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PREPARATION OF POLYESTERS

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This invention relates to the manufacture of esters of polyhydric alcohols which are substantially free of unreacted acids and also concerns a method of manufacturing synthetic ester-type lubricants having low acid numbers.

I have found that synthetic polyester lubricants produced from the esterification of mixed monobasic carboxylic acids with polyhydric alcohols have very low free acid content provided the esterification is carried out in two steps. These two steps comprise dividing the mixture of acids into a high boiling portion and a low boiling portion and then partially esterifying the polyhydric alcohol with the high boiling portion followed by completing the esterification with the low boiling portion.

The shortage of petroleum lubricating oil during World War II accelerated the research work on producing a suitable synthetic lubricant for special uses in military purposes. As a result of this work, it was found that the reaction of monobasic carboxylic acid with polyhydric alcohols gave high molecular weight esters which were found to be useful as lubricants for aircraft instruments, hydraulic and dampening fluids, and precision bearing lubricants where exceptionally low temperature fluidity properties were required. Of particular interest were the diester lubricants. However, these diesters were only useful as light oils since their viscosity was too low for anything but these special applications. Since the viscosity index was too low and the pour point too high for the very low temperatures required in military uses, they were found to be unsuitable for engine oils. Also, the method of their production was considered to be quite complex. This prior work has been done with essentially pure acids and the diesters produced were essentially a single compound. Interest in diester lubricants has been accelerated with the development of the gas turbine. Recent work has shown that when a mixture of monobasic carboxylic acids having greater than 6 carbon atoms per molecule is esterified with polyglycols that the diesters produced have unexpectedly superior qualities as engine lubricating oils as compared with the diesters produced from a single acid. Therefore, there is real incentive for producing diesters from mixed monobasic carboxylic acids that will meet government specifications for engine lubricating oils.

One of the big problems in producing satisfactory polyesters when using mixed monobasic carboxylic acids in the C_7 to C_{30} range is that the high molecular weight acids which are required for superior products are very difficult, if not impossible, to remove from the ester product when they have not reacted with the polyglycol. Government specification for lubricating oil requires that the acid number (i.e., mg. KOH/gm.) must not exceed 0.1. The normal esterification process is carried out by reacting an alcohol with an acid in the presence of an esterification catalyst, such as a strong mineral acid, and refluxing the mixture while trapping out the water of the reaction. Normally an azeotroping agent is used in the reaction to facilitate the removal of the water. When no more water is produced the reaction is complete and the product from the reaction is purified by distillation. If stoichiometric amounts have been added and the reaction has proceeded theoretically there is no excess acid or alcohol. However, as is true in most chemical reactions, the reaction product in the majority of the cases contains an excess of either the acid or the alcohol. In producing synthetic diester lubricants which are suitable as engine oils, as well as special uses, it is essential that the diester product contain no free acid or monoester. If excess acid is present it will cause corrosion of the engine when the lubricating oil is in use and if monoesters are present they will cause a reduction of viscosity and viscosity index and will increase the pour point. When esterifying mixtures of low and high boiling carboxylic acids any residual unreacted acid is very difficult, if not impossible, to remove since a portion of the residual acids will boil at a temperature above the boiling point of the lowest boiling polyesters. Experience has shown that they cannot be removed by distillation alone. The obvious answer would appear to be the use of an excess of polyglycol in the reaction, thereby reacting all the acids, both low boiling and high boiling. However, the presence of an excess amount of polyglycol during the esterification will cause the formation of monoesters, sometimes called half esters. Since some of these glycol monoesters boil as high as the diesters they cannot be completely separated from the diesters and will degrade the superior qualities of the diester synthetic lubricant. Normally an excess amount of acid is used in the reaction in order to insure that all the polyglycol will react, thereby forming the preferred diester product. Previous workers have not been faced with the difficulty of removing residual amounts of high boiling acids since their work has been done with relatively pure low boiling acids which can be removed by distillation and neutralization.

