

June 5, 1945.

J. F. HYDE

2,377,689

DIELECTRIC COMPOSITIONS

Filed May 17, 1943

Fig. 1

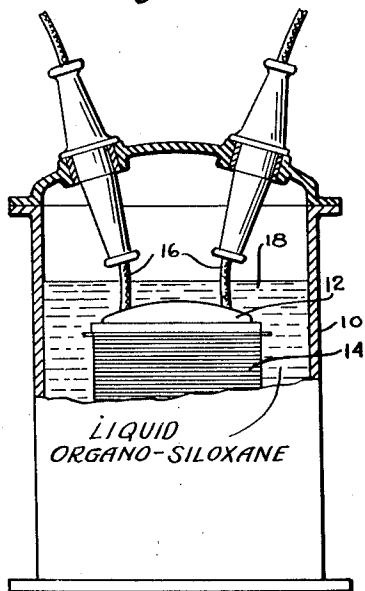


Fig. 2

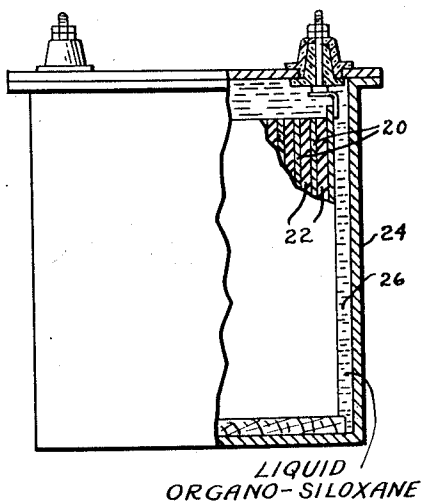
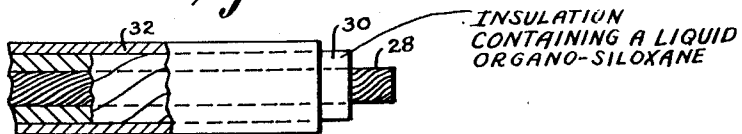


Fig. 3



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DIELECTRIC COMPOSITION

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Application May 17, 1943, Serial No. 487,375

9 Claims. (Cl. 174—17)

This invention relates to dielectric liquids for electrical apparatus.

This application is a continuation-in-part of my co-pending application Serial Number 432,528 filed February 26, 1942.

In electrical apparatus such as transformers, capacitors, cables, switches, fuses, reactors, regulators, circuit breakers, and similar equipment, it is customary to provide a liquid insulating medium which is termed the "dielectric liquid." This liquid has a substantially higher breakdown strength than air and, by displacing air from spaces in the electrical equipment between conductors, and to ground, materially raises the break-down voltage of the equipment. In the past it has been customary to use petroleum products, such as the mineral oils, as dielectric liquids. These oils have not proven generally satisfactory. Although possessing certain advantages by reason of their availability and relatively low cost the mineral oils also possess certain very serious disadvantages.

One disadvantage of the mineral oils is that they tend to form deposits, generally known as "sludge" during the period of their use. This is due to oxidation and decomposition and also results to some extent in the formation of acids which is equally undesirable. The sludging of dielectric oils during use is a serious disadvantage and requires either replacement of the oil or treatment to remove the sludge.

The most serious disadvantage of the mineral oils is the fact that they are inflammable and upon decomposition yield gases which are also inflammable and explosive when mixed with air. A fire proof insulating liquid would be highly desirable, since there exists the possibility of a fire in the event a short circuit or similar electrical defect occurs in the electrical apparatus insulated. Furthermore, the electric arc which is frequently developed in electrical equipment causes decomposition of the oils into gases which are inflammable and explosive.

A commercially satisfactory dielectric liquid should possess the following properties. It should not sludge or be inflammable. It is desirable for many applications that the liquid should have a low freezing point and a high boiling point. Its viscosity should be relatively low and should not change greatly with temperature. The liquid should be thermally and chemically stable and inert to arcing; or if sensitive to arcing it should not leave a conducting carbon path. Its ohmic resistance should be relatively high; its power factor should be relatively low and dielectric

strength high. It should also have a satisfactory dielectric constant.

The primary object of this invention is to provide a new dielectric liquid.

5 Another object of my invention is to provide an improved method of insulating elements in electrical apparatus.

A further object of my invention is to provide an improved electrical apparatus containing a dielectric medium comprising a liquid organo-siloxane.

