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FRICTION REDUCTION BY POLY(n-ALKYL METHACRYLATES) IN SOLUTION AND DRY FILMS

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2 Claims

ABSTRACT OF THE DISCLOSURE

A poly(n-alkyl methacrylate) wherein the alkyl group contains 22 carbon atoms which reduces the friction of solid surfaces when applied in solution or as a dry film.

Reference is hereby made to patent application, Ser. No. 642,673, of Henry Gisser and Marco Petronio, for "Friction Reduction by Copolymer of N-alkyl Methacrylates and Methacrylic Acid in Solution," filed May 25, 1967, assigned to the same assignee of this patent application.

This invention relates to lubricants, and more particularly relates to methacrylate polymers for reducing the friction properties of sliding surfaces when subjected to the lubricants.

The use of polymers as oil additives has been practiced for many years, but only recently has attention been given to the relationship of the polymer to the lubrication process. Early observations indicated that polymer containing motor oils reduced engine friction, i.e., lower engine friction was obtained with polymer containing oils than non-polymer containing oils of the same viscosity. This was attributed to the reduction of viscosity of polymer containing fluids at high shear rates which prevails during engine operation. The temporary reduction of viscosity of polymer solutions under high shear is well known. These early observations on reduced engine friction with polymer containing oils were confirmed when it was determined that the polymer containing oils also had a minimum in the friction-viscosity curve. The polymer containing oils also yielded less engine wear at viscosities below those corresponding to minimum friction and above these viscosities wear remained low. These observations are consistent with the classical lubrication picture in which the minimum corresponded to transition between mixed boundary and fluid film lubrication. In several instances, polymers have also been employed as dispersants in lubricating oils.

Therefore, up to the time of the instant invention, the action of polymers in friction reduction compounds has been limited to that of oil additives primarily for increasing solubility or effecting viscosity. It has been discovered, however, through a study of the friction behavior of polymer solutions in the boundary region in which surface phenomena have been isolated from volume phenomena, that polymer molecules themselves are capable of enhancing the friction properties on a solid surface. The friction behavior of polymeric compounds in the boundary region is dependent upon the interactions of the polymer with the solid surface and hence, as would be expected, is a function of the chemical structure of the polymer molecule and its conformation on the surface. This invention therefore is indicative of the strong influence of the chemical structure of polymers on friction and wear behavior.

In the past, considerable work has been done on the friction behavior of low molecular weight organic compounds in solution and in the dry state on solid surfaces, nevertheless, little work has been done with polymer solutions. The low molecular weight organic compounds al-

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though instantaneously successful in increasing the friction reduction properties of surfaces have proved extremely unsuccessful in retaining this beneficial effect for any significant period of time. This failure of an essential lubrication property is due to the inherently poor wear resistant film formed on the surface.

It is an object of this invention to provide a new friction reducing compound.

Another object of this invention is to provide polymeric friction reducing compounds.

A further object of our invention is to provide a friction reducing composition having good wear resistant properties.

In accordance with the present invention, it was found that the poly(n-alkyl methacrylate)s when the alkyl consists of a carbon chain having 1 to 22 carbon atoms, and preferably 14 to 22 carbon atoms, significantly reduces the friction on a solid surface when used either in solution or as films deposited by evaporation of solvent. The polymers were prepared thru emulsion polymerization, although various polymerization techniques can be used. The molecular weights of the various polymers are given in Table I.

TABLE I.—MOLECULAR WEIGHTS OF POLY(n-ALKYL METHACRYLATES)

	MW ¹ ×10 ⁻⁵	Relative Polymer chain length ²
Alkyl:		
Methyl.....	7.6	1.00
Ethyl.....	19.0	2.2
Butyl.....	4.3	0.43
Octyl.....	2.2	0.15
Lauryl.....	1.4	0.072
Octadecyl.....	1.9	0.073
Docosyl.....	15.9	0.53

¹ Determined by membrane osmometry.

² Relative to poly (methyl methacrylate).

Coefficient of friction was determined on a modified Bowden-Leben machine in which the tangential force was detected by strain gages mounted on a strain ring, the signals being amplified and recorded. All friction measurements were made with a ¼ in. diameter 440C stainless steel ball rider on an approximately 6 mm. thick plane substrate. Steel, copper, and glass substrates were employed for the measurements. The steel substrate was 1020 steel plate prepared by rinsing in boiling benzene, polishing successively with 400, 600, 2/0, 3/0, and 4/0 silicon carbide paper and rinsing in boiling benzene. It was then placed in a desiccator over anhydrous calcium sulphate for 24 hours before use. The copper substrate (99.98% Cu) was prepared in the same manner as the steel. The glass specimens were cut from 6 mm. thick polished plate, silvering quality soda lime glass, abraded under water successively with 400 and 600 silicon carbide paper followed by rinsing with hot distilled water. These specimens also were stored over anhydrous calcium sulphate for 24 hours before use. All measurements were made at a 100 gram load and 0.04 cm./sec. sliding speed. The length of traverse was 1.3 to 1.9 cm. for each measurement. Polymer solutions were made with benzene and xylene of spectrographic grade, although various petroleum hydrocarbon fluids can be employed. Three drops of polymer solution were placed in a continuous line along the path to be traversed by the rider, the first drop being placed at a location so that it wet the rider. The area covered by the fluid was approximately 0.9 square centimeters. Friction measurements were started 5 to 10 seconds after applying the polymer solutions. Unless otherwise indicated all measurements were made at a polymer concentration of 1.0 mg./ml. The standard deviation of the coefficient of friction measurement was 0.005.

