

July 29, 1969

F. HELD ET AL

3,458,351

PROTECTION OF ELECTRICAL CONTACTS

Filed June 19, 1964

Fig.1

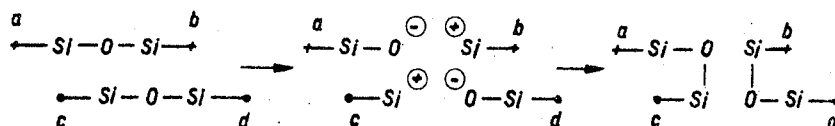


Fig.2

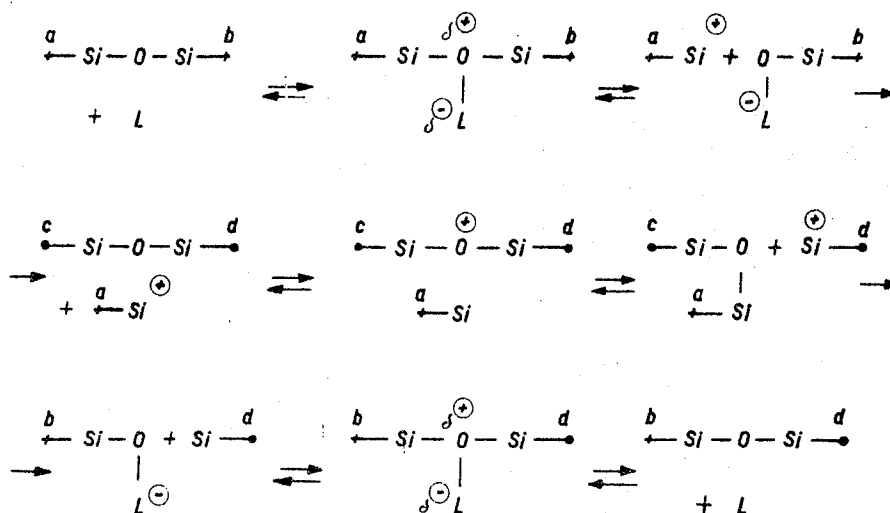


Fig.3

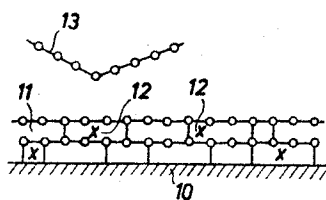


Fig.4

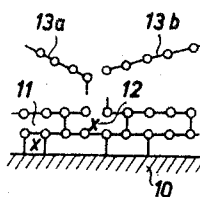
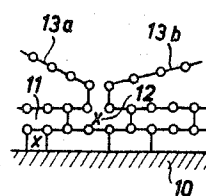


Fig.5



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PROTECTION OF ELECTRICAL CONTACTS

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Filed June 19, 1964, Ser. No. 376,520

Claims priority, application Switzerland, July 3, 1963, 8,352/63

Int. Cl. B44d 1/18

U.S. Cl. 117—212

1 Claim

ABSTRACT OF THE DISCLOSURE

For protecting electrical constructional elements having contact surfaces, the surfaces surrounding the actual contact surfaces are coated with a silicone resin composition which makes the treated surface non-wettable by organic liquids. The coating may be applied, in the form of a solution of the silicone resin in a halogenated hydrocarbon solvent, to the whole surface of the constructional element and thereafter that part of the coating which overlies the actual contact surfaces be mechanically removed.

The present invention is concerned with a process for the protection of electrical contacts, especially in communication and control equipment. As is known, the function of electric contacts is the joining together of two electric leads at any given time or the separation of such leads or the connection or disconnection of a source of current. After connection has been made, the touching pair of contacts forms a component part of the electrical lead which requires that the passage of current at the point of contact must not be hindered. In the case of satisfactory contacts, the measurable contact resistances are low and vary approximately between 5–20 $\mu\Omega$. However, even small increases of this contact resistance may be disturbingly noticeable when an electric circuit requires several or many such contacts, as is outstandingly the case in, for example, automatic telephone exchanges and many kinds of electrical control devices. The greatest part of the expenditure of time for the maintenance of such devices or equipment is due to the increased contact resistances. It is, therefore, not surprising that for a very long time a great deal of attention has been paid to this problem.

As the most important reasons for disturbances at electrical contacts, there are to be mentioned contact corrosion and contact fouling, two phenomena which can primarily be regarded as being separate. However, from a secondary point of view, it must be stated that corroded contacts inevitably become fouled and vice versa. The field of contact corrosion is concerned, in the narrowest sense of the term, with the physical and chemical changes of the contact surfaces by exchange reactions of the contact material with the air under the influence of the spark discharges produced during connection and disconnection. In the broader sense of the term, there also belong thereto the so-called burning off, as well as the surface changes which result purely by mechanical stressing during connection and disconnection. By the choice of suitable contact materials, corrosion can be prevented or at least slowed down to a large extent.

