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Description

Internal combustion engines operate under a wide range of temperatures including low temperature stop-and-go service, as well as high temperature conditions produced by continuous high speed driving. Sludges or insolubles are produced under some operating conditions and dispersants are added to the lubricating oil so that potentially insoluble materials remain dispersed in the oil.

It is known to employ nitrogen containing dispersants and/or detergents in the formulation of crankcase lubricating oil compositions. Many of the known dispersant/detergent compounds are based on the reaction of an alkenylsuccinic acid or anhydride with an amine or polyamine to produce an alkylsuccinimide or an alkenylsuccinamic acid as determined by selected conditions of reaction.

It is also known to chlorinate alkenylsuccinic acid or anhydride prior to the reaction with an amine or polyamine in order to produce a reaction product in which a portion of the amine or polyamine is attached directly to the alkenyl radical of the alkenyl succinic acid or anhydride. The thrust of many of these processes is to produce a product having a relatively high level of nitrogen in order to provide improved dispersancy in a crankcase lubricating oil composition.

A serious problem facing the lubricant manufacturer is that of seal deterioration in the engine. All internal combustion engines use elastomer seals, such as nitrile-rubber or fluorocarbon-rubber seals, in their assembly. Over time, these seals are susceptible to serious deterioration caused by the lubricating oil composition. A lubricating oil composition that degrades the elastomer seals in an engine is unacceptable to engine manufacturers and has limited value.

It is an object of this invention to provide a lubricating oil composition which does not degrade nitrile elastomer seals in internal combustion engines.

U S Patent No. 4,304,678 discloses a lubricating oil composition containing a friction modifier from the class of glycerol esters. The use of esters of glycerol and a fatty acid as an additive in lubricating oil compositions is also described in, e.g. EP-A-0,305,538 and US-A-4,304,678.

The present invention relates to the use of an ester of glycerol and an unsaturated fatty acid having from 8 to 45 carbon atoms in an oil of lubricating viscosity in order to provide nitrile elastomer seal compatibility properties.

The ester which imparts the seal compatibility properties may be a mono-, di- or triester of glycerol and may be prepared from a simple unsaturated fatty acid or a mixture of unsaturated fatty acids. In general, the fatty acid will contain from about 8 to 45 carbon atoms, preferably 12 to 30 carbon atoms. These fatty acids may be represented by the formula R-COOH in which R is an unsaturated aliphatic radical having from 7 to 44 carbon atoms.

The preferred unsaturated fatty acids have from 12 to 30 carbon atoms. Typical unsaturated fatty acids which are suitable include the following: oleic, linoleic, hexadecenoic and linolenic.

The ester additive of the invention is made by either reacting glycerol with one or more of the prescribed fatty acids or by reacting natural triglyceride oils with water or glycerol according to known methods. The ester additive may be a monoester, diester or triester or a mixture of mono-, di- and triesters. In general, it is preferable to have a high proportion of monoesters in the ester additive.

Typical glycerol esters of unsaturated fatty acids which are suitable are illustrated by the following: glyceryl monooleate; glyceryl dioleate; glyceryl trioleate; glyceryl monolinoleate; glyceryl dilinoleate and glyceryl trilinoleate and glyceryl ricinoleate.

The lubricating oils contemplated for use with the esters herein disclosed include both mineral and synthetic hydrocarbon oils of lubricating viscosity and mixtures thereof with other synthetic oils. The synthetic hydrocarbon oils include long chain alkanes, such as cetanes, and olefin polymers, such as trimers and tetramers of octene and decene. The synthetic oils, which can be used as the sole lubricating oil, or which can be mixed with the mineral or synthetic hydrocarbon oil include (1) fully esterified ester oils, with no free hydroxyls, such as pentaerythritol esters of monocarboxylic acids having 2 to 20 carbon atoms, (2) polyacetals and (3) siloxane fluids. Especially useful among the synthetic esters are those made from polycarboxylic acids and monohydric alcohols. More preferred are the ester fluids made from pentaerythritol, or mixtures thereof with di- and tripentaerythritol, and an aliphatic monocarboxylic acid containing from 1 to 20 carbon atoms, or mixtures of such acids.