All the polymers yielded considerable reduction in friction from the solvent alone. However, as the side chain

increased in length, there was a progressive reduction in the coefficient of friction. There are minor differences in behavior with the different substrates. For example, with 1020 steel, there was first a rapid reduction from the initial value which then reached a minimum in the neighborhood of 16 carbon atoms. With copper the total reduction of coefficient of friction from the methyl to the docosyl was small but significant, whereas with glass there was a uniform reduction with increasing length of the side chain. While these individual differences are probably associated with differences in intersection of the polymer with the particular substrate, the similar behavior on all substrates indicates that the general conformation of the polymers on the substrates is approximately the same insofar as friction is affected. However, whatever the particular conformation, the length of the alkyl group is a significant factor in reducing the coefficient of friction on the surface.

It should be noted that the concentration of the polymer in xylene, benzene or other solvents may vary from 0.01 to 10.0 mg./ml. without any significant effect on the coefficient of friction.

Table II gives the data for sliding the 440C stainless steel rider on the substrates with a xylene solution of the polymer. The data reported are the kinetic coefficients of friction. The coefficients of friction for the dry glass, copper and steel were 0.85, 0.39, and 0.36, respectively.

TABLE II.—COEFFICIENT OF FRICTION (μ) WITH 0.1% SOLUTION OF POLY (n-ALKYL METHACRYLATES) IN XYLENE USING A STAINLESS STEEL RIDER

	μ on Steel	μ on Copper	μ on Glass
Alkyl:			
C ₁ -----	0.215	0.257	0.232
C ₂ -----	0.200	0.250	0.225
C ₄ -----	0.190	0.250	0.217
C ₈ -----	0.179	0.244	0.202
C ₁₂ -----	0.170	0.235	0.187
C ₁₆ -----	0.150	0.230	0.156
C ₂₂ -----	0.150	0.243	0.141

As stated previously, the relationship of the polymer to friction and wear phenomena is also dependent on the interaction of the polymer with the solid surface. This interaction is primarily an adsorption phenomenon. The polymer conformation on the surface is best described by stating that most, but not all, of the carbon chain or vinyl backbone of the polymer lies fairly close and substantially parallel to the solid surface secured thereto by adsorption of the polar groups; i.e. the ester moiety, in the side chains. The alkyl groups of the side chain are oriented normal to the surface, and this orientation to the surface taken together with close packing in condensed layers, leads to a "film" which effectively prevents "metal-on-metal" contact, and thus leads to friction reduction. The remainder of the polymer carbon chain form loops oriented away from the surface and extending into the solution.

Further tests were conducted to determine whether the structural features which led to friction reduction with polymer solutions gave the same effect with dry films. Accordingly, friction measurements were made on glass and copper substrates with films deposited from 1.0 mg./ml. solutions of the poly(n-alkyl methacrylate)s in xylene. Substrate surfaces with several drops of solution were permitted to remain in air for several hours until excess solvent had evaporated, then placed in a desiccator over anhydrous calcium sulphate for 24 hours before measurement. The calculated thickness of the dry films was approximately 3500 Å. whereas the estimated thickness of the films adsorbed from solution in the presence of sol-

vents was approximately 300 Å. However, it has been determined from previous studies of friction measurements on solutions of varying concentration, that the film thickness probably does not effect the friction level in the neighborhood of several hundred angstroms and above.

TABLE III.—COEFFICIENT OF FRICTION (μ) OF DRY FILMS OF POLY (n-ALKYL METHACRYLATE)S WHILE SLIDING A STAINLESS STEEL RIDER ON COPPER AND ON GLASS

	μ on Copper	μ on Glass
Alkyl:		
C ₁ -----	0.252	0.309
C ₂ -----	0.230	0.249
C ₄ -----	0.158	0.232
C ₈ -----	0.142	0.156
C ₁₂ -----	0.165	0.125
C ₁₆ -----	0.142	0.130
C ₂₂ -----	0.136	0.110

The anti-wear properties of polyoctadecyl methacrylate were shown in the following experiment: 1% solution of the polymer was prepared in a petroleum hydrocarbon fluid, naphthenic base (viscosity of 20 centistokes at 37.5°C). Wear scar measurements in a four-ball apparatus obtained with these solutions were considerably lower (0.240 millimeter average) than corresponding wear scar diameters for the petroleum fluid having no polymer additives (0.334 millimeter average).

While the particular compositions and methods of application described herein are well adapted to meet the objects of the present invention, various modifications or changes may be resorted to without departing from the scope of the invention as defined in the claims.

We claim:

1. A method of applying a dry friction reducing film for a solid surface which comprise the steps of

(a) applying a 1.0 mg. per ml. solution of poly(n-alkyl methacrylate) in a solvent selected from the group consisting of xylene and benzene on to said solid surfaces wherein the alkyl group of said poly(n-alkyl methacrylate) has 22 carbon atoms, and a molecular weight about 1,590,000,

(b) allowing the filmed surface to remain in air until excess solvent has been evaporated therefrom, and

(c) placing the evaporated filmed surface in a moisture-free atmosphere prior to use.

2. A polymeric friction reducing composition consisting essentially of 0.1–10 mg. of poly(n-alkyl methacrylate) per ml. of a solvent, said solvent being selected from the group consisting of benzene and xylene, said poly(n-alkyl methacrylate) having a molecular weight about 1,590,000 and wherein the alkyl group of said poly(n-alkyl methacrylate) has 22 carbon atoms.

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