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RUST PREVENTIVE OIL COMPOSITION

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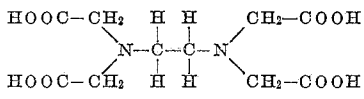
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The present invention relates to improved rust preventive oil compositions and particularly to oil compositions which contain new types of additives to render them more useful as lubricants as well as more effective in protecting ferrous metal surfaces against rust.

The rusting of ferrous metal machinery is always a serious problem, particularly in humid or tropical areas. It is often desirable that the lubricating oil used on machinery have rust preventive properties above and beyond those possessed by conventional lubricating oils. In the past various compositions have been proposed to inhibit or reduce the rusting of ferrous metals. Some of these have involved metallic salts which, although not objectionable in many instances, may be seriously objectionable where conditions of high temperature lubrication are encountered and where ash or other objectionable residues may be left when the oil is consumed.

It is an object of the present invention to provide an effective rust inhibitor for lubricating oils used in internal combustion engines and the like although the invention is not limited thereto. A still further object is to develop a rust inhibiting oil additive which also improves other properties of the oil, such as its pour point. It is a further object of the invention to provide a substantially ash free rust inhibitor for the purposes described above, although here again the invention is not necessarily limited to the ash free compositions. For some purposes metallic derivatives of the additives may be used successfully where the oil is not consumed by burning or other high temperature action, or where minor deposition of ash is not considered objectionable.

According to the present invention a nitrogen-containing complex acid such as an alkylene bis-imino aliphatic carboxylic acid, especially the di-acid, is esterified or preferably only partially esterified by a suitable alcohol. Such an acid is commercially available from the Alrose Chemical Co. under the trade name "Sequestrene AA," having the approximate formula



Preferred alcohols for esterifying such acids are the aliphatic alcohols having between about 4 and 18 carbon atoms per molecule. These are used because they lend oil solubility to the esters but it will be understood that other alcohols, such as the cyclic or aromatic alcohols may be substituted in part.

While the partial esters which are oil soluble

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are preferred for rust inhibition, the fully esterified acids have some utility, especially where pour point depression of the oil is desired. Where detergency is desirable the esters may be fully or partly saponified with a suitable metallic base such as a base of sodium, potassium, lithium, calcium, strontium, zinc or other metals.

Ordinarily the preferred products are the partial esters of ethylene-bis-imino diacetic acids, esterified with substantially saturated and unsubstituted aliphatic alcohols of the C_8 to C_{20} chain length range to the extent of one or two of the carboxyl or acid groups.

The esterifying alcohols, as noted above, are preferably of such chain length as to render the esters, preferably partial esters where rust inhibition is the primary object, oil soluble, or at least reasonably soluble in the oily medium. While alcohols of chain length as short as 4 carbon atoms may have some solubility in certain oils it is preferred to use those having at least about 8 and preferably up to about 16 or 18 carbon atoms in the aliphatic chain. A particularly effective and relatively inexpensive alcohol is the mixed alcohol widely sold under the trade name of "Lorol B" which consists of a mixture of alcohols derived from cocoanut oil and having 10 to 18 carbon atoms with an average chain length of about 13 carbon atoms. The "Oxo" alcohols of the same general character and chain length may also be used. These, as is well known, are branched chain saturated aliphatic alcohols, derived from the carbon monoxide and hydrogen treatment of olefins.

Partial esters, particularly the mono- and di-esters of ethylene-bis-imino diacetic acid, are potent rust inhibitors and can be used in proportions as small as 0.001% of the weight of the total oil composition. Ordinarily, proportions running from at least 0.005% up to about 0.2% are used. Concentrates may of course be prepared containing up to 10% or more of the additive in the oil, to be diluted with additional oil as desired.

The oily vehicle employed is normally a hydrocarbon lubricating oil, especially where the oil composition is intended to fulfill the dual purpose of lubricant and rust preventive. In some cases, however, it may be preferred to use synthetic or non-hydrocarbon oils as part or all of the lubricating oil, such as the esters of dibasic acids, other complex esters, polyglycols, ether glycols and the like which have recently come into use as lubricants and for related purposes. Also, lighter hydrocarbons than the usual lubricating oils may be used for some purposes, although in

most cases they should be of viscosity at least as great as that of ordinary kerosene. The mineral oils of ordinary lubricating grade are economical and highly satisfactory for most purposes.

While the diacetic acids have been particularly mentioned above, the acids may be derived from other low molecular weight carboxylic acids having from 1 to 4 carbon atoms in the aliphatic group. Ordinarily the acetic and propionic acid derivatives are preferred.

The invention will be further understood by referring to specific examples which have been prepared and tested.

