

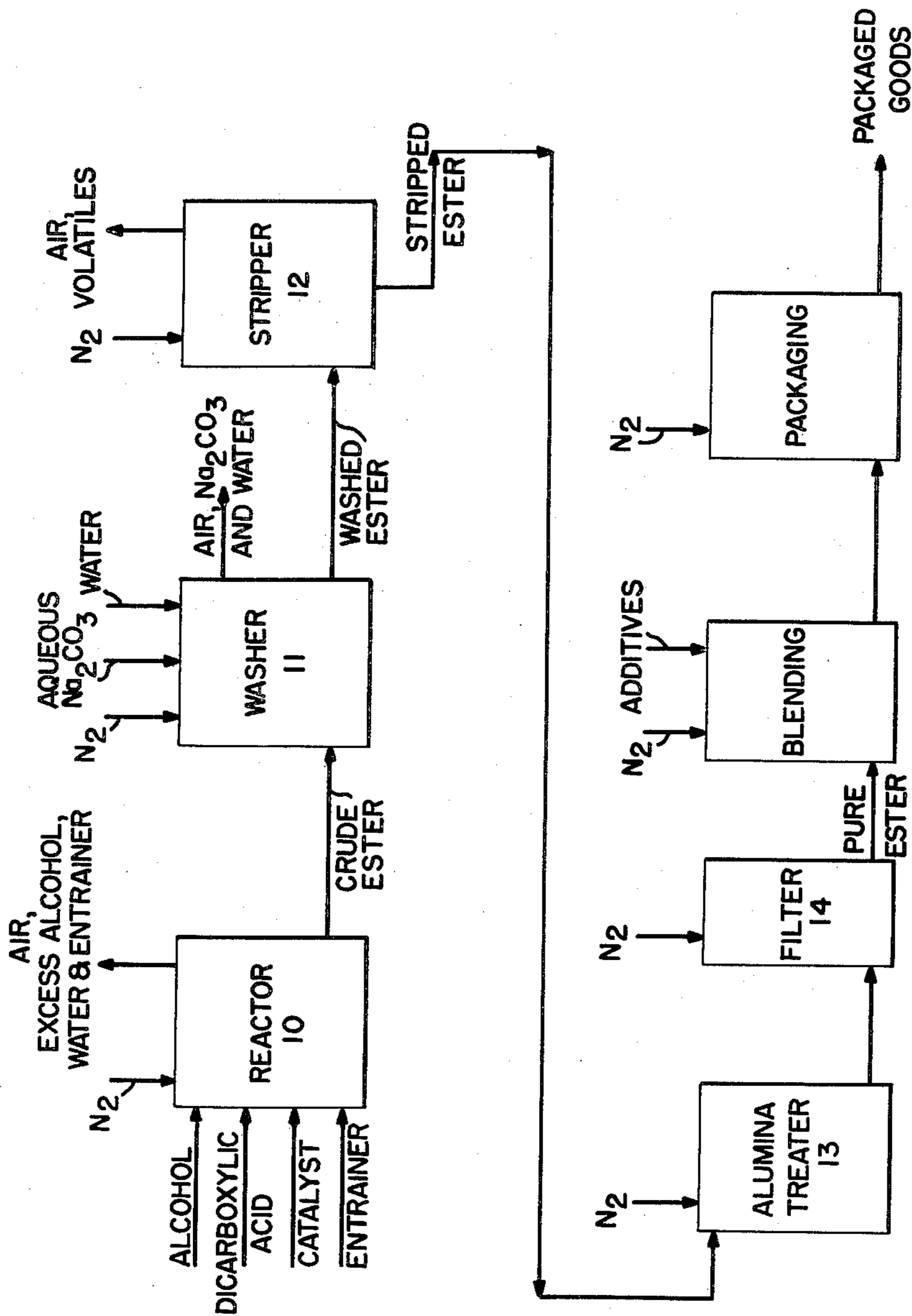
July 30, 1963

A. H. POPKIN

3,099,682

PREPARATION, TREATMENT AND STORAGE, UNDER A NITROGEN
BLANKET, OF THE DIESTERS OF DICARBOXYLIC ACIDS
AND OXO ALCOHOLS

Filed Dec. 24, 1959



Alexander H. Popkin

Inventor

By

Frank T. Johann

Patent Attorney

1

3,099,682

PREPARATION, TREATMENT AND STORAGE, UNDER A NITROGEN BLANKET, OF THE DIESTERS OF DICARBOXYLIC ACIDS AND OXO ALCOHOLS

Alexander H. Popkin, Maplewood, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Filed Dec. 24, 1959, Ser. No. 861,818

2 Claims. (Cl. 260-485)

This invention relates to a method of producing synthetic ester oils having a high degree of storage stability. Particularly, the method relates to the manufacture of diesters by esterification of dicarboxylic acids with alcohols, or by esterifying glycols with monocarboxylic acids, under an oxygen free atmosphere, whereby the formation of peroxides and deteriorating contaminants which reduce storage stability of the diester is avoided.