10 For a fuller understanding of the nature and objects of the invention, reference may be had to the following detailed description, taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a view partly in side elevation and partly in section showing the manner in which the coils and core of a transformer may be immersed in the dielectric liquids of my invention;

15 Fig. 2 is a view in side elevation of a capacitor having parts broken away to show details of the structure; and

Fig. 3 is a view in side elevation of a section of cable having parts broken away to show details of the structure.

25 I have discovered that liquid organo-silicon oxide polymers, in general, possess properties which adapt them to use as dielectric liquids. These polymers are compounds which contain organic radicals attached to silicon through a carbon atom and whose silicon atoms are joined to other silicon atoms by oxygen atoms, thus Si-O-Si. They may be prepared either by hydrolysis of hydrolyzable organo-silicanes and condensation of the hydrolysis products or by hydrolysis of a mixture of different hydrolyzable organo-silicanes and co-condensation of the hydrolysis products. In the latter method of preparation, a hydrolyzable silicane which contains no organic radicals attached to silicon through a carbon atom, such as silicon tetrachloride or ethyl orthosilicate may be included along with the hydrolyzable organo-silicanes. By hydrolyzable organo-silicanes I mean derivatives of SiH₄ which contain readily hydrolyzable radicals such as hydrogen, halogens, amino groups, alkoxy, 30 aroxy and acyloxy radicals, etc., the remaining valences of the silicon atoms being satisfied by organic radicals that are joined to the silicon atoms through carbon atoms. Examples of such organic radicals are as follows: methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl to octadecyl and higher; alicyclic radicals such as cyclopentyl, cyclohexyl, etc.; aryl and alkaryl radicals

such as phenyl, mono- and poly-alkyl phenyls as tolyl, xylyl, mesityl, mono-, di-, and tri-ethyl phenyls, mono-, di-, and tripropyl phenyls, etc.; naphthyl, mono- and poly-alkyl naphthyls as methyl naphthyl, diethyl naphthyl, tri-propyl naphthyl, etc.; tetrahydronaphthyl, anthracyl, etc.; aralkyl such as benzyl, phenylethyl, etc.; alkenyl such as methallyl, allyl, etc., and heterocyclic radicals. The above radicals may also, if desired, contain certain inorganic substituents such as halogens, etc.

Hydrolysis of the above silicane or mixtures thereof is generally accompanied by condensation to a greater or less degree depending upon the conditions of hydrolysis and the particular silicane involved. As a result of the hydrolysis and concurrent condensation, organo-silicon oxide polymers are produced which are partially or completely condensed and which have on the average up to and including three organic radicals attached to each silicon atom. The polymers so obtained vary in character some being liquids, others being crystalline solids or gels. They also vary in the ease with which they may be further polymerized by heat since they differ in the number of active functional groups retained as a result of incomplete hydrolysis and condensation. Those which are only partially condensed may be converted to higher polymers and even to solids by heat alone or even by standing at room temperature by virtue of the completion of the condensation. On the other hand, those which approach complete condensation are extremely resistant to further polymerization by heat alone. However, the latter may be further polymerized by proper acid treatment, alkali treatment or air treatment as disclosed in my copending applications Serial Number 481,155 filed March 30, 1943; Serial Number 481,154, filed March 30, 1943; and Serial Number 451,354 filed July 17, 1942, all being assigned to the assignee of the present invention. The condensed hydrolysis products of silanes or mixtures thereof and their polymerization products are now known as siloxanes. (See page 20 of Alfred Stock's book, *Hydrides of Boron and Silicon*, published 1933). This invention as shown above is concerned with the organo-substituted siloxanes, that is those siloxanes containing organic radicals attached to silicon through carbon-silicon linkages.

I have found that the liquid organo-siloxanes which are substantially completely condensed are to be preferred as dielectric media because of their great resistance to further polymerization by heat. However, the thermal stability of the partially condensed silicones may be further improved by the utilization of stabilizers. In general, the liquid siloxanes are non-hydrolyzable and substantially non-hygroscopic and better maintain their electrical characteristics under comparable moisture conditions than do hydrocarbon oils. They are relatively non-flammable and if they do burn they leave a silica ash which is electrically nonconducting as contrasted with the conducting carbon track of the carbon compounds. Their tendency to form sludge under ordinary conditions of operation is slight. They are resistant to oxidation and have little or no effect on metals, synthetic insulation coatings, varnishes and rubber, even at high temperatures. They have low freezing points, which in many instances are far below those of the hydrocarbon oils. They also have in most cases high boiling points and consequently lower vapor pressures. Their flash points are in general relatively high.