An effective amount of ester in the lubricant for nitrile seal compatibility is an amount ranging from about 0.01 to 3.0 weight percent based on the weight of the oil composition. A preferred concentration is from 0.1 to 0.75 weight percent.

Seal Compatibility Tests

An important property of a lubricating oil additive and blended lubricating oil compositions containing the additive is the compatibility of the oil composition with the rubber seals employed in the engine. Some of the nitrogen containing succinimide dispersants and other additives such as active sulfur compounds employed in crankcase lubricating oil compositions may have the effect of seriously degrading the elastomer seals in internal combustion engines. In particular, such additives are known to attack rubber seals, such as nitrile rubber and fluorocarbon rubber seals which are commonly employed in internal combustion engines. This deterioration exhibits itself by sharply degrading the flexibility of the seals and in increasing their hardness. This is such a critical problem that a number of automotive engine builders require that all crankcase lubricating oils pass a seal compatibility test before the oil composition will be rated acceptable for engine crankcase service. The seal compatibility tests used for nitrile rubbers are described below and are designed to determine the seal compatibility properties of a crankcase lubricating oil composition.

The test method for the Mercedes-Benz Seal Compatibility Test is based on the VDA 521-01 test procedure.

The seal compatibility test is conducted by soaking samples of the elastomer-rubber in the oil under investigation at an elevated temperature and then measuring the effect of the oil composition on the rubber sample for volume change, elongation change, hardness change and tensile strength change.

The specimens are weighed in air and in water to the nearest mg. After weighing in water, each specimen is dried on clean filter paper. The elongation and tensile strength of three of the specimens are measured.

The hardness of the specimens is determined with a durometer. The specimens conform to the standard S2 definition.

Six specimens are suspended in a beaker by inserting a piece of nichrome wire through the small hole in the end of each specimen. The specimens are arranged so that they do not touch each other or the beaker. The test oil is added in a ratio of 1:80 of elastomer to oil in the beaker. The elastomer specimens in the beaker are aged for 168 hours in an oven maintained at 100°C.

At the end of the test period, the beakers are removed from the oven and the specimens are removed from the beaker and cleaned with absorbent paper. Elongation and tensile strength measurements are made on each aged specimen. Each specimen is weighed in air and in water and measured for hardness.

Further details of seal compatibility test methods or nitrile elastomers required by Mercedes-Benz, CCMC and MAN are illustrated in the tables that follow.

Mercedes-Benz

Specification:	DBL 6606/6612/6615
Test Procedure:	VDA 521-01
Elastomer:	SRE NBR-34
Compound:	Nitrile
Test Temperature:	100°C
Test Duration:	168 hours
Vessel:	600 ml beaker w/cover
S2 Specimens:	3 used for rupture properties 3 used for volume/hardness properties
Limits:	SRE NBR-34
%Δ in Rupture Strength:	Max -20
%Δ in Max Elongation:	Max -35
%Δ in Volume:	0 to +10
Δ in Hardness, Shore A:	0 to -8

CCMC

Test Procedure:	CEC L-39-T-87
Elastomers:	RE4
Compound:	Nitrile
Test Temperature:	100°C
Test Duration:	168 hours
Vessel:	400 ml beaker/300 ml beaker w/covers
S2 Specimens:	3 used for rupture properties in 400 ml beakers
	3 used for volume/hardness properties in 300 ml beakers
Limits:	RE4
%Δ in Rupture Strength:	-20/0
%Δ in Max Elongation:	-50/0
%Δ in Volume:	-5/+5
Δ in Hardness, IRHD:	-5/+5

M.A.N.

Specification:	OC 13-017
Elastomer:	SRE-NBR 28
Test Procedure:	DIN 53 521
Exposure:	100°C for 168 hours
Vessel:	Elastomer/oil ratio of 1/80 in closed glass beaker
S2 Specimens:	3 used for rupture properties
	3 used for volume/hardness properties

TESTS	LIMITS
	NBR 28
Change in rupture strength, %	Max -20
Change in max elongation (ME)%	Max -30
Change in volume (V)%	0 to +10
Change in hardness, (H) Shore A	Max -10

The following examples illustrate the practice of this invention.

