

UNITED STATES PATENT OFFICE

2,499,723

LUBRICANTS CONTAINING COPOLYMERS
OF ETHYLENE AND VINYL ACETATE

Donald D. Coffman, Wilmington, Del., and John
F. Lontz, Nutley, N. J., assignors to E. I. du
Pont de Nemours & Company, Wilmington,
Del., a corporation of Delaware

No Drawing. Application July 28, 1947,
Serial No. 764,256

10 Claims. (Cl. 252—56)

1

This invention relates to new compositions of matter, and more particularly to lubricating oils having improved properties.

For many years fatty oils were used in some quantity for the lubrication of light machinery, airplane motors, and delicate mechanisms, such as watches, clocks, scientific instruments, spindles, looms, sewing machines, etc., because they possess excellent lubricating properties, high degree of adhesion to metal surfaces in the form of thin films, and great resistance to displacement of such films by water. These excellent properties are counter-balanced by poor stability under operating conditions and too great variations in viscosity with changes in temperature. For these reasons, ester-type lubricants have lost favor and have been replaced by petroleum products which can, to a large extent, be designed for specific applications. The ideal lubricant is one combining the good properties of the ester-type lubricants with those of lubricants from petroleum hydrocarbons. The present need for lubricants which would retain their lubricating properties over broad ranges of temperature, as from -70°F. to 350°F. , has again directed attention to esters which offer attractive possibilities for the development of such lubricants. Extensive investigation resulted in the discovery that diesters of the higher aliphatic dibasic acids such as adipic, sebacic, and the like, with C_8 to C_{12} primary aliphatic saturated monohydric alcohols approach the ideal lubricant. However, further improvements are required to obtain lubricants suitable for general use under the widely varying and rigorous conditions encountered in actual service.

This invention has as an object new and useful compositions of matter. A further object is the production of lubricating oils having improved low temperature characteristics. A further object is the production of lubricating oils which are obtained from esters derived from a wider range of acid and alcohol components than those successfully used in the prior practice. A still further object is a practical and economical method of obtaining these oils. Other objects will appear hereinafter.

The above objects are accomplished by incorporating into carboxylic acid esters of primary saturated aliphatic monohydric alcohols, more particularly described below, a minor amount by weight, of an ethylene/vinyl acetate polymer having an ethylene:vinyl acetate mole ratio of from 1:1 to 6:1, said esters containing at least 10 carbon atoms.

2

The ethylene/vinyl acetate polymer may be incorporated into the ester by heating or stirring or by mechanically working polymer into the ester and then heating, if necessary, or by any other means known for obtaining a homogeneous mixture or solution.

The esters used in the practice of this invention contain at least 10 and usually not more than 38 carbon atoms, and can be of natural or synthetic origin. These esters are the reaction products of aliphatic carboxylic acids, namely those having from 2 to 20 carbon atoms, with primary aliphatic saturated monohydric alcohols containing from two to 18 carbon atoms. The esters most advantageously used for the present purpose are those obtained from aliphatic dicarboxylic acids of 5 to 12 carbon atoms with a saturated aliphatic primary monohydric alcohol containing from 8 to 12 carbon atoms, and especially with branched chain alcohols of this kind wherein there is at least one side chain alkyl radical containing from 1 to 6 carbon atoms. The esters of these branched chain alcohols with sebacic acid are of particular value because of the high degree of solvency of these esters for ethylene/vinyl acetate polymers, and because of the extreme high pressure lubricating properties, low pour points, and good viscosity indices possessed by the lubricating oil obtained.

In the examples given below the viscosity measurements are made in a modified Ostwald viscosimeter as described by McCluer and Fenske (Ind. Eng. Chem. 27, 82-6 (1935)); (Procs. A. S. T. M., 38, part I, 900-908 (1938)) giving the kinematic viscosity in centistokes. Conversion to Saybolt units may be made according to McCluer and Fenske and Report of Committee D-2 on Petroleum Products and Lubricants, Panph, Pre-print A. S. T. M. meeting June 28-July 2, 1937. The viscosity index is defined by Dean and Davis in Chem. and Met. Eng., 36, 618 (1929), and is calculated from the tables in Hersh, Fisher, and Fenske, Ind. Eng. Chem., 27, 1441-6 (1935).

The examples which follow are submitted to illustrate and not to limit this invention. Unless otherwise stated, parts are expressed by weight.

Example I

To 300 parts of bis(2-ethylhexyl)sebacate is added 100 parts of an ethylene/vinyl acetate polymer containing an ethylene/vinyl acetate mole ratio of 1.2:1 and this mixture agitated with heating until solution is complete.

The above solution is diluted with a sufficient amount of bis(2-ethylhexyl)sebacate to yield a

3

blend containing 2% of the ethylene/vinyl acetate polymer. The properties of the resulting blend are as follows: viscosity at 100° F. (cts.) 17.79, viscosity at 210° F. (cts.) 4.24, viscosity index 167. The properties of the untreated ester are, viscosity 100° F. (cts.) 12.67, viscosity 210° F. (cts.) 3.33, viscosity index 154.

