Rubber Swell as a Function of Fatty Acid Ester Chain Length[1]

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ABSTRACT

A study was made of the relationship between the structure of some fatty acid esters of varying chain length and their swelling effect on standard nitrile rubber samples. The esters evaluated were: methyl esters of caprylic, capric, lauric, myristic, palmitic and isostearic acids; *n*-butyl, isobutyl, *n*-octyl, octadecyl, "tallow" and 2,2-dimethyl-1,3-propanediol esters of lauric acid and tetradecyl acetate. Federal test methods for aircraft turbine lubricants were used for the evaluations. In the esters the swelling was higher with type L rubber than with type H. The lower the equivalent weight of the ester, the higher the swell with both types of rubber. Branching in the alcohol moiety lowered the swell. Deswelling (desorption) in air of the swelled samples was also investigated. Methyl myristate, methyl palmitate and the long chain laurate esters meet MIL-L-23699 military specifications for type H rubbers. In type L rubbers the swelling is too high to meet specifications.

INTRODUCTION

The problem of elastomer compatability with fluid systems is an ever-continuing one, and the importance of rubber swell is predominant in a number of areas. To cite one example, modern methods of transportation as represented by the automobile rely on the efficiency of rubber seals in automatic transmissions, power steering and hydraulic brake systems.

The degree of rubber swell is dependent upon several properties of fluids, and some generalizations have been made with regard to this. The similarity between the structures of the liquid and the rubber is an important factor (1-3). If both liquid and rubber have polar groups (or both have nonpolar groups) as important parts of their structures, swelling is likely to be high. If one is polar and the other is nonpolar, then swelling is likely to be low (4-6). The viscosity of the liquid is less important than its polarity, although the rate of penetration into the rubber decreases as the viscosity of the swelling liquid increases (7).

Changes in molecular structure in specific compound classes have an effect on the swelling power of liquids (6,8). For example, it has been shown with nitrile rubbers that branching in the alkyl chain of alkyl halides lowers the swelling power of these liquids. On the other hand, unsaturation or the presence of cyclic structures, or both, in ketones and alkanes increases their swelling power. The nature or position of the functional group in the molecule appears to be of little importance, since the carboxyl group produces a similar degree of swelling in nitrile rubbers, as do Br, Cl, CO, CN and NO_2. The presence of a hydroxyl group in a molecule surprisingly causes little swelling, and alcohols cause as little swelling as alkanes or less. In the latter instance, internal hydrogen bonding in the liquid is apparently stronger than hydroxyl-nitrile interaction (6).

Synthetic esters, which are commonly used in turbine, transmission and hydraulic fluids, typically have fairly high molecular weights, but their equivalent weights are often quite low. These fluids are known to swell several common elastomers severely, and perhaps for this reason esters in general have been accused of causing excessive rubber swell. The volatility of low molecular weight monoesters makes them unsuitable for use in functional fluids, and higher monoesters which have suitable volatilities are usually solids at operational temperatures.

TABLE I

Test Data for Esters

	Per cent rubber swell		Kinematic viscosity, centistokes				Wear scar diameter, mm
Ester	Type H	Type L	78 F	100 F	130 F	210 F	
Methyl caprylate	83.8	132.5	1.45	1.19	0.96	0.61	0.843
Methyl caprate	57.9	114.7	2.25	1.81	1.39	0.84	0.578
Methyl laurate	37.0	90.8	3.37	2.64	1.93	1.14	0.663
Methyl myristate	24.4	64.1	4.56	3.43	2.52	1.35	0.698
Methyl palmitate	17.8	55.4	← Solid →				0.587
Methyl isostearate	17.9	51.2	7.57	5.60	3.86	1.84	0.547
Bis-(2-ethylhexyl) sebacate	---	53.5	20.0	12.8	8.08	3.37	0.830
100 Paraffin oil[a]	---	26.4	93.9	46.3	22.06	5.94	0.803
n-Butyl laurate	17.4	53.7	4.54	3.52	3.08	1.40	0.642
Isobutyl laurate	16.2	49.6	4.61	3.69	2.59	1.40	0.725
Neopentyl laurate	11.7	39.8	6.00	4.53	3.21	1.64	0.595
2-Ethylhexyl laurate	9.1	30.4	7.57	5.40	3.74	1.84	0.587
n-Octyl laurate	11.1	35.8	8.18	5.84	4.09	2.02	0.827
Octadecyl laurate	0.15	8.1	Solid	Solid	10.61	4.39	0.465
"Tallow" laurate	2.07	16.4	---	---	---	---	0.487
2,2-Dimethyl-1,3-propanediol dilaurate	5.20	27.5	24.32	16.06	9.86	3.97	0.597
Tetradecyl acetate	17.6	60.9	5.63	4.27	3.04	1.56	0.880

[a] Refined Pennsylvania Oil with a viscosity of 100 Saybolt seconds at 100 F. MIL-L-23699 Specifications—% swell (10% minimum-25% maximum), viscosity centistokes at 210 F, 5.0 minimum-5.5 maximum, at 100 F 25 min.

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It occurred to us some time ago that the rubber swelling tendency of esters may be related not so much to the ester group itself as to the concentration of that functional group in the molecule, i.e., the equivalent weight of the ester. Boehringer and Trites (9) recently synthesized a series of liquid esters having equivalent weights in excess of 500. These gave low swell with type L rubber. The present paper attempts to provide more information regarding the relationship of the structure and molecular weight of monoesters and their swelling effect on synthetic rubber.