EXAMPLE I

The base oil employed in this example was a refined oil (NMP SN 100/200) which was fully formulated with a conventional detergent-inhibitor package. The fully formulated oil (Oil 1) and a modification containing 0.55 weight percent glyceryl monooleate (Oil 2) were tested for their effect on a nitrile rubber (NBR-34 formulated from an acrylonitrile-butadiene copolymer containing about 34 percent of acrylonitrile) in the Mercedes-Benz Seal Compatibility Test. The percent change in tensile strength (TS) and in elongation (E) were reported.

Table 1

Mercedes-Benz Seal Compatibility Test

	Oil 1	Oil 2	Test Limits
Change TS, %	-17.3/-21.8	-5.0	-20 max
Change E, %	-36.3/-40.8	-22.3	-35 max

Oil 2 containing the glyceryl monooleate exhibited excellent nitrile seal compatibility properties.

EXAMPLE II

A fully formulated lubricating oil composition designated as Oil 1 was employed in the CCMC Seal Test, the Mercedes-Benz Seal Test and the MAN Seal Test. Modifications of this oil, designated as Oil 2 containing 0.20 weight percent glyceryl monooleate and Oil 3 containing 0.55 weight percent glyceryl monooleate, which was supplied by C. P. Hall, were also employed in the CCMC Seal Test. The elastomer tested was a nitrile rubber. The test results are indicated in Table 2 below.

Table 2

Oil No.	1	2	3	Test Limits
CCMC Seal Test Results				
RE 4 (NBR Nitrile)				
Change in TS, %	-23.3	-6.2	0.1	-20/0
Change in ME, %	-46.6	-35.2	-24.8	-50/0
Change in H, IRHD	-8	-4	-4	-5/+5
Change in V, %	3.1	3.9	4.2	-5/+5
Mercedes-Benz Seal Test Results (NBR-34)				
Change in TS	-34.5	-13.9	-9.5	-20 max
Change in ME, %	-47.4	-32.6	-25.7	-35 max
Change in H	-5	-3	-5	-8 max
Change in V, %	-18.6	3.9	4.3	0/+10
MAN Seal Test Results				
NBR-28				
Change in TS, %	-29.9	-14.3	-8.5	-20 max
Change in ME, %	-45.7	-32.6	-28.7	-30 max
Change in H	-4	-3	-3	-10 max
Change in V, %	6.1	4.0	4.1	0/+10

The additive oils of the invention containing glyceryl monooleate exhibited excellent improved nitrile seal compatibility properties.

EXAMPLE III

The lubricating oil employed in this example was a fully formulated gasoline engine oil and is designated as Oil 1. Oil 2 contains 0.20 weight percent of glyceryl monooleate, Oil 3 contains 0.55 weight percent of glyceryl monooleate and oil 4 contains 0.20 weight percent of Radiasurf 7150, another brand of glyceryl monooleate. These oils were tested in the Mercedes Benz Seal Test and the results are set forth in Table 3 below.

Table 3

Oil No.	1	2	3	4	Test Limits
Change in TS, %	-19.0	-10.9	-14.0	-14.8	-20 max
Change in ME, %	-39.3	-32.1	-33.6	-23.7	-35 max

All of the oils containing the glyceryl monooleate exhibited excellent nitrile seal compatibility properties.

EXAMPLE IV

A commercial Ford Factory Fill lubricating oil composition was tested in the CCMC Seal Compatibility Test. A modified oil or variant was prepared containing 0.20 weight percent of glyceryl monooleate. A nitrile rubber was used in the test. The results are reported in Table 4 below.

Table 4

	FORD FF/PL	Variant	Test Limits
RE4 (NBR Nitrile rubber)			
Change in TS, %	-28.9	-15.9	-20/0
Change in E, %	-50.1	-42.7	-50/0

The foregoing results demonstrate that the modified oil containing 0.20 percent of glyceryl monooleate gave excellent results in the CCMC Seal compatibility Test for the nitrile rubber.