The above experiment is duplicated using an ethylene/vinyl acetate polymer containing an ethylene/vinyl acetate mole ratio 2.3/1. Viscosity 100° F. (cts.) 24.69, viscosity 210° F. (cts.) 5.95, viscosity index 172. The corresponding properties of the untreated ester are those given in the preceding example.

The above experiment is duplicated employing an ethylene/vinyl acetate polymer containing an ethylene/vinyl acetate mole ratio of 5.6/1. The resulting product is a viscous oil having good lubricating properties.

Example II

To 24 parts of bis(isobutyl) 2,9-dimethyl-4,7-dithiasebacate there is added 0.5 part of an ethylene/vinyl acetate polymer containing an ethylene/vinyl acetate mole ratio of about 1.2:1 and the mixture is stirred at about 120° C. until solution is complete. The blend has a viscosity at 100° F. (cts.) of 98.94, a viscosity at 210° F. (cts.) of 14.65, and a viscosity index of 136. The untreated control has a viscosity at 100° F. (cts.) of 9.26, a viscosity at 210° F. (cts.) of 2.31, and a viscosity index of 58.

Example III

To 98 parts of methyl oleate there is added 2 parts of an ethylene/vinyl acetate polymer containing an ethylene/vinyl acetate mole ratio of 2.4:1 and the mixture is stirred and heated at 190° C. until solution is complete. The blend has a viscosity at 100° F. (cts.) of 20.91, a viscosity at 210° F. (cts.) of 6.01, and a viscosity index of 191. The untreated control (the ester) has a viscosity at 100° F. (cts.) of 6.29, a viscosity at 210° F. (cts.) of 2.13, and a viscosity index of 152.

Example IV

To 98 parts of 2-ethylhexyl laurate there is added 2 parts of an ethylene/vinyl acetate polymer containing an ethylene/vinyl acetate mole ratio of 2.4:1, and the mixture is stirred and heated at 220° C. until solution is complete. The blend has a viscosity at 100° F. (cts.) of 7.61, a viscosity at 210° F. (cts.) of 2.70, and a viscosity index of 201. The untreated control (the ester) has a viscosity of 100° F. (cts.) of 5.24, a viscosity at 210° F. (cts.) of 1.83, and a viscosity index of 136.

Example V

The behavior of the polymer-modified esters of this invention under severe conditions of mechanical shear is demonstrated by the following experiments. A one-percent solution of an ethylene/vinyl acetate polymer having an ethylene/vinyl acetate mole ratio of 2.3:1 is prepared in di-(2-ethylhexyl)sebacate. This solution is circulated by means of a high-pressure centrifugal pump through a small orifice, where mechanical shearing stress occurs, and then through a cooling heat exchanger, a meter, and a reservoir before repassing through the pump to the orifice. With all mechanical variables of the system standardized, e. g., pressure, type of pump, circulation rate, number of cycles, temperature, size of orifice, etc., a convenient bench test is provided for predicting the viscosity stability in serv-

4

ice. At 5000 cycles the total loss in viscosity of the above di-(2-ethylhexyl)sebacate-ethylene/vinyl acetate polymer blend is only 7.1%. Under the same conditions, and at the same concentration, a blend of di(2-ethylhexyl)sebacate with a commercial viscosity index improver shows a 23% loss in viscosity after 5000 cycles.

The optimum proportions of the ethylene/vinyl acetate polymers to the ester will range from 1% to 10% by weight of the ester, but improved results can be obtained with amounts of the polymer ranging from 0.5% to 30% by weight of the ester.

Examples of suitable esters other than those mentioned in the examples are ethylenehexanoate, 2-propylheptyl-2,9-diethyl-4,7-dithiasebacate, 2-ethylhexylsebacate, 2,4-dimethyloctylbenzoate, 2,5-dibutyldecylterephthalate, 2-propylheptylethyladipate, octylsebacate, heptyl-2,9-dimethyl-4,7-dioxasebacate bis(3,5,5-trimethylhexyl)azelate bis(3,5,5-trimethyl-hexyl)glutarate, and the like.

The alcohols used in the synthesis of the esters may be branched or straight chain monohydric alcohols. Examples are heptanol-1, octanol-1, 2-ethylhexanol, 2-propyl-heptanol, 3,5,5-trimethylhexanol, 2-ethyl heptanol-1, 2,4-dimethyl octanol-1, dodecanol-1, tetradecanol-1 and 2,5-dibutyl decanol-1.

Examples of carboxylic acids which can be esterified by the above mentioned alcohols to obtain esters of the kind used in the practice of this invention are hexanoic, decanoic, dodecanoic, 2-methylpentanoic, 4-methyl decanoic, malonic, glutaric, adipic, azelaic, sebacic, methyl adipic, ethyl adipic, 2,9-dimethyl-4,7-dithiasebacic, 2,9-diethyl-4,7-dithiasebacic, 2,9-dimethyl-4,7-dioxasebacic, suberic, 3,8-dibutyl suberic, arachidic, hexahydroterephthalic terephthalic, o-phthalic, benzoic, naphthalene dicarboxylic, and octadecanedicarboxylic acid.