EXPERIMENTAL PROCEDURES

Materials

The standard rubber samples were obtained from the Naval Air Development Center, Department of the Navy, Warminster, Pa. The formulations used in their fabrication are given in U.S. Air Force Specification Bulletin no. 539 (10).

All of the esters used, with the exception of methyl isostearate and "tallow" laurate, had purities, as estimated by GLC, of 98% or greater. Methyl caprylate, methyl caprate and methyl myristate were purchased as the best laboratory grade available, redistilled or fractionated, or both, to yield material of suitable quality. All of the other esters were synthesized in this laboratory by conventional esterification techniques. For the methyl isostearate preparation, a sample of Emery 875 isostearic acid obtained from Emery Industries was used. The tallow alcohols used in the tallow laurate preparation were a sample of Adol 42 from Ashland Chemical Co. These Alcohols, according to the supplier's literature, are a mixture of cetyl and oleyl alcohols and have the following specifications: IV 45-55, OH value 211-221 and cloud point 30-36 C.

Testing Methods

Kinematic viscosities were measured according to ASTM D-445-65 using Cannon-Manning semimicro viscometer tubes. For determining the wear scar diameters of the esters, the Precision-Shell four-ball wear test was used. The samples were tested at 120 C under 50 kg load for 1 hr as described by Peale et al. (11). The rotation of the upper ball was 600 rpm.

Rubber swelling was determined by Federal Test Method Standard No. 791a with some modifications.

RESULTS AND DISCUSSION

Preliminary tests showed that half-size rubber samples could be used without loss of accuracy or precision. We therefore used 1 x 1 in. samples in all of the tests, maintaining the ratio of ester to rubber specified in the test procedure. Previous studies on rubber sample size showed that only a variation in sample thickness altered the results.

The test data for the methyl esters used in the study are given in Table I.

Included, for comparison, are similar data for bis-(2-ethylhexyl) sebacate (DOS) and 100 Paraffin Oil. For type H rubber, the amount of swell decreased with increase in the chain length of the ester. The concentration of the polar group within the ester decreased with increase in chain length and consequently had less effect on the high nitrile content rubber. The per cent swell for type H rubber in methyl myristate, methyl palmitate and methyl isostearate was low enough to meet military specifications as set forth in MIL-L-23699 (10% minimum and 25% maximum).

For the low nitrile (Type L) rubber, the rubber swell was again an inverse function of chain length. Notably, the amount of swell for each ester was relatively high in comparison to the high nitrile rubber. The extent of swelling with type L for all esters was too high to meet MIL-L-23699 specifications. The same minimum and maximum amounts of swell that applied to type H apply also to type L. These results indicate that these esters resemble type L rubber more nearly with respect to polarity than they do type H.

Also listed in Table I are the viscosity and wear scar data for the methyl esters. The rates of swelling and deswelling of the rubber samples depend upon the viscosity of the swelling medium and not upon the structure of the medium. The viscosities of the esters were also determined after the rubber swell tests. The viscosities changed very little and this shows that the esters were stable in the presence of the rubber samples at the test temperature (158 F). It also indicates that little if any material was extracted from the rubber.

The wear scar diameters indicate suitable antiwear properties for the esters and suggests that some of them may be used in making blends in order to obtain proper swelling characteristics for meeting specifications.

Deswelling of the samples was also investigated. The volume of the swelled samples was redetermined after exposure to air. The samples were allowed to stand at room temperature in air to determine how long it would take for the absorbed ester to separate from the rubber. The amount of deswelling per unit time indicates the rate of penetration of an ester into the rubber during the swelling process, and the rates of swelling and deswelling are dependent upon the viscosity. It was found that the rate of deswelling was faster for the short chain esters than for the long chain esters. This suggests that the vapor pressure of the ester may have an effect on the rate of deswelling. The volumes of some rubber samples were smaller after deswelling that they were originally. This was so with methyl caprylate and indicates that this ester dissolved or extracted a portion of the rubber.

Table I contains the test data for the lauric acid esters. Also included in the table are the data for the diester 2,2-dimethyl-1,3-propanediol dilaurate and tetradecyl acetate. Examining the type H rubber swell results, two trends can be observed. First, as noted earlier, rubber swell decreased with increase in equivalent weight of the ester. Second, in the same equivalent weight range, branching in the alcohol moiety of the ester decreased the amount of swell. It is noteworthy that the amount of swell for type H rubber in *n*-butyl laurate and tetradecyl acetate (same equivalent weights) is almost identical. The amount of swell in the C_4 and C_8 alcohol laurates was within the limits of the specifications in MIL-L-23699.

When type L rubber was tested with the laurate esters, as expected, rubber swell was high. The amount of swell decreased with increase in chain length of the alcohol portion of the ester, i.e., with increasing equivalent weight. Again, isobutyl laurate and 2-ethylhexyl laurate induced a smaller amount of swell in the rubber than their straight chain isomers. In all but two instances the per cent swell exceeded MIL-L-23699 specifications, and only one of these had sufficient swell to meet specifications. Octadecyl laurate almost makes the lower limit for acceptable swell. The wear scar data for this ester is indicative of good antiwear properties. It is conceivable that blending this ester with one having high swell would provide a combination which meets specifications and a product with good lubricant potential would result. Tallow laurate seems to have these properties without any additional blending. The rate of deswelling for a swelled sample of type L rubber that was exposed to tallow laurate is also unusual. After exposure to air at room temperature for 720 hr, the swelled sample still retained 11.7% swell.

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