EXAMPLE V

A variety of glycerol esters were tested in the same lubricating oil employed in Example II. In all cases, the glycerol ester was employed in a concentration of 0.20 weight percent. The following table lists the oils tested and the particular glycerol ester.

Oil No.
1 Radiasurf 7150 Glyceryl Monooleate
2 Radiasurf 7140 Glyceryl Monostearate, approx. 35% monoglycerides
3 Radiasurf 7600 Glyceryl Monostearate, approx. 52% monoglycerides
4 Radiasurf 7153 Glyceryl Monoricinoleate
5 None (Ref. oil)

These oils were tested in a Mercedes-Benz Seal Compatibility Test and the results are set forth in Table 5 below.

Table 5

Mercedes-Benz Seal Compatibility Test Results (NBR-34)

Oil No.	1	2	3	4	5	Test Limits
Change TS, %	-10.6	-28.1	-26.9	-16.8	-20.1	-20 max
Change ME, %	-24.8	-31.5	-35.8	-27.3	-36.8	-35 max

The test results show that there is criticality in the nature of the glycerol ester. The esters formed from glycerol and a saturated fatty acid, namely glyceryl monostearate, fail to pass the test limits for the Mercedes-Benz Seal Compatibility Test while the oils containing a glycerol ester of an unsaturated fatty acid gave excellent nitrile seal compatibility properties.

Claims

1. The use of an ester of glycerol and an unsaturated fatty acid having from 8 to 45 carbon atoms in an oil of lubricating viscosity in order to provide nitrile elastomer seal compatibility properties.

2. The use as claimed in Claim 1 in which said ester is a mono-, di- or triester of glycerol or a mixture thereof.

3. The use as claimed in Claim 1 or Claim 2 in which said ester is predominantly a monoester of glycerol.

4. The use as claimed in Claim 1 in which said ester is glyceryl monooleate, glyceryl ricinoleate or glyceryl linoleate.

5. The use as claimed in any one of the preceding Claims in which from 0.01 to 3 weight percent of said glycerol ester is present in said oil of lubricating viscosity.

Patentansprüche

1. Die Verwendung eines Esters aus Glycerin und einer ungesättigten Fettsäure mit von 8 bis 45 Kohlenstoffatomen in einem Öl mit Schmierviskosität, um Nitrilelastomerdichtungskompatibilitätseigenschaften bereitzustellen.

2. Die Verwendung, wie beansprucht in Anspruch 1, wobei besagter Ester ein Mono-, Di- oder Triester von Glycerin oder eine Mischung derselben ist.

3. Die Verwendung, wie beansprucht in Anspruch 1 oder Anspruch 2, wobei besagter Ester überwiegend ein Glycerin-Monoester ist.

4. Die Verwendung, wie beansprucht in Anspruch 1, wobei besagter Ester Glycerylmonooleat, Glycerylricinoleat oder Glyceryllinolsäureester ist.

5. Die Verwendung, wie beansprucht in irgendeinem der vorangehenden Ansprüche, wobei von 0,01 bis 3 Gew.-% von besagtem Glycerinester in besagtem Öl mit Schmierviskosität vorhanden sind.

Revendications

1. Utilisation d'un ester du glycérol et d'un acide gras insaturé ayant de 8 à 45 atomes de carbone dans une huile d'une viscosité lubrifiante afin de conférer des propriétés de compatibilité avec les joints en élastomère nitrile.

2. Utilisation selon la revendication 1, dans laquelle ledit ester est un mono-, di- ou triester du glycérol ou un mélange de ceux-ci.

3. Utilisation selon la revendication 1 ou 2, dans laquelle ledit ester est de façon prédominante un monoester du glycérol.

4. Utilisation selon la revendication 1, dans laquelle ledit ester est le mono-oléate de glycéryle, le ricinoléate de glycéryle ou le linoléate de glycéryle.

5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle de 0,01 à 3 pour cent en poids dudit ester du glycérol est présent dans ladite huile de viscosité lubrifiante.