

1

2,836,611

END-BLOCKED LINEAR POLYSILOXANES

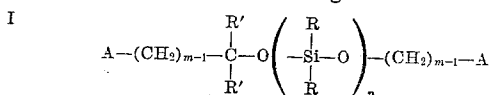
Lawrence J. Exner and Peter L. De Benneville, Philadelphia, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

No Drawing. Application March 30, 1955
Serial No. 498,110

15 Claims. (Cl. 260—448.8)

This invention relates to the production of novel polysiloxane derivatives which are of liquid oily character and are adapted to serve as hydraulic media for the transmission of power, such as in systems which serve for operating brakes or other mechanical devices, by the exertion of hydraulic forces thereon. The new compounds are also useful as lubricants and for other purposes as will be pointed out hereinafter.

The new compounds of the present invention have the structure of Formula I following:

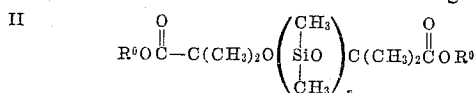


in which m is an integer having a value of 1 to 3, n is a positive number having an average value from 2 to 9, A is selected from the group consisting of $-\text{CN}$ and $-\text{COOR}^0$ where R^0 is selected from the group consisting of cyclohexyl and alkyl groups of 1 to 18 carbon atoms, R' is selected from the group consisting of H and alkyl groups having 1 to 8 carbon atoms, and R is a lower alkyl group having 1 to 5 carbons.

The number n preferably has an average value of 3 to 4. Some or all of the R' radicals are either the same or different. All R' radicals are preferably methyl groups. Examples of the lower alkyl representing R are methyl, ethyl, propyl, isopropyl, butyl, and amyl.

The new polysiloxane oils are characterized by low loss of viscosity through shear breakdown under continuous load at high speed; chemical inertness even at 300°F ; freedom from corrosion against common materials of construction, such as iron, steel, aluminum and so forth; and retention of adequate fluidity even at low temperatures. In general, they are heat stable oils having various viscosities and showing somewhat increased, but not unduly excessive increase, in viscosity at extremely low temperatures, such as on the order of -60°F . Thus they serve as the hydraulic transmission medium in hydraulic systems such as in hydraulic lifts and brakes. They also serve in shock absorbers and recoil mechanisms of the type which employ hydraulic media. They are also useful for reducing icing or frosting of the windshields, wings and so forth of automobiles, airplanes and other vehicles.

A preferred group of the new compositions are those having the structure of Formula II following:



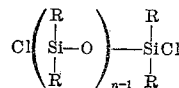
where the symbols have the same meaning as above.

These preferred compounds may be generally termed α -(alkoxycarbonyl)alkyl ethers of dimethyl polysiloxanes. The presence of the tertiary carbon atoms attached to the oxygen atoms of the siloxane chain imparts enhanced stability thereto. Depending upon the size of the R^0 radical, the preferred group of compounds exhibit various degrees of lubricity.

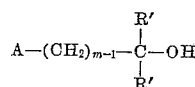
2

The compounds of the present invention may be prepared by the reaction of a compound having the structure of Formula III following with a compound having the structure of Formula IV following:

5 III



10 IV

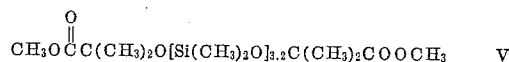


in which the symbols have the same meaning as previously set forth. For convenience, when reference is hereinafter made to the number of siloxane units in compounds of Formula III, the number refers to the value of the term " n " even though one of the silicon atoms of the formula lacks a corresponding oxygen atom. Compounds of Formula IV which may be used advantageously include esters of lactic acid, glycolic acid, α -hydroxybutyric acid, α -hydroxyisobutyric acid, α -hydroxy- n -valeric acid, α -hydroxyisovaleric acid, β -hydroxypropionic acid, β -hydroxybutyric acid, γ -hydroxybutyric acid, and α -hydroxydecanoic acid. Examples of the hydroxy nitriles of Formula IV which may be used include glycolonitrile, ethylenecyanohydrin, lactonitrile, and acetone cyanohydrin. Generally, the reaction may be carried out without a solvent though, if desired, an organic solvent may be used, such as benzene, toluene, xylenes and so on. The amount of hydroxy ester or hydroxy nitrile of Formula IV that is used may be equivalent to the chlorine atoms in the dichloropolysiloxane of Formula III. However, it is generally preferred to have a substantial excess even up to as much as 50% to 60% of the compound of Formula IV. Reaction is generally effected by heating with stirring and it is continued until the theoretical amount of HCl is substantially completely evolved. This may require from 10 to 20 hours at temperatures of 200° to 250°C . Lower temperatures down to room temperature may be employed provided additional time is taken. When a solvent is used, temperatures of 0° to 35°C may be employed provided a condensing agent, such as a tertiary amine, is added. Examples of tertiary amines include trimethylamine, triethylamine, pyridine, diethylaniline and so on. The use of the tertiary amine also has the advantage of combining with the hydrogen chloride liberated which reduces the opportunity for degradation of the compound formed during the reaction. The products may be isolated as oils by filtering the reaction mixture to remove the hydrochloride salt of the tertiary amine when such agent is used and then stripping the filtrate to remove all unreacted esters, and solvent if such is used.