I have now discovered a new technique for producing polyesters by the reaction of mixtures of low and high boiling monobasic carboxylic acids with polyglycols which method, after normal purification of the product, produces synthetic diester lubricants containing essentially no residual acid. The method comprises first dividing the mixture of acids into a low boiling portion and a high boiling portion; mixing the polyglycol with the high boiling acid portion in a reaction vessel along with an esterification catalyst; carrying out the esterification until all acids in the high boiling portion have completely reacted, leaving unreacted hydroxyl groups in the partially esterified polyglycol; adding the low boiling acid portion to the reaction mix and resuming the esterification until all the hydroxyl groups of the polyglycol have reacted to form polyesters, and leaving an excess of unreacted low boiling acids in the polyester product mix. In the product work-up the low boiling acids can be easily removed by distillation. In this manner the disadvantages of the prior art are overcome and polyester synthetic lubricants of a very low acid content are produced.

An example of a mixture of carboxylic acids which are suitable for producing diesters for use as lubricating oils is a portion of those acids which are produced by the hydrogenation of carbon monoxide. The carboxylic acids used in making synthetic lubricants have at least 7 carbon atoms in the molecule and up to as many as 30 carbon atoms per molecule. The mixture contains many carboxylic acids differing in the extent of unsaturation and branching in the hydrocarbon chain. This process is commonly known as the hydrocarbon synthesis process or synthol process. The typical conditions used in the synthol process are as follows. Synthesis gas (fresh feed) consisting of 95–98% carbon monoxide and hydro-

gen in a molar ratio of hydrogen to carbon monoxide of between 1.0–2.5:1 is contacted at a temperature between 450° and 750° F., preferably between 600° and 700° F., with an iron-type catalyst. While pressures of between 100 and 700 p.s.i.g. may be used, pressures higher than about 250 p.s.i.g., preferably between 325 and 425 p.s.i.g. are preferred. Gaseous recycle ratios of between about 1 to 2 volumes of recycle gas per volume of fresh feed may be employed. Space velocities of between 5 and 15 s.c.f. CO/hr./lb. of catalyst are generally satisfactory. While the operating conditions set forth above are those which are usually considered preferable, it is to be strictly understood that any of the known conditions used in the synthol process for producing hydrocarbons and oxygenated chemicals by reacting carbon monoxide and hydrogen at 450°–750° F. and between 100 and 700 p.s.i.g. over an iron-type catalyst may be used. Catalysts suitable for use in the synthol process are any of those iron-type catalysts known to be useful for producing liquid hydrocarbons and oxygenated chemicals. More detailed descriptions of the synthol process may be found in U.S. 2,681,924 to M. B. Kratzer and Encyclopedia of Chemical Technology by Kirk-Othmer, volume 6, pages 972–983 (1951).

The effluent from the reactor is cooled and separated into a gas stream and two liquid streams. The liquid streams consist of an aqueous phase containing water-soluble oxygenated compounds and a hydrocarbon phase containing oil-soluble oxygenated compounds. Usually about 10 to 20% of the total product will consist of oxygenated compounds. The synthol acids employed in preparing highly useful diesters are oil-soluble acids recovered from the hydrocarbon phase. Any of a number of methods may be practiced in recovering the oil-soluble carboxylic acids from the hydrocarbon phase. The alcohols, aldehydes, and ketones may be separated from the hydrocarbon phase by extracting with an aqueous solution of a water-soluble bisulfite, followed by extracting the hydrocarbon raffinate with an aqueous solution of a mild alkali such as sodium carbonate (note U.S. 2,457,257) to separate the carboxylic acid salts and then springing and recovering the acids from the salt solution. Other methods of recovering the oil-soluble carboxylic acids from the hydrocarbon phase are detailed in U.S. 2,670,366 and U.S. 2,645,655.

The mixture of oil-soluble carboxylic acids which is recovered from the hydrocarbon phase consists primarily of acyclic monocarboxylic acids. The mole percent unsaturation of the carboxylic acids may range between 2 and 35%. The mixture contains both straight and branched chain acids. It may contain between 10 and 60% of straight chain acids and between 90 and 40% of branched chain acids, the percentage of branched chain acids increasing with the number of carbon atoms in the acid molecule. Analysis of the types and structures of the various carboxylic acids produced during the synthol process, as well as a discussion thereof, is presented in I. and E. Chem., volume 45, pages 359–362 (February 1953).