The position is, however, quite different in the case of contact fouling. By this there is understood a fouling with substances which do not originate from the contact material, i.e. its burning off or oxidation products. These substances are mostly of an organic nature, for example, dust, oils, greases and the like, which undergo changes on the contact surfaces, the reasons for which vary. Under

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the influence of the sparking which always occurs but the intensity of which varies more or less according to the manner of use of the contacts, there takes place a stepwise breakdown via decomposition products, to carbon and gaseous oxidation products. Furthermore, liquid materials can polymerise or condense due to the catalytic effect of the contact metal or due to the action of peroxides formed by the contact sparking.

The effect of these alterations is always the same, regardless of the actual cause; the contact resistance increases due to the secondarily-formed substances until actual contacting is no longer possible.

It follows from this that the most effective means of protection against these detrimental alterations of the contact surfaces must be the prevention of fouling by foreign matter by keeping away organic substances.

The question then arises how these substances are, in any case, able to get on to the contact surfaces at all, provided, of course, that the contacts leave the production process in a clean state. The most obvious measure of producing the contacts under carefully tested, dust-free conditions showed that only a part of the disturbances disappear. Another possibility for the contamination is that these organic substances reach the contact via the gaseous or vapour phase. In the forefront of such substances are the relatively readily volatile materials originating from organic insulating materials, such as only partially reacted resin components, plasticisers and the like.

Experiments in artificially produced vapour atmospheres of substances of this type indeed show an effect in the direction of a relatively rapid deterioration of the contacts. However, the elimination of the influences of dust and readily volatile substances does not have the desired result: the described disturbances arise as before, not only in the laboratory but also in communication and control equipment.

Consequently, it had to be considered whether still other substance transport mechanisms played a part. It is known that on solid body surfaces non-polar and weakly polar oils spread widely on their substrates, i.e. when put on to a substrate, a drop of oil continuously increases its diameter until the drop has covered the whole of the substrate with a layer of uniform thickness or until the substrate is covered with a monomolecular layer, provided, of course, that the substrate is large enough.

Thermodynamically this phenomenon is easy to understand when it is borne in mind that binding forces and thus the surface tensions in a solid body are, from the point of view of energy, considerably stronger than those of a liquid. In most cases, therefore, the increase of energy by the adsorption of a molecule of a liquid on the boundary surface of a solid body is greater than the energy required for overcoming the surface tension which results in the spreading of the liquid.

The transport of substances and its velocity brought about by this spreading or creeping is a function of various physical substance properties, as well as of the surface in question. Vapours of organic substances which have been deposited as condensates, for example on the contact holders, or substances which have even been deposited there during production, can now, according to this phenomenon, reach the contact surfaces. A donor effect in this sense is possessed by all constructional elements which are in direct mechanical contact with the contacts. It can readily be appreciated that in this manner, from the point of view of amount, a far greater quantity of substances is to be reckoned with than that due to the amount of substances which can condense on the contact surfaces. This is particularly so when it is borne in mind that, from the point of view of surface area, this substance deposition exceeds the contact sur-

faces by several orders of magnitude. Since this substance deposition is continuously maintained, on the one hand, by condensation and, on the other hand, by contact with synthetic resins which contain volatile components, an availability of substances is ensured. There are also to be mentioned again residues of substances which have served as auxiliaries during the production.

From the knowledge of this substance transport, as well as of the substance accumulation effect of certain constructional elements, there results the following possible preventative measure: cutting off the solid body surface tension of the decisive constructional elements.

This measure of cutting off or screening the surface tension is a process which is frequently used in the horological industry and is called epilamisation. This process consists in that a thin layer of, for example, a saturated, straight-chained hydrocarbon containing 15–20 carbon atoms which has a terminal polar group, for example a carboxylic acid group, such as stearic acid, a substance frequently used for this purpose is applied on the surface to be protected. This thin layer is called epilam. The protective effect is hereby twofold: the surface tensional forces are weakened by partial neutralisation by the polar groups and spaced out by the hydrocarbon chains standing vertically to the surface.

This measure is of outstanding effectiveness for a period of several years against contamination by all oils of a purely organic nature. It has also been successfully used for the improvement of the contacting of electrical contacts, as is indicated, for example, in Swiss patent specification No. 242,030 and in German patent specification No. 945,278. Nevertheless, relay contacts carrying parts treated by this process sometimes fail in practice where, in certain cases, and unchanged and rapid deterioration of the contacts has been observed.