In the following examples, which are illustrative of the present invention, the parts are given by weight unless otherwise designated:

EXAMPLE 1

(a) Preparation of



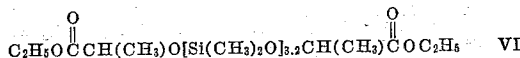
In a 3-liter, 3-neck flask equipped with a stirrer, thermometer, condenser and dropping funnel were placed 198 parts of methyl α -hydroxyisobutyrate, 170 parts of triethylamine and 310 parts of dry benzene. The solution was cooled on an ice bath and with the inside temperature at 0 to 5°C . added dropwise a solution of 204.4 parts of α,ω -dichloropolydimethylsiloxane having an average of 3.2 siloxane units in 185 parts of benzene. When addition was completed the bath was removed with the stirring being continued. After one hour at room

3

temperature the reaction began to exotherm and reached 39° C. Much solid precipitated. The mixture stirred overnight. The dark amber mixture was filtered, washed with 350 parts of dry benzene. The triethylamine hydrochloride obtained was 187 parts, theory=192.5 parts.

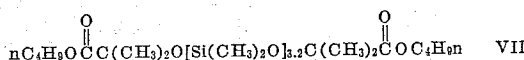
The filtrate was stripped to a vapor temperature of 45° C./7 mm. Hg. The concentrate, 270.4 parts of a dark brown oil, was dissolved in 700 parts of naphtha. This solution was boiled for a few minutes after adding 10 parts of activated carbon. The pale yellow filtrate was stripped at a pot temperature of 100° C. at 15 mm. Hg for one hour yielding 258 parts (81%) of a tan oil.

(b) The procedure of part (a) is repeated substituting ethyl lactate for the ester used in (a). An oily product is obtained having the structure



EXAMPLE 2

(a) Preparation of

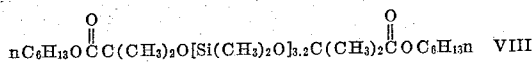


In a one-liter, 3-neck flask equipped with a stirrer, thermometer and reflux condenser which was connected by means of a CaCl_2 filled tube to two water traps in series were placed 288 parts of n-butyl α -hydroxyisobutyrate and 175.2 parts of α,ω -dichloropolydimethylsiloxane having an average of 3.2 siloxane units. The stirred solution was slowly heated on a glass-col mantle so that the reaction temperature reached 100° C. in 3.5 hours and 186° C. in a total of 7.5 hours. HCl was evolved after the temperature reached 64° C. The mixture was allowed to stand overnight. Heating was continued for a total of 18.5 hours. The maximum temperature reached was 202° C. 86.8% of the theoretical HCl was trapped. The reaction mixture was distilled until the vapor temperature reached 100° C./15 mm. The original butyl ester distilled at 103° to 110° C./62 mm. The 251 parts of amber colored concentrate was dissolved in 630 parts of naphtha. Added 10 parts of activated carbon and boiled the solution a few minutes. The very pale yellow filtrate was stripped at a pot temperature of 100° C. at 20 mm. for 1.5 hours, yielding 246 (76%) parts of an almost colorless oil.

(b) The procedure of part (a) is repeated substituting 238 parts of butyl glycolate for the ester of part (a).