Synthetic diester lubricating oils have become widely used for the lubrication of turbo-prop, turbojet and pure jet aircraft engines. These synthetic ester oils have low pour points, excellent viscosity-temperature characteristics at both low and high temperatures, and other desirable characteristics. While the use of diester oils in commercial aircraft is constantly increasing, the primary use remains in military aircraft. For military aircraft use it is desired that the synthetic diester oil have an exceptionally long storage life, up to 3 years or more, so that an adequate stock pile of oil is available. In the past, these storage requirements have been difficult to meet and have previously constituted a practical bar to the use of certain synthetic esters. Thus, from an economical and availability standpoint, it is desirable to prepare the diesters from Oxo alcohols with dicarboxylic acids such as adipic acid and azelaic acid. Unfortunately, diesters prepared from these components by conventional techniques have been somewhat poorer with regard to long storage stability, being inferior in this regard to the better known di(2-ethylhexyl) sebacate. Based upon recent research, it is believed that this poor storage stability is the result of formation of peroxides due to exposure of the diester to air. These peroxides are believed to catalyze the breakdown of diester to half esters which materially increase the corrosivity of the lubricant to the lead in the lead bearings present in the aircraft engines. Furthermore, deposit formation and corrosiveness to other engine metals are increased as the amount of contaminants correspondingly increases as the diester ages. It has now been found that manufacture and storage of synthetic diesters in an oxygen-free atmosphere, (for example under a nitrogen blanket) greatly improves the storage stability of the diester.

While manufacture and storage under an oxygen-free atmosphere considerably improves oxidation stability, the stability of the oil may be even further improved by the use of certain absorbents to remove other contaminants from the diester. Exactly what contaminants are removed by absorbents is not clearly understood at this time. Even further improvement can be made by use of a certain select combination of oxidation inhibitors which will later be described in detail.

The synthetic diesters which may be made in accordance with this invention are those of the general formulae:



wherein R represents a C₆ to C₁₂ alkyl radical while R' represents a C₄ to C₁₀ saturated aliphatic hydrocarbon group. The above types of esters may be prepared from glycols and monocarboxylic acids or alcohols and dicarboxylic acids. Examples of such esters include di-

2

propylene glycol dipelargonate, di(C₈ Oxo) adipate, di(C₁₀ Oxo) adipate, C₈ Oxo/C₁₀ Oxo adipate, di(2-ethylhexyl) azelate, di(C₈ Oxo) azelate, di(C₉ Oxo) sebacate, etc. While all esters of the above formula may be made by the method of the invention, the method is particularly effective with diesters prepared from the Oxo alcohols which otherwise exhibit relatively poor oxidation stability. These Oxo alcohols are an isomeric mixture of branched chain primary alcohols produced by the Oxo process. In this process, an olefin (usually polymers and copolymers of propylene and butylene) is reacted with carbon monoxide and hydrogen in the presence of a catalyst, usually a cobalt carbonyl catalyst, to form a mixture of aldehydes having one carbon more than the starting olefin. This reaction is usually carried out at pressures of about 200 to 400 atmospheres at temperatures of about 300° to 400° F. The aldehyde mixture is then hydrogenated to form the Oxo alcohols which are then recovered by distillation. The Oxo process is well known and has been described in various U.S. patents, e.g. U.S. 2,327,066 and U.S. 2,593,428.