EXAMPLE I

One mol of Lorol B alcohol (207 g.) together with one-half mol (146 g.) of ethylene bis-iminodiacetic acid ("Sequestrene AA") and 200 cc. of toluene were placed in a three necked round bottom flask. The mixture was refluxed with stirring and nitrogen gas flowing and water was removed by means of a water trap. After refluxing at 128–130° C., for one-half hour only 0.1 cc. of water came off. Thereafter the reaction ingredients and vessel were cooled and 3 g. of sulfosalicylic acid was added as a catalyst. The flask was heated again until the contents refluxed at 130° C. The esterification was very slow and only one-half cc. of water was removed after one and one-half hours of refluxing. 130–140 cc. of the toluene was next distilled off and the temperature rose to 190–200° C. After 7 hours the full theoretical amount of water was recovered. The product was filtered through a finely divided silicious material, "Hyflo" filter aid, and the remainder of the toluene was distilled off. The yield obtained was as follows:

Weight of material added:

Lorol B alcohol	grams	207
Ethylene bis-iminodiacetic acid	do	146
Catalyst	do	3
Total	do	356

Weight of recovered material:

Esterified product	grams	265
Water	do	23
Total	do	288
Loss	grams	68
Yield	per cent	81

The product contained 3.33% nitrogen.

A blend of the partial ester of Lorol B alcohol and the ethylene bis-iminodiacetic acid ("Sequestrene AA") in an extracted Mid-Continent lubricating oil having a viscosity of 43 S. S. U. at 210° F. was tested for rust inhibiting properties by the procedure of ASTM Rust Test D665–46T. This test method is intended to indicate the ability of steam-turbine oils, including those used for steam-turbine gears, to aid in preventing the rusting of ferrous parts should water become mixed with the oil.

The result obtained is compared with the uninhibited oil in the table that follows:

Composition	Results
0.1% Partial Ester 0.4% Alkyl phenol type antioxidant 99.5% Oil	Pass.
0.4% Alkyl phenol type antioxidant alone in Oil	Heavy Rusting.

An additional example was prepared, making the tri ester first and thereafter preparing the barium salt as in the following:

EXAMPLE II

Product A.—Tri Lorol ester of "Sequestrene AA"

A mixture of 146 grams of "Sequestrene AA," 300 grams of Lorol B alcohol, 1 gram of sulfosalicylic acid and 500 cc. of xylene were charged to a 2 liter, 3 necked flask equipped with stirrer, thermometer, and water trap. The mixture was heated for 5 days at a reaction temperature 155–230° C. During the heating, an additional 5 grams of sulfo-salicylic acid was added. 33.5 cc. of water was removed. The xylene was then distilled off and the product filtered. The product was then heated for 2 hours at 160–170° C. and blown with nitrogen in order to remove remaining xylene and light ends. The yield was 361.5 grams of ester. This product contained 3.31% nitrogen.

Product B.—Ba salt or tri ester of "Sequestrene AA"

84 grams of Tri Lorol ester of "Sequestrene AA" and 97 grams of a naphthenic lubricating oil having a viscosity of 40 S. S. U. at 210° F. were stirred and heated in a beaker at 125° C. Then 3 drops of a silicone polymer foam depressant and 32 grams of $Ba(OH)_2.8H_2O$ were slowly added to the ester. Product B was then blown with N_2 at 150° C. for one-half hour to remove remaining water and was filtered through "Hyflo" diatomaceous earth filter aid. The yield was 82.3 grams.

Product "B" contained 1.47% of barium by weight.

(a) Rust test

The above product passed the ASTM rust test using distilled water. The ester was blended in 0.2% concentration by weight in an extracted Mid-Continent oil having a viscosity of 43 S. S. U. at 210° F., containing 0.4% di tertiary butyl para cresol as an antioxidant. The blends gave no rusting in the liquid phase, with slight trace of rusting at interface and vapor phase. The oil containing no rust inhibitor gave heavy rusting in all three phases. This product was also tested for detergency in an internal combustion engine lubricating oil with the following results:

(b) Detergency test.—25 hour Lauson engine test

Blend	Varnish	Bearing Wt. Loss, Gms./ Bearing
3 Wt. Percent Product B in Mineral Oil of 60 S. S. U. viscosity at 210° F	3.50	0.085
Oil Alone	4.75	0.092

In general, for the lubrication of engines and the like where detergency is desirable the ester of this invention may either be saponified with a suitable metal base or conventional detergents may be added, or both. Thus, the product tested for detergency above was also tested with the addition of calcium sulfonate and barium phenol sulfide, the latter being a combined anti-oxidant and detergent. These additional agents improved the performance of the oil composition as an engine lubricant, reducing both varnish and bearing weight loss in standard Lauson engine tests. Even for rust inhibiting purposes alone it may be desirable to add minor proportions, prefer-

ably between 0.05 and 4.5% of an oil soluble soap, preferably an oil soluble petroleum sulfonate of calcium, barium, sodium, or potassium. These materials tend to promote rust resistance as well as to improve detergency but they should not be used where emulsification is undesirable.