Further investigations disclosed the limit of the classical epilamisation protection: the size of the value of the surface tension. Common mineral oils, synthetic greases, and oils of vegetable and animal origin exhibit surface tensions which preponderantly lie in the region between 32–35 dyne cm^{-1} . If the surface tension is less than about 25 dyne cm^{-1} it no longer suffices for the holding together of the liquid even on epilamised surfaces and for the prevention of spreading. Other epilamisation substances which even show an effect in this range are hitherto unknown. Liquid silicones which are finding an ever increasing use in the most varied kinds of preparations, such as mould release agents, floor polishes, furniture polishes, hand creams and the like, exhibit, according to the molecular weight, a surface tension of 17–21 dyne cm^{-1} and the spreading thereof cannot be prevented by any physically-acting epilam in the described manner.

Investigations of the effect of silicone oils on relay contacts show that liquid silicones are to be regarded as actual contact poisons. Whereas the decomposition of purely organic substances takes place via carbon, which can at least be partially converted into electrically conductive graphite due to the influence of sparking, to carbon monoxide or carbon dioxide, i.e. gaseous end products, the end product in the case of silicones is silicone dioxide, a highly insulating substance of very low volatility which is formed on the contact point, remains there and puts the contact out of action by increased resistance.

The wide use of silicone oils and their extraordinary tendency to spread would lead, at the very outset, to the belief that measures for keeping silicones away from contact surfaces are illusory. Thus, the problem arises of finding a new process which effectively prevents the spreading of silicone oils. From the above-described situation, it appeared to be less promising to employ further physical methods. Therefore, the attempt was made to achieve a repellent measure against silicones by chemical means.

The solution of the problem posed was found in the process according to the present invention which essential-

ly consists in that the surfaces surrounding the actual contact surfaces of the constructional elements having the contacts are covered with a protective layer of a solid polymeric compound which contains Si bonds. A protective layer of this kind makes surfaces non-wettable by organic liquids and, at the same time, is able to chemically transform liquid silicone compounds so that they lose their mobility.

The protective layer can expediently be formed from a pure silicone resin or a solid organic polymeric compound containing a silicone resin, in that a thin to thinnest possible coating of a dilute solution of the polymeric compound is applied on to the surface to be treated by any of the known lacquering technics and then allowed to dry.

If the constructional elements having contacts are treated in the described manner, then the molecules of liquid silicones are chemically bound to the cross-linked compound forming the protective layer in such a manner that they become a component part of the compound. The mobility of the silicone molecule is thus removed and its transport to the contact prevented. Since the activity of the layer can be maintained over a long period of time and this protective layer is also non-wettable by non-silicone oils, the problem of the protection of contacts against contamination by liquids can be regarded as being solved by the process according to the present invention. Because of its "getter" action, the protective layer produced by the process according to the present invention is, in the following, referred to in this sense as a "getter layer."

If, in a macromolecule of a polymeric compound, there are present substituents, such as alcoholic or phenolic hydroxyl groups, carboxylic acid groups, primary amino groups, epoxy groups, —Si—H groups, —Si—C=CH_2 groups, Si—O—C groups etc., then, under certain conditions, a reaction with a linear polysiloxane molecule is to be expected. The number of functional groups in the macromolecule of the polymeric compound, as well as their reactivity, play a decisive part for the effectiveness of the getter layer. The reaction known in silicone chemistry as equilibration can be utilised for this purpose and leads to the solution of the chemical side of this problem.

In the following, the present invention is explained by way of example, with reference to the accompanying drawings, in which:

FIGURE 1 shows schematically the splitting of an Si—O bond and the exchanged combination of the parts produced by the splitting;

FIGURE 2 shows, in principle, the same as FIGURE 1 but with an indication of the mechanism in the presence of a catalyst (electron-theoretical explanation); and

FIGURES 3–5 show schematically the course of the formation of the binding of a linear, polymeric siloxane to a cross-linked polysiloxane (getter layer).

5% of a silicone resin is dissolved in a halogenated hydrocarbon, for example, perchloroethylene. The resultant liquid lacquer is applied, with the aid of a buckskin dipped therein, in a thin layer to the whole surface of a constructional element having contacts up to a distance of about 4 cm. from the contacts. After the lacquer layer has dried, the layer is removed, by means of a fine file, from the actual contact surfaces where electric contact is to be made, but not from the surfaces of the contacts and leads so that finally the lacquer-free actual contact surfaces are surrounded with much larger surfaces carrying a protective layer of silicone resin. The protective layer may contain a catalyst.

A silicone resin suitable for the described use is marketed by the General Electric Company under the trade name Dri-Film 103 as a protective agent for buildings. This latter is a 70% solids solution in an aromatic solvent of a methylmethoxypolysiloxane resin, as described in Krantz Patent 2,810,704. This is a precondensed silicone resin which, by the action of catalysts,

hardens completely at about 20° C. As catalysts there can be used, for example, cobalt and lead salts, preferably the naphthenates, individually or in combination. However, for hardening at room temperature, tin salts, such as tin octoate and tin maleate, appear to be particularly effective.