The diesters of the invention are prepared by the reaction of alcohol and dicarboxylic acid, or by reaction of glycol and monocarboxylic acid, by straight esterification procedures, but in an oxygen-free atmosphere. Generally, an entraining agent such as toluene or heptane will be used to help remove the water of the reaction. In the case of diesters of alcohols and dicarboxylic acids, an excess of alcohol can be used to insure complete reaction of the acid. In the case of a synthetic ester made from a glycol and primary acid, excess of acid is used to assure complete reaction. Esterification catalysts such as sodium methylate, metallic sodium, sulfuric acid, sodium acid sulfate, toluene sulfonic acid, zinc oxide, etc. can be used to hasten the reaction. The acidic esterification catalysts, such as sodium acid sulfate, sulfuric acid and toluene-sulfonic acid, have been found most useful in carrying out the esterification. However, when an acidic catalyst is used, it is generally desirable to treat the crude ester obtained with a neutralizing agent, followed by water washing. Frequently, a diluent aqueous solution of sodium carbonate is used to neutralize the acid catalyst as well as any acidic by-products that may form during the esterification reaction, followed by water-washing and a stripping distillation to obtain a dry product and remove volatiles.

Reference is now made to the drawing which illustrates a preferred form of the process of the invention directed to the manufacture of diester of alcohol and dicarboxylic acid. The alcohol, dicarboxylic acid, catalyst and entraining agent are added to the reactor 10. Heat is applied and as the vapors form, the air in the reactor is driven out. The water of reaction, entrainer and any excess alcohol is removed overhead. The water can be separated and the alcohol and entrainer may be used again. After completion of the esterification by removal of the excess alcohol, entrainer and water of reaction, contents of the reactor are allowed to cool thereby condensing any vapors in the reactor. As the vapors condense, nitrogen is admitted to restore the reactor to atmospheric pressure and prevent the entrance of air. The diester is then passed into the washer 11, as additional nitrogen is admitted to the reactor to prevent a vacuum. The washer 11 also operates under a nitrogen blanket which is obtained by first filling the washer completely with nitrogen, thereby displacing all air, and then in turn displacing the necessary amount of nitrogen by the crude diester reaction product from the reactor. A diluent solution of about 10 wt. percent sodium carbonate in water is added, while displacing nitrogen, to neutralize any acidity in the crude ester which may be due to the catalyst or to the

3

formation of acidic bodies during the esterification. Next, the washer contents are allowed to remain quiescent so that an aqueous layer and an ester layer forms. The aqueous layer is then drawn off and discarded while additional nitrogen is vented into the washer. Next, water may be admitted to the washer, stirred, allowed to form a water layer, then the water layer is drawn off and discarded. It will be apparent that by the above procedure, several washings and neutralizing stages can be carried out until the desired final neutralization number of about .01 to 0.08 mg. KOH/gm. ester is obtained. The washer contents are continuously maintained under a nitrogen blanket by the addition or venting of nitrogen as the washing and neutralizing solution is withdrawn or added to the washer. Next, the washed ester is piped into the vacuum stripper 12. Again the vacuum stripper may be initially filled with nitrogen to displace any air, while a portion of the nitrogen in turn is displaced by the incoming batch of washed ester. Upon the application of heat and vacuum to the stripper any volatile material such as water, unreacted alcohol, or entraining agent is drawn off. Upon completion of the stripping operation, the contents are cooled and nitrogen can be passed into the stripper 12 so as to displace the stripped ester which is then passed into a nitrogen filled alumina (Al_2O_3) treater 13, where it is stirred for about 1 to 10 hours, preferably 3 to 6 hours, in contact with finely divided alumina having a particle size of about 48 to 100 mesh. About 1 to 15% by weight of alumina or aluminum oxide, based on the weight of ester, is used and the treating can be carried out at temperatures of about 50 to 250° F., preferably 100–110° F. Next, the alumina treated ester is passed through a filter 14 to filter out the alumina. The alumina treated ester is passed into a blending tank where any additive or base oil materials may be added to form the finished composition. From the blender the composition is pumped to a storage tank which is nitrogen blanketed or may be directly packaged in drums or cans. A nitrogen atmosphere is maintained in all operations including the alumina treater, filling, blending and packaging by means previously described, e.g. in the case of the drums or cans, nitrogen is passed into the container in order to displace the air and then the ester composition is passed into the drum or container to displace the nitrogen and the container is sealed. As evidenced by the above described method, air is prevented from coming into contact with the ester composition at any stage of its preparation.

While the above method utilizes an individual reactor, washer, stripper and alumina treater, it is possible to carry out all of these functions in the same vessel as will be later illustrated by the working example.

