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REACTION PRODUCTS OF OXIDIZED OIL AND PCl_3

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The present invention relates to products obtained by the reaction of an oxidized oil and phosphorus trichloride and more particularly to extreme pressure lubricants comprising such a reaction product and to a soluble oil comprising a neutralized reaction product of oxidized oil with phosphorus trichloride.

It is generally known, in machine operations such as cutting and grinding, that emulsions of water with so-called "soluble oils" may be used effectively to remove heat generated and chips formed during the operations, prolong tool life and improve the finish of the work piece. In use, machining fluids are usually poured in a steady stream over the tool and the work piece, the oil content of the fluid being relied upon to provide lubricity between the work and the tool and thus counteract the heavy pressure therebetween, and the water component being relied upon to carry away the great amount of heat generated during the machining operation.

It has now been found that it is possible to react a highly refined, oxidized petroleum oil with phosphorus trichloride and to obtain thereby a clear, light-colored product useful as such as an extreme pressure lubricant and capable of neutralization with a suitable base to yield a semi-solid soap emulsifiable with water and therefore eminently suitable as a so-called "soluble oil" for machining metals.

This discovery is quite surprising in view of the fact that satisfactory products are not obtained when compounds such as phosphorus pentachloride, phosphorus pentasulfide, phosphorus sequisulfide and phosphorus sulfur trichloride, heretofore proposed as members, without discrimination or criticality, of a common group in making cutting oils, are used in place of phosphorus trichloride.

The initial oil utilized in the method of this invention may be any solvent-extracted or white petroleum oil of high or low viscosity, oxidized to have a saponification number between about 20 and 80 and a neutralization number between about 9 and 25. The viscosity of the oil, before oxidation, may vary between about 75 and 600 SSU at 100° F. The initial oil, before oxidation, should have an ASTM aniline point of at least 105° C., an aromatic content below about 12% and a total sulfur content of less than 0.2%.

The oxidation may be carried out by any suitable method such as by passage of air through the oil. One preferred method of oxidizing highly refined solvent-extracted and white petroleum oils is that of passing air through the oil in the presence of a catalyst, such as manganese naphthenate or manganese stearate, while the oil is maintained at a temperature of about 200 and 350° F. If the oil is less highly refined, it is preferable to add, at the beginning, or bleed in slowly

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and in minor amounts immediately after the start of the operation, a strong base such as potassium or sodium hydroxide or carbonate in the form of an aqueous solution or a solid. If the oil is more highly refined, e. g. when white oil having an ASTM aniline point of about 117° C., or more is utilized, no catalyst is required although it is started more readily in the presence of the above-mentioned catalysts or a milder catalyst such as cumene hydroperoxide.

The oxidation is carried out for several hours until the desired saponification number and ASTM neutralization number have been reached. The oxidation will proceed at atmospheric or higher pressure. Superatmospheric pressure is not required but shortens the time required for the oxidation without affecting the product.

The reaction of the oxidized oil with phosphorus trichloride is carried out by slowly adding the phosphorus trichloride to the oil while stirring, generally at about room temperature or below the boiling point of the phosphorus trichloride. This results in an evolution of hydrogen chloride which diminishes after about one-half hour. Inasmuch as the reaction of the oxidized oil with phosphorus trichloride is exothermic and the boiling point of the latter is 76° C., it is desirable, for maximum economy and efficient use of the phosphorus trichloride, to add the trichloride sufficiently slowly to control the reaction temperature. If desired, the mixture may then be heated to a temperature of between about 150 and 350° F. for a period of up to about one hour or more, or until the evolution of hydrogen chloride has ceased. After that, the reaction mixture is subjected to moderate air blowing at room temperature or at a higher temperature to remove occluded volatile matter.

The amount of phosphorus trichloride reacted with the oxidized oil may be any amount up to about 20% by weight of the oil. Amounts in excess of 20% have no harmful effect on the product but serve no useful purpose inasmuch as they are lost in the reaction. Satisfactory results are obtained by adding between 5 and 16% by weight of phosphorus trichloride. For optimum results and most economical practice consistent with such results, the amount added should be between about 10 and 15% by weight.

The product thus obtained is strongly acid and clear. The lower the temperature employed in the treatment with phosphorus trichloride, the lighter the product will be. Even at temperatures of the order of 350° F., however, the product will not be much darker than the original oil.

The product thus obtained may then be neutralized, preferably with a strong base such as sodium or potassium hydroxide, the amount of neutralizing agent being sufficient to neutralize the product of reaction between oxidized oil and

phosphorus trichloride but not in an excess sufficient to raise the pH of the neutralized product above about 10. The neutralization is preferably carried out in the presence of a mutual solvent for the reactants and the products of reaction. The mutual solvent may be water, alcohol or the like.

The neutralized product is a semi-solid soap which forms a clear soapy frothing solution with water that is eminently suitable as a machining fluid in metal cutting operations.

It is believed that the results of the reaction of oxidized oil with phosphorus trichloride are particularly surprising in view of the very different results obtained by reacting other materials normally considered the equivalents of phosphorus trichlorides. Thus, for example, a reaction of the same oxidized oil with phosphorus pentachloride results in very dark and strongly fuming products from which a considerable amount of sludge is precipitated. Neither thiophosphorylchloride nor phosphorus sesquisulfide will react with the oxidized oil even at temperatures as high as 400° F. The oil is greatly darkened but analysis shows that the increase in phosphorus content of the oil is negligible. Reaction of the oxidized oil with phosphorus pentasulfide yields very dark and foul smelling products.