Not only is their temperature-viscosity slope relatively flat but their temperature-viscosity coefficients are constant. They possess high ohmic resistance, high dielectric strength, and low power factors. Many of them are excellent heat transfer media as well. Furthermore, they are compatible with many of the common organic dielectric liquids so that, if desired, mixtures of the organo-siloxanes and other dielectric liquids may be used. In general they possess properties which in combination render them greatly superior to conventional dielectric fluids for a wide variety of applications.

The following examples illustrate representative liquid organo-siloxanes which possess desirable characteristics for dielectric liquids. A brief description of the preparation of the siloxanes is also given in each example for better establishing their identity.

Example 1

Trimeric phenyl ethyl silicone was prepared by the hydrolysis and condensation of phenylethylsilicon dichloride. It was a liquid having a viscosity of about 80 centistokes. Its specific inductive capacity was determined to be 2.7 and its power factor at 1 megacycle to have a value of 0.075%. A parallel plate variable air-condenser was immersed in the silicone and increasing potential applied across the two sets of plates until break-down occurred. Values of 500, 1450 and 720 at a .035 inch gap were noted on three successive break-downs. No deterioration of the silicone was apparent. With the same arrangement, break-down occurred at 600, 625 and 700 volts with a good grade of transformer oil.

Example 2

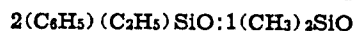
Bis-phenyldimethylsilicyl oxide,



was prepared by hydrolysis and condensation of phenyldimethylethoxysilicane. It is a liquid of low viscosity. Its specific inductive capacity was determined to be 2.5 while its power factor was .015% at 1 megacycle. Its break-down voltage over a .1 inch gap was 25 kv. on the first test and 28.5 kv. on the fifth successive test. After each test the liquid was stirred before making the next measurement.

Example 3

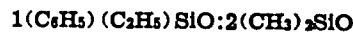
A liquid copolymer having the composition



was prepared in the following manner. A mixture of dimethyldiethoxysilicane and phenylethylsilicon dichloride in the proper proportions was added to a solution of water and ethanol and stirred. An oil and aqueous layer were produced and then separated. The oil was dissolved in ether and washed with water until acid free. The silicone was then dried by heating to 150° C. under 15 mm. pressure. Its viscosity was 29.6 centistokes at 25.0° C. The power factor of this silicone was 0.054% at one megacycle and room temperature and its specific inductive capacity was 3.05. Its break-down voltage across .1 inch gap at room temperature and 60 cycle frequency was 34.5 kv. on the first test and 29.0 kv. on the second test.

Example 4

A copolymer having the composition

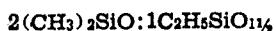


was prepared in a manner similar to that em-

played in Example 3. The liquid product had a viscosity of 23.0 centistokes at 25.0° C. Its power factor at room temperature and 1 megacycle frequency was approximately 0.022% while its specific inductive capacity was 2.85. Its break-down voltage across a .1 inch gap at room temperature and 60 cycle frequency was 31.7 kv. on the first test and 23.5 kv. on the second test.

Example 5

A copolymer having the composition



was prepared as described in Example 3, except that the water was added to the mixture of silicane which comprised essentially dimethyldiethoxysilicane and ethyltriethoxysilicane. The product was a liquid having a viscosity of 54.8 centistokes at 25.0° C. Its power factor at room temperature and 1 megacycle frequency was approximately 0.035% while its specific inductive capacity was 2.83. Its break-down voltage across .1 inch gap at room temperature and 60 cycle frequency was 34.0 kv. on the first test and 17.5 kv. on the second test.

Example 6

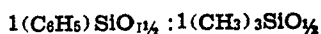
A copolymer having the composition



was prepared by adding a mixture of phenyldimethylethoxysilicane and methyltriethoxysilicane in the proper proportions to a .5% solution of hydrochloric acid. The oily product was taken up in ether and washed acid free. The solvent was then removed and the product dried. The viscosity of the product was 18.3 centistokes at 25.0° C. Its power factor at room temperature and 1 megacycle frequency was approximately 0.026% while its specific inductive capacity was 2.85. Its break-down voltages across .1 inch gap at room temperature and 60 cycle frequency on first and second break-downs were 33.5 kv. and 26.2 kv.

Example 7

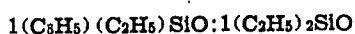
A copolymer comprising essentially the composition



was prepared by mixing phenyl silicon trichloride and a solution of trimethylethoxysilicane in benzene and alcohol. The mixture was diluted with diethyl ether. Water was added with stirring. The product was taken up in ether, washed, concentrated and dried. The viscosity of the product at 25.0° C. was 112.3 centistokes. Its power factor at room temperature and 1 megacycle frequency was 0.42% while its specific inductive capacity was 3.29. Its break-down voltages across .1 inch gap at room temperature and 60 cycle frequency were 29.5 kv. on the first test and 17.5 kv. on the second test.