In forming a final usable lubricant composition the di-ester oil, as noted above, may be blended with various additives, and even other base oils. For example, diester prepared under a nitrogen atmosphere can even be blended in minor amounts, e.g. 5 to 25 wt. percent, based on the total weight of diester, of other diester materials not made under an inert atmosphere but which are per se relatively storage stable, such as di-(2-ethylhexyl) sebacate and di-(2-ethylhexyl) adipate. Also various complex esters prepared by esterification reactions between glycols, dicarboxylic acids, and alcohols can be added to the base diester oil. The most useful of the complex esters are those having the formula:

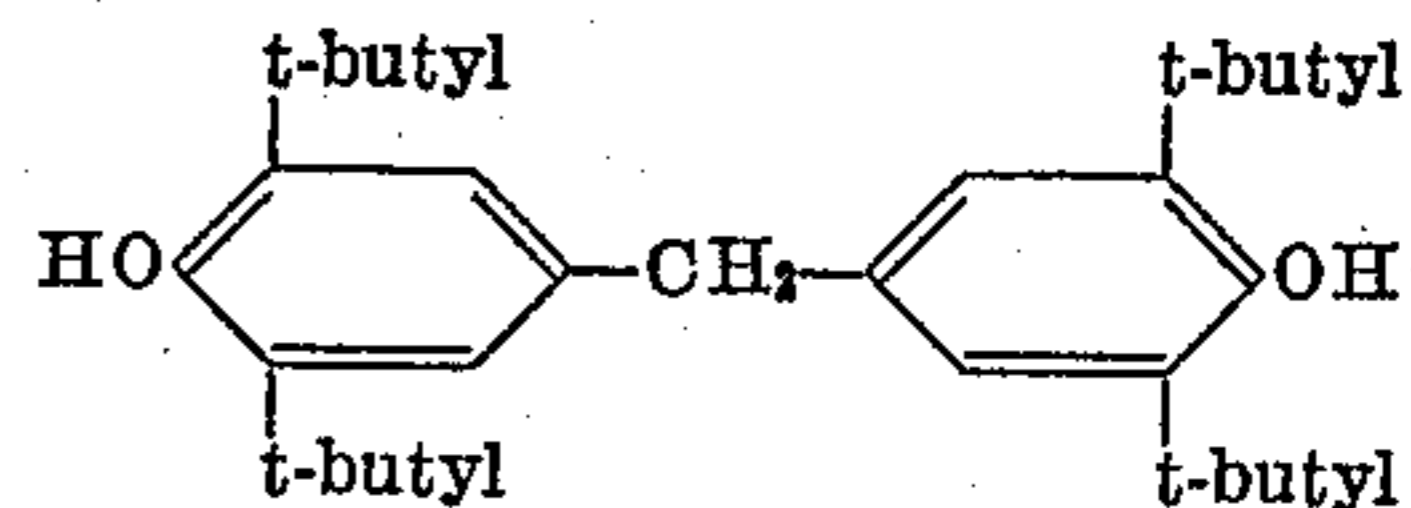


wherein all the said R's are saturated, aliphatic hydrocarbon radicals and x is a number averaging about 1 to 6. R_1 and R_5 are C_6 to C_{12} alkyl radicals of alkanols; R_2 and R_4 are saturated hydrocarbon groups or saturated oxyhydrocarbon groups of 2 to 20 carbon atoms derived from glycols or polyglycols respectively; while R_3 is the satu-

4

rated hydrocarbon group having 4 to 10 carbon atoms of an alkandioic acid.

Various additives in an amount of .01 to 10.0 wt. percent, preferably .1 to 4.0 wt. percent, of each additive, based on the weight of the final composition, may be included in the final composition. Such additives include load-carrying agents such as tricresyl phosphate, polymeric silicones of 1,000 to 100,000 molecular weight, sebacic acid and di-(C_8 Oxo) diesters of pyromellitic acid dianhydride; anti-foamants such as polymethylene silicone having a viscosity at 25° C. of about 60,000 centistokes; anti-oxidants such as phenothiazine, and Bisphenol A which is a commercially available material of the formula:



It has been further found that a particularly effective oxidation inhibitor combination is about 0.1 to .85 wt. percent, preferably 0.5 to 0.75 wt. percent, of phenothiazine and about .005 to 0.5 wt. percent, preferably 0.05 to .15 wt. percent, of Bisphenol A, (said wt. percents being based upon the total weight of the composition). This combination of additives is more effective than a like amount of any of the two additives alone.