The glycol used in the esterification can be ethylene glycol, propylene glycol, diethylene glycol, or triethylene glycol. The diesters produced from these glycols can be used as synthetic lubricants in aircraft or automobile engines. Other types of polyhydric alcohols, such as dipropylene glycol, trimethylolethane, trimethylolpropane, pentaerythritol and the like, can be used; however, the esters produced are less satisfactory as engine lubricants. These latter esters are used in special applications where both a high viscosity index and a low pour point are not required.

As an example of my invention, the esterification of triethylene glycol with a mixture of synthol acids will be described. A mixture of hydrogenated synthol acids boiling in the range of 150° to 500° C., which contained about 80% C_7–C_{12} and about 20% C_{12}–C_{30} monobasic acids was fractionated to produce two portions. One contained the acids boiling below 90° C. at 1 mm. (about 250° C. at 760 mm.) and the other contained the acids boiling above 90° C. at 1 mm. (about 250° C. at 760 mm.). Each portion contained about 50% by volume of the acids. At the 50% cut point the C_7 acids up to about C_9 were taken overhead and the bottom portion contained the C_9+ acids up through about C_{30} to C_{35}. The molecular weight of these higher acids is not known with precision since they cannot be segregated due to their high boiling points. This fractionation step does not need to be performed with precision since only a rough separation of the acids is necessary. For the purposes of my invention, the separation can be made in the range of 5 to 95% depending upon the character of the mixed acids being fractionated and the quality of the ester product desired. If high viscosity is an important factor, it will be desirable to separate the acids into a larger high boiling portion and a smaller low boiling portion, as for example, by preparing a 5 to 30% portion of the low boiling acids. Thus, in the first step of my esterification method where the higher boiling acids (i.e., the higher molecular weight) are reacted in the presence of an excess of hydroxyl groups, all of these higher boiling acids will be esterified. Thus, when the lower boiling portion is added and the esterification is completed with an excess of acid, this excess of acid will be in the form of the very low boiling acids (i.e., lower molecular weight).

In preparing the diesters the higher boiling portion of the mixed synthol acids was added to approximately an equal molar amount of triethylene glycol. About 2 weight percent of toluene sulfonic acid (based on the amount of glycol) was used as the catalyst and xylene was used as an entraining agent. The entire mixture was refluxed while the water of reaction was removed by a trap in the overhead reflux condenser. The reaction was allowed to proceed at reflux temperature until no more water was taken overhead, thus indicating that all of the high boiling acids had been completely esterified. Since the acid to glycol molar ratio was about 1:1, there was an excess of unreacted hydroxyl groups in the reaction mix. These hydroxyl groups were contained in the form of unreacted glycols and monoesters. Next, the low boiling portion of the synthol acids previously separated were added to the reaction mix bringing the total amount of acid added (both high boiling and the low boiling portions) to an acid to glycol molar ratio of about 2.5:1. The esterification was resumed and once again the water of reaction was withdrawn until no more was produced. Since avoiding the formation of the monoester is essential to obtaining a diester with good viscosity index and pour point making it suitable for synthetic lubricants, it is essential that there be an excess of acid in the final esterification step. This insures complete esterification of the glycol. The product was removed from the reaction vessel and distilled under vacuum to remove the bulk of the unreacted low boiling synthol acids and the entraining agent. The acids are believed to be in the C_7–C_8 range. A diester having an acid number of about 50 to 100 (mg. of KOH/gm.) was obtained. This fractionated diester was dissolved in n-pentane and filtered through Attapulgus clay and silica gel, and the solutions were then distilled to recover the purified diesters. Evaluation of the diesters produced from the reaction of synthol acids with triethylene glycol in accordance with my invention as described above, along with esters prepared by conventional means and the Government specification for synthetic lubricants are shown in Table I. Run 1 shows the properties of a sample prepared in accordance with my invention, that is a two-step esterification. For comparison, run 2 shows the properties of a diester produced by esterifying in one step the total synthol acid mixture with triethylene glycol followed by the same purification method as used in run 1. The

purified diester from run 2 was further purified in an attempt to remove the residual acids. About 8% of the low boiling portion of the purified diester was removed by distillation under vacuum and the remainder of the diester was treated with Attapulgus clay and silica gel in the same manner as runs 1 and 2. The properties of this product are shown in run 3. The last column of Table I gives Government specifications.