The procedure to be followed in preparing the products of the present invention and the utility of said products will become more apparent from the detailed description in the following examples:

EXAMPLE 1

500 grams of white oil having a viscosity of 368 SSU at 100° F. and an ASTM aniline point of 119.5° C. were oxidized to a saponification number of about 80 by blowing air through it for eight hours in the presence of 15 grams of cumene hydroperoxide, the temperature of the oil during oxidation being maintained at 284° F.

50 grams of phosphorus trichloride were then added to the oxidized oil, while stirring, in the course of one-half hour and at room temperature. The treated oil was then blown, at room temperature, with air for four days and thereupon neutralized with 75 cc. of an 11.4 N solution of potassium hydroxide.

The neutralized product was light in color, transparent and was found, upon analysis, to contain 1.5% phosphorus, 2.1% chlorine and 13.2% ash.

A 5% aqueous emulsion of the neutralized product thus obtained by reacting oxidized oil with PCl_3 at room temperature, as described above, and a 5% aqueous emulsion of a well known commercial soluble oil, available on the market, containing sulfonates as the primary emulsifying agent were subjected, for comparison, to severe surface finish and tool wear tests on a heavy lathe.

In each test the emulsion tested was used to lubricate a 18–4–1 HSS (18% tungsten, 4% chromium and 1% vanadium high speed steel) single point tool cutting a test piece of SAE 1015 steel, the depth of cut in each test being 0.25 inch and the rate of feed being 0.0025 inch per revolution of the work piece. A conventional "Brush" surface analyzer was used to measure the finish both perpendicular and parallel to the feed giving peak-to-valley and root mean square values. Two peak-to-valley and two root mean square values were obtained for each test and averaged. The value obtained with the commercial type of said emulsion was reduced to 1.00 as a standard and the relative value for the emulsion of the invention was obtained by dividing the figure obtained with that emulsion by the figure obtained with the commercial emulsion.

The wear of the tool in each test was measured by weighing the tool before and after each test, the loss in weight resulting from the use of the commercial emulsion being adjusted to a value of 1.00 to serve as an index and the loss of weight resulting from the use of the emulsion of the invention being divided by the loss of weight resulting from the use of the commercial emulsion to obtain a figure comparable with the index value of 1.00 for the commercial emulsion.

The results of these tests are tabulated:

Table I

LATHE EVALUATION OF CUTTING FLUIDS

Soluble Oil	Finish Index Average	Wear Index Average
Commercial	1.00	1.00
Neutralized product of oxidized oil and PCl_3	0.98	0.54

The data in Table I is believed to show that a 5% water emulsion of the soluble oil of the present invention compares favorably and in fact is somewhat superior to the commercial 5% water emulsion with reference to the smoothness of the finish obtained on a work piece and particularly with reference to the amount of wear on the cutting tool.

EXAMPLE 2

6000 grams of a solvent-extracted oil having a viscosity of 115 SSU at 100° F. and an ASTM aniline point of 105° C. were oxidized overnight to a saponification number of 48 and a neutralization number of 12.3 by blowing air therethrough in the presence of 12 grams of manganese naphthenate and 12 grams of sodium carbonate, the temperature of the oil during oxidation being maintained at 255° F.

15.7 grams of phosphorus trichloride were added, while stirring, to each of two 100 gram samples of the oxidized oil, the stirring being continued for about one-half hour, by which time the evolution of hydrogen chloride had slowed down very considerably. One sample was heated to a temperature of 212° F. and the other sample was heated to a temperature of 302° F. These temperatures were maintained for one hour, after which moderate air blowing was begun and continued for an additional hour. The products were clear and not much darker than the original oil. The analyses of the reaction products, before neutralization, are given in Table II below:

Table II

ANALYSIS OF REACTION PRODUCT OF SOLVENT-EXTRACTED OIL AND PCl_3

Temp., ° F.	Percent P	Percent Cl	Calc. $\frac{\text{Atoms Cl}}{\text{Atoms P}}$
212	2.46	1.51	0.53
302	2.18	1.10	0.44

It is evident from the data in the table that approximately two-thirds of the phosphorus added as phosphorus trichloride remained in the final product, the other third probably having been volatilized as oxychlorides of phosphorus.

The strongly acid reaction products were each neutralized with a 50% aqueous potassium hydroxide. The resulting products were semi-solid soaps which formed clear, soapy, frothing solutions with water. The performance of these solutions in lathe tests is similar to that of the solution prepared in accordance with Example 1.

It is to be anticipated that many changes and alterations will become apparent to those skilled in the art upon reading the present description. All such changes and modifications are intended to be included within the scope of this invention as defined in the appended claims.

I claim:

1. A method of preparing a soluble oil which comprises reacting phosphorus trichloride with a highly refined petroleum oil oxidized to have a saponification number between about 20 and 80 and a neutralization number between about 9 and 25, and then treating the reaction product with an aqueous solution of a strong inorganic base in an amount sufficient to neutralize the reaction product but not in an excess sufficient to raise the pH of the neutralized product above about 10.

2. The method defined in claim 1 wherein the neutralization is effected with an aqueous solution of a base selected from the group consisting of potassium hydroxide and sodium hydroxide.

3. The method defined in claim 1 wherein the neutralization is effected in the presence of a mutual solvent for the reactants and the products of reaction.

4. The reaction product of phosphorus trichloride and a highly refined petroleum oil oxidized to have a saponification number between about 20 and 80 and a neutralization number between about 9 and 25, said reaction product having been neutralized by treatment with an aqueous solution of a strong inorganic base and said reaction product having a pH not above about 10.

5. A machining fluid comprising a water emulsion of the reaction product defined in claim 4.

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