The invention will be further understood by reference to the following example:

EXAMPLE I

A mixed diester was prepared in two stages. In the first stage one molar proportion of adipic acid was reacted with one molar proportion of a C_{10} Oxo alcohol to make the C_{10} Oxo adipate half ester. One molar proportion of the C_{10} Oxo adipate half ester was then reacted with 1.1 molar proportion (10% excess) of C_8 Oxo alcohol to make a mixed C_8/C_{10} Oxo adipate ester. The C_{10} Oxo alcohol used was prepared from subjecting tripropylene to the Oxo process, while the C_8 Oxo alcohol was correspondingly prepared from a C_7 olefin derived from a propylene-butylene feed.

In the first stage of the esterification, C_{10} Oxo alcohol and adipic acid were charged to a reactor equipped with a condenser in equi-molar quantities. 0.25 wt. percent, based on the theoretical yield of ester, of anhydrous sodium acid sulfate ($NaHSO_4$) was added as a catalyst. 5.0 vol. percent, based on the total charge, of benzene was added as a water entraining agent. The reaction mixture was brought to reflux temperature of about 270°–280° F. and the reaction was continued until the theoretical amount of water was removed overhead. C_8 Oxo alcohol was then piped into the reactor and reflux was continued until an acid value of 1.0 mg. KOH/gm. is obtained. The reaction mixture was then cooled to 110°–125° F. while nitrogen was admitted to the reactor to prevent the formation of vacuum. Next, an aqueous sodium carbonate solution containing about 6 wt. percent sodium carbonate, was pumped into the reactor. The actual weight of sodium carbonate used was equal to 2% by weight of the total initial charge to the reactor. After agitating for one and a half hours, the reactor contents were allowed to separate and the alkaline layer was drawn off. The remaining crude ester was washed twice with water by pumping in water, agitating it with the ester, allowing the layers to separate and then drawing off the water layer. The excess alcohol and benzene entraining agent were next removed at 300° F. under vacuum until the remaining product has a flash point of 420° F. minimum. 4 wt. percent based on the weight of ester, of F-1 Alumina was added to the reactor. The F-1 Alumina is an activated alumina which is a porous

5

form of aluminum oxide (Al_2O_3) of relatively high purity. Typical analysis and properties are as follows:

| Analysis: | F-1 alumina |
|---|-------------|
| Alumina (Al_2O_3), percent | 92.00 |
| Soda (Na_2O), percent | <0.8 |
| Silica (SiO_2), percent | <0.1 |
| Titania (TiO_2), percent | <0.02 |
| Iron Oxide (Fe_2O_3), percent | <0.10 |
| Moisture (loss on ignition), percent | 7.00 |
| Density: Pounds/cu. ft. (approx.) | 50 |

After stirring the alumina with the ester for 4 hours at 110°F ., the mixture was filtered. 0.05 wt. percent, based on the weight of ester, of Bisphenol A anti-oxidant was then added to the resulting product. Except for the filtering, the preparation of the ester described above was carried out in a single reactor tank under a nitrogen atmosphere by either exhausting nitrogen from the tank as additional ingredients were added or by blowing nitrogen into the tank as materials were removed.

Under a nitrogen blanket, a lubricating oil composition was prepared by mixing 79 vol. percent of the C_8/C_{10} Oxo adipate coester prepared as described above with 20 vol. percent of di-2-ethylhexyl sebacate and 1 vol. percent of a complex ester. The complex ester was prepared by simultaneously reacting one molar proportion of polyethylene glycol of about 200 average molecular weight (PEG), 2 molar proportions of C_8 Oxo alcohol and 2 molar proportions of adipic acid. The formula for the resulting complex is:



where x averages about 1.7. To 100 parts by weight of the above synthetic oil blend there was added by simple mixing, 1 part by weight of tricresyl phosphate, 0.75

6

The weight loss of the lead strip during the time on test is then determined and reported in terms of milligram weight loss per square inch of lead surface.

The accelerated storage test was carried out by storing the oil composition at a temperature of 185°F . for 42 days (which is equivalent to about 3 years normal storage) and then running the lead corrosion test described above.

The engine test was run on a J-57 turbo-jet engine and a sample of the oil was withdrawn after every 25 hours engine operation and tested for lead corrosivity.

