Patented Mar. 9, 1954 2,671,760

UNITED STATES PATENT OFFICE

2,671,760

LUBRICATING OIL COMPOSITIONS

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No Drawing. Application May 18, 1951, Serial No. 227,096

3 Claims. (Cl. 252—56)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to us of any royalty thereon.

This invention relates to lubricating compositions and particularly to the improvement of lubricating oil compositions by the incorporation therein of copolymeric additives which improve their viscosity index.

In recent years, because of increased use of complex machines operating through wide temperature ranges, necessity has arisen for the ready availability of lubricating oils having improved viscosity-temperature characteristics. The ideal lubricant, of course, would show little or no viscosity change with temperature. Various attempts have been made to impart improved viscosity-temperature characteristics to lubricating oils. The improvement in viscosity index which can be obtained from increased refining and from mixing of petroleum stocks is limited and, therefore, other methods must be used. It is accordingly an object of this invention to provide improvements in the viscosity properties of lubricating oils and lubricating oil compositions.

The viscosity of a high polymer solution depends on the size of the polymer, the extent of the intra- and intermolecular interaction of the polymer molecules, the extent of the interaction between the polymer molecules and the solvent, the concentration of the polymer and the nature of the solvent. In general, a polymer having a high degree of polymerization, because its higher molecular volume acts to impede the liquid flow, gives a solution of higher viscosity than does a low molecular weight polymer. If the intramolecular forces are high and the degree of solvation is low (i. e. a "poor" solvent), the internal attracting forces will cause the polymer molecules to curl up in compact form decreasing the effective volume and surface area of contact, giving solutions of low viscosity.

In polymer solutions where the intra- and intermolecular forces are low, and the solvation forces are high (i. e. a "good" solvent), each polymer molecule is sheathed by solvent molecules and tends to uncurl into long chains increasing the effective volume and the surface area of contact, giving solutions of higher viscosity than in a "poor" solvent.

According to the invention, a lubricating oil composition having an improved viscosity index may be obtained by incorporating in the lubricating oil a linear heteropolymer, particularly a

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copolymer, prepared by the copolymerization of two or more monomers. We have discovered that it is possible to prepare copolymers having gradually changing solubility in any given lubricating oil by merely controlling the relative proportions of each of the monomers introduced into the polymer chain and that such copolymers are desirable additives for lubricating oils. The monomers used in preparing the heteropolymer are chosen in such a manner that one of them gives a homopolymer having high solubility in lubricating oils whereas the other gives a homopolymer having substantially no solubility in lubricating oils. An example of suitable monomers are vinyl palmitate which gives a homopolymer quite soluble in lubricating oils and vinyl acetate which gives a homopolymer quite insoluble in lubricating oils. Monomers which give polymers having considerable solubility in lubricating oils may be chosen from the group of vinyl esters and ethers having from about 8 to 22 carbon atoms per molecule. Monomers which give polymers having substantially no solubility in lubricating oils may be chosen from the group of vinyl esters and ethers having less than 6 carbon atoms per molecule. Other monomers suitable for use in accordance with our invention will be obvious.

We have found that when a vinyl ester of a fatty acid such as vinyl palmitate is copolymerized with vinyl acetate a product results which has unusual value for improving the viscosity index of an oil to which it is added. By varying the proportions of each of the monomers used in preparation of the copolymer to be added, it is possible to control the solubility of the polymer in the base oil to a considerable degree. Copolymers having molecular weights in the range of about 5,000 to 100,000 are most valuable for this purpose. This invention makes it possible to provide an effective additive for lubricants substantially regardless of the solvent powers of the base stock. Hitherto only two methods were available for improving the viscosity index of lubricating oils to a significant degree. These were, first, the use of polymers having a very high degree of polymerization and, second, addition to the oil of insolubilizing agents which render the additive less soluble. The first of these methods is limited by several factors, of which an important one is the tendency of high molecular weight additives to shear and break down under stress. The second of these methods, the addition of insolubilizing agents is expensive and difficult to control and therefore has not been used generally.

The following examples are illustrative of the nature of our invention, but our invention is not restricted to these examples.

Example 1.—Polyvinyl palmitate

A solution of 141.2 g. of vinyl palmitate and 0.605 g. of benzoyl peroxide in 97.5 g. of benzene was heated in a nitrogen atmosphere for 6.5 hours at 75° C. The solution was then diluted with 500 ml. of benzene and poured into 3 l. of acetone to precipitate the polymer. A 58% conversion was obtained.