EXAMPLE 3

(a) Preparation of



In a one-liter, 3-neck flask equipped with a stirrer, thermometer and reflux condenser which was connected by means of a CaCl_2 filled tube to two water traps in series were placed 338.4 parts of n-hexyl α -hydroxyisobutyrate and 175.2 parts of α,ω -dichloropolydimethylsiloxane having an average of 3.2 siloxane units. The stirred solution was slowly heated on a glass-col mantle so that the reaction temperature reached 144° C. in 5 hours. After standing overnight the reaction was heated an additional 16 hours. The maximum temperature of 203° C. was reached after 15 hours of heating. 80.6% of the theoretical HCl was trapped. The mixture was stripped until the vapor temperature was 142° C. at 10 mm. The 246 parts of brown oil concentrate was dissolved in 560 parts of naphtha and boiled a few minutes with 10 parts of activated carbon. The pale yellow filtrate was stripped at a pot temperature of 100° C. at 1.5 mm. yielding 242 parts (68%) of a yellow oil.

(b) The procedure of part (a) is repeated substituting 362 parts of cyclohexyl α -hydroxyisovalerate for the ester of part (a). An oily product is obtained.

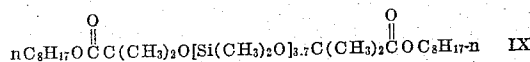
(c) The procedure of part (a) is repeated replacing

4

one-half the ester of part (a) with t-octyl α -hydroxyisobutyrate. An oily product is obtained which retains its fluidity over a wide range of temperatures.

EXAMPLE 4

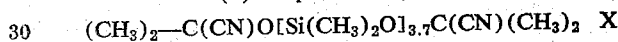
Preparation of



In a 2-liter, 3-neck flask equipped with a stirrer, thermometer and condenser which was connected by means of a CaCl_2 filled tube to two water traps in series were placed 649 parts of n-octyl α -hydroxyisobutyrate and 328 parts of α,ω -dichloropolydimethyl siloxane having an average of 3.7 siloxane units. The stirred solution was slowly heated on a glass-col mantle so that the reaction temperature reached 218° C. in 12 hours. It was heated an additional 9 hours at 230° to 235° C. with evolution of 84% of the theoretical HCl. The mixture was stripped until the vapor temperature reached 147° C./1.2 mm. The 541 parts of dark brown concentrate was dissolved in 700 parts of naphtha, heated to boiling for a few minutes with 10 parts of activated carbon. The clear yellow filtrate was stripped at a pot temperature of 100° C. at 1.1 mm. yielding 532.5 parts (77.6%) of oil.

EXAMPLE 5

(a) Preparation of



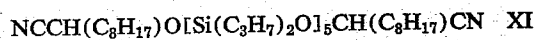
In a 500 cc. 3-neck flask equipped with a stirrer, thermometer, condenser and dropping funnel were placed 30.6 parts of acetone cyanohydrin, 36.4 parts of triethylamine and 66 parts of dry benzene. The solution was cooled on an ice bath and with the inside temperature at 0° to 5° C. there was added dropwise a solution of 49.3 parts of α,ω -dichloropolydimethyl siloxane having an average of 3.7 siloxane units in 40 parts of benzene in approximately forty-five minutes. The bath was removed, allowed to stir one hour, and then stood overnight. The reaction mixture was then filtered. The triethylamine hydrochloride was washed well with benzene yielding 42 parts (theory 41.3 parts) of salt. The yellow filtrate was stripped at 100° C./30 mm. Hg yielding 60.5 parts (95% yield) of yellow oil. The concentrate was dissolved in 140 parts of naphtha, heated to boiling for a few minutes with 5 parts of activated carbon. The filtrate was stripped at a pot temperature of 100° C. at 2.7 mm. yielding 56 parts (88% yield) of a yellow oil having the structure of Formula X above.

(b) The procedure of part (a) is repeated in successive runs, substituting for the ester used in (a):

- (1) 20.5 parts of glycolonitrile
- (2) 25.6 parts of ethylenecyanohydrin, and
- (3) 25.6 parts of lactonitrile respectively

In each case an oily product is obtained which retained its fluidity over a wide range of temperatures at least down to -40° C. and at least as high as 300° C.

(c) Preparation of



In a reaction vessel provided with an agitator, there are provided 169 parts of 3,3,5-trimethylhexaldehyde cyanohydrin, 150 parts of triethylamine and 100 parts of dry benzene. The solution is cooled in an ice bath to an inside temperature of about 0° to 5° C. and then there was gradually added a solution of 352 parts of α,ω -dichloropolydiisopropyl siloxane having an average of 5 siloxane units in 300 parts of dry benzene. Thereafter, the general procedure of part (a) is followed and the yield of the yellow oily product of Formula XI above is about 430 parts.