The test results of the tests on the freshly made oil along with tests of one of the prior best commercial oils are summarized below:

Table I

| Lubricant | After indicated months stored at ambient temperature | Cumulative lead corrosion (mgs./in. ²) in indicated hours on test | | | |
|--|--|---|------------|-------------|--------------|
| | | One hour | Four hours | Eight hours | Twelve hours |
| Oil composition of invention made and stored under nitrogen... | 12 | 0 | 0 | 0 | 0 |
| Same oil composition but made and stored under air..... | 4 | 0 | -568 | -1,107 | -1,887 |

The above test shows the excellent results obtained with the oil composition of the invention which was made under nitrogen.

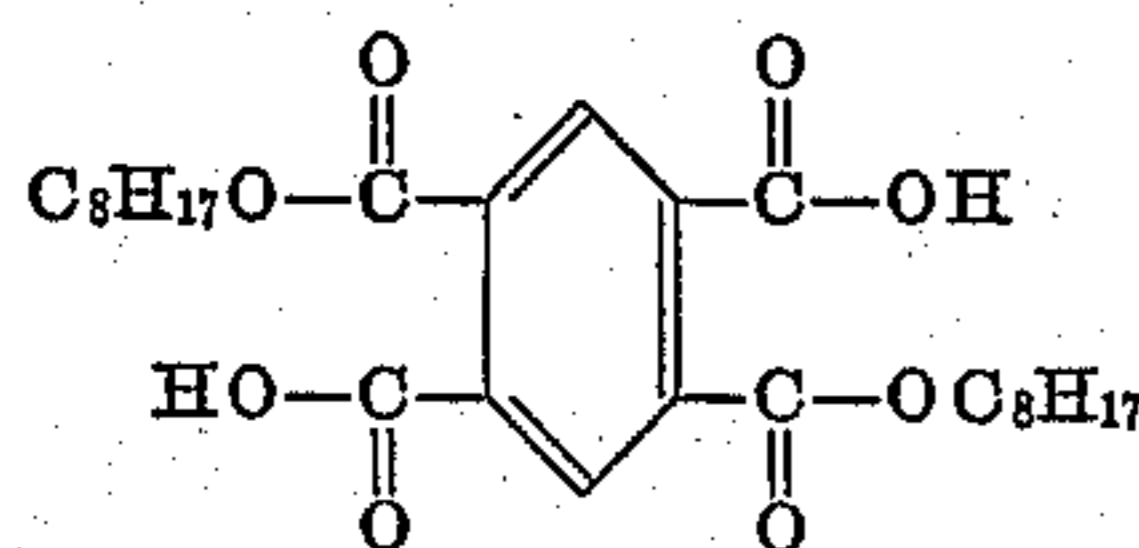
In the accelerated storage test, three samples of the invention made under nitrogen were tested along with three samples of the exact same composition, but made under exposure to air. The results are given in Table II below:

Table II

| Days at 185°F . | MIL-L-7808 requirement | Storage at 185°F ., nitrogen blanket | | | Mgs./sq. in. lead corrosion, Exposed to Air | | |
|-------------------------------|---|--|------|------|---|------|------|
| | | I | II | III | I | II | III |
| None..... | | -0.2 | -0.2 | -0.3 | -0.5 | 0 | 0 |
| 7..... | | -0.2 | -0.2 | -6.0 | -0.6 | 0 | -32 |
| 14..... | 25 mgs. max..... | -0.2 | -0.2 | -0.2 | -133 | -85 | -148 |
| 28..... | | -90 | -71 | -67 | -193 | -116 | |
| 42..... | | -59 | -65 | | -75 | -75 | |
| | 150 mgs. max. at 45 days ¹ | | | | | | |

¹ The 45 day result is obtained by plotting the results of the test after 0, 7, 14, 28, 42 days and extrapolating.

parts by weight of phenothiazine, 0.7 parts by weight of the C_8 Oxo diester of pyromellitic dianhydride, 0.015 parts by weight of sebacic acid and 0.001 parts by weight of polymethyl phenol silicone having a viscosity at 25°C . of 60,000 cs. The C_8 Oxo diester of pyromellitic dianhydride has the structure:



The final oil blend described above was then stored under nitrogen in drums.

The above composition of Example I was tested for lead corrosivity: (1) after storing at ambient temperature, (2) after an accelerated storage test, and (3) after normal storage for 2 months followed by use in a test engine.

The lead corrosion test in all three cases was carried out by rapidly rotating a bimetallic strip consisting of a lead strip and a copper strip bound together, in an oil sample maintained at 325°F ., while air is bubbled through the sample for one hour, or as long as indicated.