The ethylene/vinyl acetate polymers can be made by reacting ethylene with vinyl acetate at temperatures in the range of 100 to 400° C. and pressure in excess of 500 atms. as disclosed in U. S. Patent 2,200,429 or by reacting ethylene with vinyl acetate in an aqueous medium in the presence of a peroxy compound catalyst as disclosed in U. S. Patents 2,334,195, 2,388,178, 2,396,677 and 2,391,920. When the ethylene and vinyl acetate is thus reacted in contact with aqueous medium and polymerization catalyst both the minimum pressure and temperature can be considerably lower than in the case of the first mentioned patent. Thus, in accordance with Patent 2,396,677, the present ethylene/vinyl acetate polymers can be obtained at pressures in excess of 50 atmospheres at temperatures of 20° C. to 350° C. It is necessary in obtaining the improved lubricating oils described herein that the mole ratio of ethylene to vinyl acetate be within the range previously given.

The following is typical of the preparation of an ethylene/vinyl acetate polymer coming within the scope of our invention:

Ninety two hundredths lbs./hr. of ethylene and 1.25 lbs./hr. of vinyl acetate containing 300 P. P. M. benzoyl peroxide separately pressured to 1000 p. s. i., are mixed at this pressure, and then pressured to 2000 atms. At 2000 atms. pressure, 5.1 lbs./hr. of water is injected into the reaction stream. The mixture is passed through a tubular $\frac{1}{8}$ " I. D. stainless steel reactor which is surrounded by boiling water at 110° C. In a contact time of 8.8 minutes, at a conversion of

42% ethylene and 39.5% vinyl acetate, 0.88 lb. of ethylene/vinyl acetate polymer with a mole ratio of 2.5 is obtained. The product is steamed free of vinyl acetate monomer and then worked on a rubber mill at elevated temperature until essentially free of water.

The present invention makes possible the controlled production from readily available esters of lubricating oils having the desired properties of good lubricity and viscosity index characteristics and having high stability under conditions of operation in which they are subjected to severe mechanical shear. As a result of the unusual resistance of these polymers to physical degradation by mechanical shearing action lubricating compositions of which they are components undergo less change in viscosity characteristics during use than similar compositions containing certain commercial types of viscosity index improvers.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A composition of matter consisting essentially of an ethylene/vinyl acetate polymer and an ester which contains at least 10 carbon atoms and which is an ester of an aliphatic carboxylic acid and a primary aliphatic saturated monohydric alcohol, said polymer being completely soluble in said ester and having an ethylene:vinyl acetate mole ratio of from 1:1 to 6:1 and being contained in said composition in amount from 0.5% to 30% by weight of said ester, said polymer being that obtained by polymerizing a mixture of ethylene and vinyl acetate in excess of 50 atmospheres in contact with a polymerization catalyst.

2. A composition of matter consisting essentially of ethylene/vinyl acetate polymer and an ester which contains at least 10 carbon atoms and which is an ester of an aliphatic dicarboxylic acid containing from 5 to 12 carbon atoms with a saturated aliphatic primary monohydric alcohol containing from 8 to 12 carbon atoms, said polymer being completely soluble in said ester and having an ethylene:vinyl acetate mole ratio of from 1:1 to 6:1 and being contained in said com-

position in amount from 0.5% to 30% by weight of said ester, said polymer being that obtained by polymerizing a mixture of ethylene and vinyl acetate in excess of 50 atmospheres in contact with a polymerization catalyst.

3. The composition defined in claim 2 in which said alcohol is a branched chain alcohol wherein the branched chain is an alkyl radical containing from 1 to 6 carbon atoms.

4. The composition defined in claims 2 in which said acid is a sebacic acid and in which said alcohol is a branched chain alcohol containing at least one side chain alkyl radical of from 1 to 6 carbon atoms.

5. The composition defined in claim 1 in which said polymer is contained in said composition in amount of from 1% to 10% by weight of said ester.

6. The composition defined in claim 2 in which said polymer is contained in said composition in amount of from 1% to 10% by weight of said ester.

7. The composition defined in claim 3 in which said polymer is contained in said composition in amount of from 1% to 10% by weight of said ester.

8. The composition defined in claim 4 in which said polymer is contained in said composition in amount of from 1% to 10% by weight of said ester.

9. The composition defined in claim 5 in which said polymer is contained in said composition in amount of from 1% to 10% by weight of said ester.

10. The composition defined in claim 2 in which said ester is an ester of a dithiicarboxylic acid.

DONALD D. COFFMAN.
JOHN F. LONTZ.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,091,627	Bruson	Aug. 31, 1937
2,104,408	Wiezevich	Jan. 4, 1938
2,200,429	Perrin	May 14, 1940
2,327,705	Frollich	Aug. 24, 1943
2,417,281	Wasson	Mar. 11, 1947