EXAMPLE 6

In a 500 cc. 3-neck flask equipped with dropping funnel, thermometer and condenser placed 22.2 grams (0.22 mole) of dry triethylamine, 78.5 grams (0.22 mole) of n-octadecyl- α -hydroxyisobutyrate and 50 cc. of dry benzene. Added 60.8 grams (0.1 mole) of α,ω -dichloropolydimethyl siloxane having an average of about 7.5 siloxane units at 0° to 5° C. After the addition was completed the reaction was stirred at room temperature 1.5 hours slowly becoming tan and then stood overnight. The filtered weight of $(C_2H_5)_3N \cdot HCl = 27.1$, theory = 30.2. Heated the filtrate to reflux yielding another 3.1 grams of solid. Stripped the filtrate to 178° C./1.5 mm. The residue was heated to boiling for a few minutes with activated carbon in 150 cc. of a solvent naphtha. It was then stripped at 128° C./6.5 mm. Hg to yield a clear golden oil.

When the preparation of the compounds is such as to leave the compound with an acid number, it is preferable to reduce the acid number by washing the compound with aqueous sodium carbonate, potassium carbonate or the like, and then stripping at reduced pressures, such as on the order of 10 to 30 mm. Hg. When so treated, the compositions have a negligible corrosive effect on such common materials as iron, steel, magnesium, copper, and aluminum. However, corrosion inhibitors may also be added, such as phenothiazine in amounts of about 0.5 to 1% on the weight of the polysiloxane.

When the compounds of the invention are employed as lubricants or hydraulic transmission media, they may be used alone or they may be compounded with other lubricating materials. For example, they may be compounded with fatty acid esters of higher alcohols, such as the esters of alcohols from octyl to octadecyl with fatty acids of 4 to 18 or more carbon atoms. They may also be compounded with diesters of aliphatic dicarboxylic acids, such as the diesters formed from diacids having from 6 to 12 carbon atoms with monohydric alcohols having 6 to 10 carbon atoms or mixtures of such alcohols. Examples of the esters that may be employed include butyl stearate, dodecyl pelargonate, dioctyl sebacate, dioctyl adipate, and so on. The compounds of the present invention may also be incorporated into liquids of hydrocarbon type to provide lubricating oils or hydraulic transmission media, again in amounts of 10% to 90% of each component. The proportions of the polysiloxane compounds of the present invention relative to the esters or other lubricating materials may vary from 10% to 90% of each on the total weight of the mixture. Lubricity-enhancing agents and wear-reducing agents may also be incorporated into the polysiloxane derivatives of the present invention whether they are used alone or in conjunction with other lubricating agents. Examples of such auxiliary materials include phosphoric acid or phosphorus acid esters such as triphenyl phosphate, tricresyl phosphate, tricyclohexyl phosphate, trioctyl phosphate, or the corresponding phosphites or corresponding phosphonates. From 1% to 10% by weight of the total composition may be composed of such auxiliary wear-reducing or lubricity-enhancing agents.

EXAMPLE 7

The product of Example 4(a) when tested as a lubricant was capable of sustaining a load up to 700 pounds before seizure. This compares with unmodified hydrocarbon oils having an SAE 20 which sustained loads of 800 to 1000 pounds before seizure. The incorporation of 6.5% of tricresyl phosphate with the polysiloxane product obtained in Example 4(a) raised the load capacity to 850 pounds before seizure. A mixture of 50 parts by weight of dioctyl sebacate with 47 parts by weight of the polysiloxane product of Example 4(a) and 3 parts

by weight of tricresyl phosphate showed a capacity for sustaining loads up to 2300 pounds before seizure.

EXAMPLE 8

The kinematic viscosities at various temperatures, the Dean and Davis (ASTM) viscosity indexes and ASTM slopes were determined by standard methods on the polysiloxane products obtained in Examples 1(a), 2(a), 3(a), 4(a) and 5(a) with the results set forth in the accompanying Table I.