Example 2.—Polyvinyl acetate : palmitate

A solution of 105 g. of vinyl palmitate, 95 g. of vinyl acetate and 1.78 g. of benzoyl peroxide in 288 g. of benzene was heated in a nitrogen atmosphere for 7 hours at 70–73° C. The resulting solution was poured into 2.6 l. of methanol to precipitate the copolymer. The yield of copolymer after a total of three precipitations was 66%. The copolymer contained about 75 mole percent of vinyl acetate.

Example 3.—Polyvinyl acetate : palmitate

A copolymer containing approximately 50 mole percent of vinyl acetate was prepared by heating a solution of 153.2 g. of vinyl palmitate, 46.8 g. of vinyl acetate and 1.31 g. of benzoyl peroxide in 210 g. of benzene, as described in Example 2. The yield of copolymer after purification was 59%.

Example 4—Polyvinyl acetate : palmitate

A copolymer containing approximately 25 mole percent of vinyl acetate was prepared by heating a solution of 181.4 g. of vinyl palmitate, 18.6 g. of vinyl acetate and 1.04 g. of benzoyl peroxide in 168 g. of benzene, as described in Example 2. The yield of copolymer after purification was 60%.

Example 5.—Polyvinyl acetate : palmitate : oleate

The procedure of Example 4 was repeated except that 27.2 g. of vinyl acetate, 16.7 g. of vinyl palmitate, 6.1 g. of vinyl oleate, 77.0 g. of benzene and 0.48 g. of benzoyl peroxide were employed, and the precipitating solvent was methanol.

Five percent solutions in each of two lubricating oils were prepared from the copolymers described in the previous examples. The following table shows the viscosity index of the resulting solutions and that of the test oils.

Polymer	Viscosity Index * of Treated and Untreated Lubricating Oils	
	A	B
None	90.2	79.1
From Example 1 (homopolymer)	123.7	98.5
From Example 4	130.6	106.6
From Example 3	132.5	104.7
From Example 2	136.5	

* Calculated from tables of Dean and Davis [Chem. & Met. Eng 36, #10, 618 (1929)].

It is evident that the improvement in viscosity index obtained by copolymers is significantly greater than that obtained by addition of a homopolymer (from Example 1). It is also obvious that the copolymer from Examples 2 and 3 tends to be superior to that from Example 4 for oil A whereas the copolymer from Example 4 would be preferred over that of Example 3 for addition to oil B.

Although the examples given above describe the copolymerization of the mixed monomers in benzene solution using benzoyl peroxide as a catalyst, we have found that equally valuable products can be prepared by bulk, emulsion, reductive-activation or dispersion polymerization techniques. Other solvents and chain transfer agents may also be employed and other peroxide or free radical type catalysts may be used.

The copolymerization temperature may be varied over wide limits. Temperatures much in excess of 75° C. often cause the copolymerizations to proceed too rapidly for effective control. The preferred operative temperatures are in the range of about 20 to 85° C.

The isolation of the copolymer can be effected in a variety of known ways depending mainly on the copolymerization technique employed. When solution polymerization is employed, the polymer may be isolated, if desired, by evaporation and recovery of solvent; alternatively, the copolymerization solution may be added directly to the petroleum base stock followed by removal of residual solvent in the usual ways.

We have found that the copolymers which are valuable for additives to lubricating oils may be prepared from monomer mixtures containing up to about 50 mol percent of the insolubilizing monomer. Below about 5 mol percent of the insolubilizing monomer we have not observed the desired effect on viscosity index. We prefer to employ copolymers prepared from mixed monomers containing between 25 mol percent and 50 mol percent of the insolubilizing monomer.

We have found that the operable range of copolymer concentration in the lubricating oil is somewhat dependent upon the solvent power of the petroleum base stock as well as upon the specific composition of the copolymer being used. We prefer to add the copolymers in amounts varying from about 1% to about 10% of the base stock.

We claim:

1. A lubricating oil composition having an improved viscosity index comprising a lubricating oil having incorporated therein a linear heteropolymer having a molecular weight of about from 5,000 to 100,000 and having been prepared by polymerizing a mixture containing, as polymerizable components, monomeric vinyl acetate and monomeric vinyl palmitate.

2. A lubricating oil composition having an improved viscosity index comprising a lubricating oil having incorporated therein a linear copolymer of vinyl acetate and vinyl palmitate having a molecular weight of about from 5,000 to 100,000.

3. A lubricating oil composition having an improved viscosity index comprising a lubricating oil having incorporated therein a linear heteropolymer of vinyl acetate, vinyl palmitate, and vinyl oleate having a molecular weight of about from 5,000 to 100,000.

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