Example 8

A copolymer having the composition



was prepared by hydrolyzing and condensing a mixture of diethylsilicon dichloride and phenylethylsilicon dichloride in the manner described in Example 1. The liquid product had a power factor at room temperature and 1 megacycle frequency of 0.086% and a specific inductive capacity of 2.77. Its break-down voltage across a .1 inch gap at room temperature and 60 cycles was

31.0 kv. on the first test and 18.5 kv. on the second test.

Example 9

Liquid diethyl silicone was prepared by the hydrolysis of diethylsilicon dichloride followed by condensation of the hydrolysis product. Its specific inductive capacity was determined to be 2.65 while its power factor was found to be .130% at 1 megacycle and room temperature. Its break-down voltage over a .1 inch gap at room temperature and 60 cycle frequency was 32.5 kv. on the first test and 27.0 kv. on the second test.

The liquid organo-siloxanes of my invention are well adapted to be used as dielectric media in such electrical apparatus as transformers, capacitors, cables, switches, fuses, reactors, regulators, circuit breakers, and similar equipment. Examples of electrical apparatus which may contain the dielectric liquids of my invention are shown in the drawing. Referring to Fig. 1 of the drawing, a transformer casing or tank 10 is shown with a core 12 carrying coils 14, all arranged in accordance with standard practice. The coils 14 are provided with terminal conductors 16. As illustrated, the casing contains a sufficient amount of the dielectric liquid 18 to completely immerse the coils 14. Referring to Fig. 2 of the drawing, a capacitor is shown with plates 20 made of some suitable conducting material, such as aluminum foil and the like, the plates being separated by sheets 22 of insulation or dielectric material, such as paper which is treated with a dielectric liquid of my invention. The entire assembly is supported in a casing 24 and immersed in a liquid dielectric 26 of my invention. Referring to Fig. 3, a cable is shown with a conductor 28 which has applied thereto some suitable insulating material 30, such as paper wrapping. A lead sheath 32 may be applied for protecting the insulation. The paper insulation is treated with a liquid organo-siloxane of my invention.

One of the outstanding advantages of the liquid siloxanes as dielectric media is their resistance to high temperature which is such that they may be used at temperatures hitherto impossible with conventional dielectrics. In order to take full advantage of the heat resistance of the liquid siloxanes, their flash points may be raised as high as 250° C. or higher either by removal of volatile lower polymers or by polymerization of the lower polymers to higher, less volatile polymers. It should be pointed out that the flash points of these polymers are not true flash points but rather are the temperatures at which depolymerization and liberation of lower boiling polymers occurs.

In general, I have found that the properties of the liquid organo-siloxanes may be so controlled as to fit them for a wide variety of applications as dielectric media. Those siloxanes which have an oxygen to silicon ratio between 0.5 and 1.0 and particularly those containing lower alkyl radicals have been found to be especially well adapted for use as dielectric liquids. Whereas in some respects they may not be superior to ordinary dielectrics, in other respects, they are definitely superior so that for many dielectric applications these liquid organo-siloxanes represent a distinct advance over commercial dielectrics now being used.

I claim:

1. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during

operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium comprising a liquid organo-siloxane whose organic substituents consist essentially of organic radicals attached to silicon through carbon-silicon linkages.

2. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium comprising a liquid organo-siloxane whose organic substituents consist essentially of mono-valent hydrocarbon radicals attached to silicon through carbon-silicon linkages.

3. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of a substantially completely condensed liquid organo-siloxane whose organic substituents consist essentially of mono-valent hydrocarbon radicals attached to silicon through carbon-silicon linkages, said organo-siloxane having an oxygen to silicon ratio of between $\frac{1}{2}$ and one.

4. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of a substantially completely condensed liquid organo-siloxane whose organic substituents consist essentially of mono-valent hydrocarbon radicals attached to silicon through carbon-silicon linkages.

5. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during

operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of a substantially completely condensed liquid organo-siloxane whose organic substituents consist essentially of lower alkyl and phenyl radicals attached to silicon through carbon-silicon linkages.

10 6. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of a substantially completely condensed liquid organo-siloxane whose organic substituents consist essentially of lower alkyl radicals attached to silicon through carbon-silicon linkages.

15 7. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of a liquid polymeric phenyl ethyl silicone.

20 8. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of a liquid polymeric diethyl silicone.

25 9. Electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of said apparatus to have a difference in electrical potential therebetween and a liquid medium interposed between said elements for insulating one from the other, said medium consisting of bis-phenyl-dimethyl-siliclyl oxide.

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