EXAMPLE III

75 grams of "Sequestrene AA" (¼ mol) was combined with 207.5 grams (1 mol) of "Lorol B" alcohol and 300 cc. of toluene. These materials were charged to a 3-necked 1 liter flask equipped with a stirrer, a thermometer, a water trap and a reflux condenser. On heating, the reaction went very slowly so the toluene was distilled off and replaced by xylene, adding 10 grams of toluene sulfonic acid. The mixture was refluxed for 5 hours at 300° F., yielding 4.5 cc. of water. An additional 10 grams of toluene sulfonic acid was added and the mixture refluxed for 6 hours at 300° to 330° F. A total of 18.2 cc. of water was collected. A further 5 grams of toluene sulfonic acid was added and the mixture further refluxed for 5 hours at 330° F. The total water collected rose to 21.4 cc. The resulting product was washed three times with a 5% sodium carbonate solution and three times with clear water until the water was neutral to litmus.

The mixture was heated and blown with nitrogen overnight on a stream bath to evaporate the water and left a yield of 234.5 grams. The product, which appeared to be substantially fully esterified was designated "Lorol B ester of Sequestrene AA." It had a viscosity of 56.8 S. S. U. at 210° F. and a nitrogen content of 2.41% as against 2.66% theoretical. It was tested for its pour depressing effect on various mineral base lubricating oils of SAE 10 grade with the following results:

	Pour point, ° F.
Conventionally refined Pennsylvania, V. I. 100, vis. 45.3 S. S. U. at 210° F	+ 5
Same, with 1% Example III	+ 5
Solvent extracted Mid-Continent neutral with added Bright stock—V. I. 103, vis. 46.1 S. S. U. at 210° F	+20
Same, with 1% Example III	− 5
Conventionally refined Mid-Continent neutral with added Bright stock, 95 V. I., vis. 43.6 S. S. U. at 210° F	+30
Same, with 1% Example III	0

It will be noted that the substantially fully esterified "Sequestrene AA" was an effective pour point depressant in the Mid-Continent oils but not in the Pennsylvania stock.

It will be understood that conventional antioxidants and other agents such as degras, waxes and the like may be added where a film type rust preventive material is to be prepared. As indicated above various oils and mixtures of oil may be used as will be obvious to those skilled in the art.

What is claimed is:

1. An improved oil composition comprising a major proportion of a liquid oily vehicle and a minor rust inhibiting proportion of at least one oil-soluble material selected from the group which consists of the full esters, partial esters and metal salts of partial esters of ethylene bis-imino aliphatic carboxylic acid having 1 to 4 carbon atoms in the aliphatic group, the esterifying group being C_8 to C_{18} unsubstituted aliphatic alcohol.

2. A rust preventive composition comprising a major proportion of a hydrocarbon oil and a minor proportion of an oil-soluble metal salt of at least a partially esterified ethylene bis-imino di aliphatic carboxylic acid having 1 to 4 carbon atoms in the aliphatic group, the esterifying group being C_8 to C_{18} unsubstituted aliphatic alcohol.

3. A rust preventive composition comprising a major proportion of a hydrocarbon oil and a minor proportion of an oil-soluble at least partially esterified ethylene bis-imino diacetic acid, the esterifying group being C_8 to C_{18} unsubstituted aliphatic alcohol.

4. Composition according to claim 2 wherein said carboxylic acid is acetic acid.

5. Composition according to claim 2 wherein said carboxylic acid is propionic acid.

6. A rust preventive oil composition comprising a major proportion of a liquid oily vehicle of viscosity at least as great as kerosene and between 0.001 and 10% by weight based on the total composition, of a C_8 to C_{18} unsubstituted aliphatic alcohol ester of ethylene bis-imino diacetic acid.

7. Composition according to claim 6 wherein the proportions of ester are between 0.005 and 0.2%.

8 Composition according to claim 6 wherein at least one but not more than two acid groups are esterified.

9. Composition according to claim 6 wherein the esterifying aliphatic alcohol is a mixture of alcohols substantially within the C_{10} to C_{18} range.

10. A rust inhibiting oil composition comprising a major proportion of an oil of lubricating grade, a minor proportion of a C_8 to C_{18} unsubstituted aliphatic alcohol partial ester of ethylene bis-imino diacetic acid, and a minor proportion of an oil-soluble metal base soap selected from the group consisting of oil soluble metal sulfonates and barium phenol sulfide.

11. A rust inhibiting oil composition comprising a major proportion of an oil of lubricating grade, a minor proportion of a mixed C_{10}–C_{18} unsubstituted aliphatic alcohol partial ester of ethylene bis-imino diacetic acid, and a minor proportion of an oil soluble metal base sulfonate.

12. A rust inhibiting composition consisting essentially of 95 to 99.9% by weight of mineral base lubricating oil, 0.05 to 4.5% oil-soluble metal base petroleum sulfonate, and 0.005 to 1% of aliphatic alcohol esters of ethylene bis-imino diacetic acid having at least 8 and not more than about 18 carbon atoms in each alcohol group.

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