One possibility of explaining the effective mechanism achieved by the protective layer can be by means of the reaction known in silicone chemistry which forms the basis of the equilibration of siloxanes. Equilibration is preponderantly used in technology where mixtures of non-functional polysiloxane molecules of various sizes (terminally blocked) are to be converted into a product of uniform molecular weight.

The process is explained in that molecular fragments resulting by the splitting of siloxane molecules at an Si—O bond combine with other such fragments so that, in effect, an exchange takes place. If, for example, the two fragments of a molecule are designated by *a* and *b* and those of another molecule by *c* and *d*, then these fragments can combine with one another in such a manner that one molecule afterwards consists of the fragments *a* and *c* and the other of the fragments *b* and *d*. This process is schematically illustrated, by way of example, in FIGURE 1.

Reactions which are based on the fact that, under the same conditions, Si—O bonds are split and again formed anew, are common in silicone chemistry. They take place relatively quickly, even at room temperature when catalysts, such as acids, bases or Lewis acids, are present. A mechanism in the presence of a catalyst, for example, of a Lewis acid L, is schematically illustrated in FIGURE 2.

If a cross-linked polymeric siloxane molecule enters into reaction with a linear, polymeric siloxane molecule by equilibration, then the linear, polymeric molecule becomes attached to the cross-linked material, i.e. to the getter layer. By the splitting of an Si—O bond in the cross-linked molecule, two moveable fragments do not result because the molecule is held together by further points of cross-linkage but there are merely formed two points of connection, each of which can now be linked again with a fragment of a linear polymeric siloxane. It is thereby immaterial on which molecule the catalyst acts. This process, which can be regarded as a grafting of a linear polysiloxane on a cross-linked polysiloxane, is schematically illustrated by way of example in FIGURES 3 to 5.

According to FIGURE 3, the surface of a contact spring is provided with a thin layer of silicone resin 11, the getter layer, with cross-linked molecules and embedded molecules of catalyst 12. FIGURE 3 also shows a linear, polymeric siloxane molecule 13 which acts as a contact poison. Due to the presence of the catalyst 12, a chemical reaction takes place in which an Si—O bond of a cross-linked silicone resin molecule and of a linear, polymeric siloxane molecule 13 are split (FIGURE 4) and the two resultant fragments 13a and 13b of the linear, polymeric siloxane are bound by new Si—O—Si bonds to the points of connection of the cross-linked sili-

cone resin layer 11 (FIGURE 5). In this manner, the substance 13 which is harmful for the electrical contact is prevented from wandering to the contact surface. Since the thermodynamic equilibrium of this reaction lies by the high molecular weight compound, the reverse reaction can be neglected.

Corrosion products, such as cobalt, iron and tin salts, present on the essential metallic constructional elements can possibly act as catalysts.

Furthermore, very thin layers of cross-linked polysiloxanes (silicone resins also have the great advantage that they are not wettable by a large number of organic liquids. Consequently, they also possess, to an outstanding degree, the previously mentioned physical blocking or retarding action against the creeping and spreading of liquid organic substances.

Other functional groups present in the cross-linked siloxanes, such as Si—OH, Si—OR (wherein R is an alkyl, alkylene, aryl or acyl radical and Si—H, as well as organo-functional groups, can, of course, also react, according to various mechanisms, with linear, polymeric siloxanes and also with hydrocarbon compounds containing functional groups. With the poly-functional behaviour of cross-linked polysiloxanes regarding the previously described reaction, there are connected important advantages with regard to the number of centres of reaction which are difficult to achieve by other conceivable systems.

Further advantages of this composition or reaction system are the chemical stability with regard to other compounds, as well as their resistance to ageing and the impossibility of a depletion of the centres of reaction because the chemical construction of the getter layer is not altered by the grafting of linear siloxanes.

What we claim is:

1. A process for the protection of an electrical contact, of a constructional element having an electrical contact area, against fouling by a liquid silicone contaminating material, which comprises coating that portion of the surface of the constructional element entirely surrounding said electrical contact area with a thin coating of a layer of a silicone resin varnish consisting of a solution of a silicone resin, containing Si—O bonds, in a volatile solvent for said silicone resin, allowing said solvent to evaporate and said resin to harden leaving a very thin protective film entirely surrounding said contact area, and cleaning from said electrical contact area, only, any of the coating inadvertently applied thereto, said silicone resin being a cross-linked organopolysiloxane capable of chemically combining with and inhibiting the mobility of such a liquid silicone contaminant material.

No references cited.

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U.S. Cl. X.R.

117—8, 102, 201