was exposed to air. Staining tendency was observed over a period of 24 hours. In each case, the phosphate ester and the triethanolamine, together with from about 15 to about 25 parts of water, by weight, were blended at a temperature of 150° F. The remaining portion of the water was then added, and this base formula was diluted with from about 1 part to about 20 parts of distilled water prior to running the staining tests. The various phosphate esters that were evaluated, and the data obtained are shown in the following Table I.

TABLE I

Example No.	Amine Reactant	Phosphate Ester Reactant	Results of Aluminum Stain Test at 1-20 Dilution of Base Formula at 70° F.	
			1 Hour	24 Hours
1*-----	Triethanolamine..	None-----	Gray stain-----	Dark gray stain.
2-----	do-----	Mono ester octyl alcohol plus 2 moles ethylene oxide. $\text{C}_8\text{H}_{17}-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_2-\text{P}(\text{OH})_2$	Gray line at liquid/air interface.	Black line at liquid/air interface.
3-----	do-----	Diester nonylphenol plus 4 moles ethylene oxide. $[\text{C}_6\text{H}_5\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_4]_2-\text{P}(\text{OH})_2$	No stain-----	No stain.
4-----	do-----	Mono ester nonylphenol plus 10 moles ethylene oxide. $\text{C}_6\text{H}_5\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{10}-\text{P}(\text{OH})_2$	do-----	Do.
5-----	do-----	Diester nonylphenol plus 10 moles ethylene oxide. $[\text{C}_6\text{H}_5\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{10}]_2-\text{P}(\text{OH})_2$	do-----	Do.

*Base formula modified to contain triethanolamine, 25% by weight, and water, 75% by weight.

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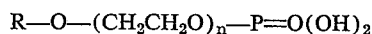
From Table I, above, it will be apparent that the use of the reaction product of the amine and the ester reactant, containing an organyl radical having less than 9 carbon atoms, as shown in Example 2, or in the absence of the ester reactant, as shown in Example 1, results in producing a stain condition on the metal surface. On the other hand, as shown in Examples 3, 4 and 5, where the ester reactant contains organyl groups having more than 8 carbon atoms, no staining of the metal occurs. It will be, of course, apparent that other ester reactants of the type described can be substituted for those of the foregoing examples, having more than 9 carbon atoms per organyl group, and thus result in obtaining similar improvement in avoiding corrosion or metal staining. Furthermore, lubricating vehicles may be substituted for those shown in the examples, which are hydrocarbon in nature and which would normally, in their untreated state, affect corrosion or staining of metal surfaces.

Although the present invention has been described with preferred embodiments, it will be understood that various modifications and adaptations thereof may be resorted to, without departing from the spirit and scope of the invention, as those skilled in the art will readily appreciate.

What is claimed is:

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1. A composition comprising the reaction product of triethanolamine and an ester selected from the group consisting of mono-esters having the formula



and di-esters having the formula



wherein R is nonyl phenol and n is an integer from about 3 to about 30; the proportions of triethanolamine and ester being such that a neutral product is produced.

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