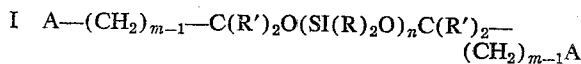
TABLE I

Product of Example	Kinematic Viscosity Centipoises				Viscosity Index	ASTM Slope
	210° F.	100° F.	-40° F.	-65° F.		
1(a)-----	2.52	6.93	149	545	199	0.634
2(a)-----	2.55	6.92	162	594	203	0.625
3(a)-----	3.10	8.98	268	1060	214	0.604
4(a)-----	3.20	9.58	333	1318	211	0.609
5(a)-----	2.19	5.62	75.9	-----	199	0.637

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

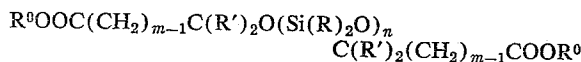
We claim:

1. A composition comprising a compound having the general formula



in which m is an integer having a value of 1 to 3, n is a positive number having an average value from 2 to 9, A is selected from the group consisting of $-CN$ and $-COOR^0$ where R^0 is selected from the group consisting of cyclohexyl and alkyl groups of 1 to 18 carbon atoms, R' is selected from the group consisting of H and alkyl groups having 1 to 8 carbon atoms, and R is a lower alkyl group having 1 to 5 carbon atoms.

2. A composition of matter comprising a compound having the structure of the formula



where

R^0 is an alkyl group having 1 to 18 carbon atoms

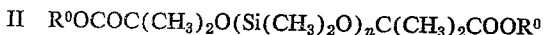
m is an integer having a value of 1 to 3

R' is an alkyl group having 1 to 8 carbon atoms

R is an alkyl group having 1 to 5 carbon atoms, and

n is an integer having a value of 2 to 9

3. A composition comprising a compound having the general formula



wherein R^0 is an alkyl group having 1 to 18 carbon atoms, and n is a positive number having an average value from 2 to 9.

4. A composition as defined in claim 3 in which R^0 is methyl.

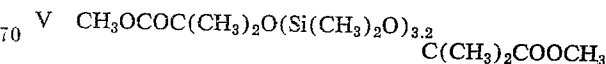
5. A composition as defined in claim 3 in which R^0 is butyl.

6. A composition as defined in claim 3 in which R^0 is hexyl.

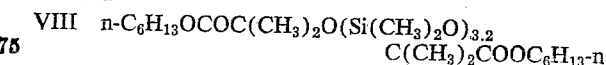
7. A composition as defined in claim 3 in which R^0 is octyl.

8. A composition as defined in claim 3 in which R^0 is dodecyl.

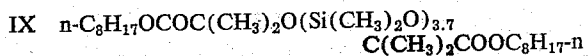
9. A composition comprising a compound having the formula



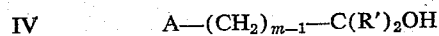
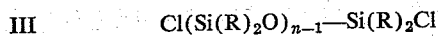
10. A composition comprising a compound having the formula



11. A composition comprising a compound having the formula



12. A method comprising the step of reacting a compound of Formula III following with a compound of Formula IV following:



in which m is an integer having a value of 1 to 3, n is a positive number having an average value from 2 to 9, A is selected from the group consisting of —CN and —COOR^0 where R^0 is selected from the group consisting of cyclohexyl and alkyl groups having 1 to 18 carbon atoms, R' is selected from the group consisting of H and alkyl

groups having 1 to 8 carbon atoms, and R is a lower alkyl group having 1 to 5 carbons.

13. A method as defined in claim 12 in which the reaction is effected in an anhydrous organic solvent.

14. A method as defined in claim 12 in which the reaction is effected in the presence of a tertiary amine at a temperature of 0 to 35° C.

15. A method as defined in claim 12 in which the reaction is effected at a temperature between room temperature and 250° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,381,366	Patnode	Aug. 7, 1945
2,415,389	Hunter	Feb. 4, 1947
2,657,226	Frisch	Oct. 27, 1953

UNITED STATES PATENT OFFICE
Certificate of Correction

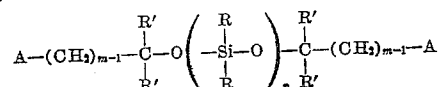
Patent No. 2,836,611

May 27, 1958

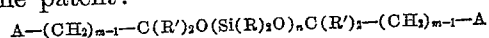
Lawrence J. Exner et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 25 to 29, Formula I should appear as shown below instead of as in the patent:



column 6, lines 28 and 29, claim 1, Formula I should appear as shown below instead of as in the patent:



Signed and sealed this 19th day of August 1958.

[SEAL]

Attest:

KARL H. AXLINE,

Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.