TABLE I

Triethylene glycol esters of C_7+ synthol acids

Run No.	1	2	3	MIL-L-6082 A and MIL-L-7808 B [1]
Wt. C_7+ Acids Reacted, gm.	2,492	1,005		
Wt. Triethylene Glycol Reacted, gm.	1,275	450		
Product Analysis:				
Acid No. mg. KOH/gm.	0.06	4.5	4.8	0.1
Sap. No. mg. KOH/gm.	263	256	287	
Mol. Wt.			417	
Kin. Vis., 100° F., cs.	10.9	10.3	10.4	11
Kin. Vis., 210° F., cs.	3.0	2.9	2.9	3
ASTM Slope	0.71	0.76	0.69	0.71
VI	149	145	162	146
Pour Pt., ° F.	<−70	<−70	−50	−75
Flash Pt., ° F., COC.	450	440	460	350

[1] U.S. Government military specifications.

An examination of the data reported in Table I shows that the diesters produced in accordance with my invention, as reported in run 1, pass all Government specifications including the acid number specification of 0.1. The acid number in run 1 is 0.06, while run 2 shows that the diester produced by conventional methods gives an acid number of 4.5. Despite the sacrifice in yield by removing the first 8% of the purified diester from run 2 in an attempt to reduce its acid number below 4.5, run 3 shows that the acid number increased to 4.8. These results indicate that the acids are distributed throughout the diester boiling range and after considerable effort no method was found to reduce their concentration to the desired low level by further refining of the purified diester product.

While I have shown that the use of synthol acids in preparing diesters suitable as synthetic lubricants for aircraft and automotive engines, I want to emphasize that my invention can be practiced using other mixtures of monobasic carboxylic acids to produce satisfactory lubricants. An example of other acid mixtures which are satisfactory are those produced by the oxo process which is the reaction of carbon monoxide and olefins followed by oxidation. Though I have stressed that the diesters

having a low acid number are particularly suited for use as an engine lubricant where high viscosity index, low pour point and low acid number are required, it should be understood that my method can be used in preparing diesters for any use where these requirements must be met. Neither do I want to be bound by the use of only triethylene glycol as the polyhydric alcohol. As I have pointed out previously, other polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, triols, etc., can be used where producing a suitable diester requires a mixture of monobasic carboxylic acids having a low acid number. Examples of other uses of my invention are in the production of plasticizers for polyvinyl resins, such as polyvinyl chloride, copolymers of vinyl chloride with vinyl acetate, copolymers of vinyl chloride with vinylidine chloride, and the like.

Thus having described my invention, what is claimed is:

1. The method of producing synthetic polyesters having low free acid contents from a polyhydric alcohol and a mixture of acyclic monocarboxylic acids containing both straight and branched chain acids and having more than 6 carbon atoms per molecule, which method comprises (1) distilling the mixture of acids into a high boiling portion and a low boiling portion, (2) partially esterifying the polyhydric alcohol with an amount of said high boiling portion of the acids insufficient to effect complete esterification of the polyhydric alcohol, (3) adding the lower boiling portion of acids to the partially esterified polyhydric alcohol in an amount more than sufficient to effect complete esterification, and completing the esterification of the partially esterified polyhydric alcohol, (4) removing unreacted low boiling acids from the esterification product by distillation, (5) and recovering a purified low free acid content synthetic polyester.

2. The method of claim 1 wherein the polyhydric alcohol is a polyglycol.

3. The method of claim 1 wherein the polyhydric alcohol is triethylene glycol.

4. The method of claim 1 wherein the mixture of monobasic carboxylic acids is a mixture of synthol process acids.

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