The above table shows that not only did the lubricating oil of the example have a very low initial corrosivity to lead, and pass the severe 14 days requirement of 25 mgs./in.² maximum lead corrosion, but even after storage equivalent to 3 or more years at ambient temperatures, the lead corrosivity was still low.

The test results obtained from using the composition of the invention in the engine showed practically no lead corrosivity. Thus, samples of the used oil showed 0.02 mg. loss after 25 hours; 1.06 mgs. loss after 50 hours; 1.02 mgs. loss after 75 hours and 0.18 mg. loss after 100 hours engine operation. The results were very surprising, since all prior diester lubricating oil compositions show a rapid increase in lead corrosivity after about 50 hours engine operation to give about 40 to 100+ mgs./in.² weight loss, followed by a tapering off in weight loss to about 10 mgs. at the end of 100 hours. This tapering off in corrosivity is due to the reaction of the corrosive materials with lead in the engine, and further degradation of the corrosive half ester to alcohol and diacid, which are not corrosive to lead.

What is claimed is:

1. A method for the preparation of a synthetic diester

useful as a lubricating oil and having a high degree of storage stability, wherein said diester has the formula:



wherein R' is a C₄ to C₁₀ saturated aliphatic hydrocarbon group, and R is a C₆ to C₁₂ alkyl radical of a branched chain primary alcohol produced by the reaction of an olefin with carbon monoxide and hydrogen in the presence of a catalyst to form a mixture of aldehydes, which aldehyde mixture is then hydrogenated to form said alcohol, which comprises heating said alcohol and a C₆ to C₁₂ dicarboxylic acid in a reactor to esterify and remove the water of condensation until the esterification is substantially complete, admitting nitrogen into the reactor as the reactor contents are cooled in order to restore the reactor to atmospheric pressure and prevent the entrance of air, neutralizing and water washing the ester product under a nitrogen blanket, heating said ester product in a reactor to strip said product of undesired volatile material, admitting nitrogen into the stripping reactor as the ester product is cooled in order to restore the reactor to atmospheric pressure and prevent the entrance of air, and then storing said ester product under nitrogen, and wherein the contacting of air with said ester product is avoided during said method.

2. A method for the preparation of a synthetic diester useful as a lubricating oil and having a high degree of storage stability, wherein said diester has the formula:



wherein R' is a C₄ to C₁₀ saturated aliphatic hydrocarbon group, and R is a C₈ to C₁₀ alkyl radical of a branched chain primary alcohol produced by the reaction of an olefin with carbon monoxide and hydrogen in the presence of a catalyst to form a mixture of aldehydes, which aldehyde mixture is then hydrogenated to form said alcohol,

which comprises heating said alcohol and a C₆ to C₁₂ dicarboxylic acid in a reactor along with an esterification catalyst and a water entraining agent to esterify and remove the water of condensation until the esterification is substantially complete, admitting nitrogen into the reactor as the reactor contents are cooled in order to restore the reactor to atmospheric pressure and prevent the entrance of air, neutralizing and water washing the ester product under a nitrogen blanket, heating said ester product in a vacuum stripping reactor to strip said product of undesired volatile material, admitting nitrogen into the vacuum stripping reactor as the ester product is cooled in order to restore the reactor to atmospheric pressure and prevent the entrance of air, treating the ester product with alumina under a nitrogen blanket, adding antioxidant while under a nitrogen blanket, and then packaging said ester product in containers under a nitrogen blanket, wherein the contacting of said ester product with air is avoided during said method.

References Cited in the file of this patent

UNITED STATES PATENTS

| | | |
|-----------|---------------|---------------|
| 2,327,066 | Roelen | Aug. 17, 1943 |
| 2,457,111 | Gresham | Dec. 28, 1948 |
| 2,571,332 | Brooks | Oct. 16, 1951 |
| 2,621,158 | Teeter | Dec. 9, 1952 |
| 2,645,658 | Reeves | July 14, 1953 |
| 2,673,212 | Young et al. | Mar. 23, 1954 |
| 2,703,811 | Smith | Mar. 8, 1955 |
| 2,710,877 | Young et al. | June 14, 1955 |
| 2,778,849 | Ackelsberg | Jan. 22, 1957 |
| 2,909,562 | Hughes et al. | Oct. 20, 1959 |

FOREIGN PATENTS

| | | |
|---------|---------------|---------------|
| 744,816 | Great Britain | Feb. 15, 1956 |
|---------|---------------|---------------|