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PLASTICS MADE CONDUCTIVE WITH COARSE METAL FILLERS

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The portion of the term of the patent subsequent to July 7, 1981, has been disclaimed
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U.S. Cl. 252—514 33 Claims

ABSTRACT OF THE DISCLOSURE

This invention pertains to metal filled electrically conductive plastics in the form of gaskets, caulking compounds or seals useful for waveguide assemblies, weather-tight R.F. (radio frequency) enclosures and the like. It is more particularly concerned with electrically conductive seals based on a compressible plastic filled or loaded with a coarse metal powder of select size, shape and surface area. The thus filled plastic is used to form a joint or closure seal that is both electrically and hermetically tight.

This application is a continuation-in-part of Ser. No. 232,566 now Pat. No. 3,194,860, "Conductive Plastic Gasket" filed Oct. 23, 1962, and Ser. No. 227,944 "Metal Filled Electrically Conductive Plastics" filed Oct. 2, 1962, now abandoned. This application is also a continuation of Ser. No. 534,919 filed Mar. 16, 1966, now abandoned, which was a continuation of Ser. No. 292,978, filed July 5, 1963, now abandoned.

There has been a need for a sealing material based upon a plastic-form material that is highly electrically conductive. Previous methods for forming electrical joints or connections have several disadvantages. For example, soldered joints are not easily broken for repairs or modification. Woven wire gaskets when properly placed in a flange make an effective electrical joint, but unless special composite rubber-wire gaskets are used they are not weather tight. Also, woven wire gaskets tend to "disappear" at high frequencies because of the spaces between the individual wires. There is a type of metal-rim waveguide gasket available that has knurling on the metal surfaces which gouges and makes electrical contact with the flange faces. This gasket may have an O-ring molded into a special channel in the metal rim to effect a pressure tight seal. This composite gasket is bulky and can be used reliably only once. It is not too effective in high power applications although generally speaking it has been up to now the best type of seal available for microwave flanges.

It has now been found that unusually effective seals for electrical closures can be formed from a compressible or resilient plastic loaded or filled with metal particles. The metal particles are held in electrical particle-to-particle contact by the plastic binder or matrix. Current can thus flow through the plastic matrix via the metal particles. Volume resistivities are below 10 ohm.-cm. and can be as low as 0.001 ohm.-cm. or lower.

The seals of this invention can have a variety of shapes to match the closure to be sealed. For example, the conductive plastics can be in the form of molded O-ring seals, cast strips for sealing container openings, gaskets die-cut from sheet stock formed in a platen press, or putty-like caulking compounds.

It has been known to load epoxy adhesives with silver powder to form "plastic solders." These solders have been used for such purposes as attaching leads and terminals as on electroluminescent panels, or for patching cracks and crevices in waveguides. The art has not appreciated up to now, however, that exceedingly effective conductive seals can be fabricated from an elastomer or other types of compressible plastics loaded with a coarse metal powder having a low surface area.

Until the present invention the tendency was to use rather fine noble metal pigments to fill the plastic and impart conductivity. While finely-divided pigments give a smooth unctuous mass or paste, they have several disadvantages. The high surface area to volume ratio of fine pigments limits the solid loadings that can be used while still retaining a workable plastic mixture. The solid loadings used in the past were in the order of 50 to 70 weight percent. Such low loadings influences the reliability and level of conductivity that is secured. Because of the high surface area of the pigments, the viscosity of the base resin is important to the stability of the system. This viscosity will change with temperature and a system stable at room temperature may undergo solids settling when heat cured i.e. become insufficiently filled and thus an insulating layer of resin will form on the upper surfaces of the mass or between the contiguous particles.

The surface effects of the coarse solids of this invention are negligible and viscosity of the resin does not influence to any appreciable extent the stability of the system. The solids loading can be so high that there will be no settling of solids even when the system is heated to an elevated temperature. Thus, there is no "excess" resin to wet and form an insulating film on the metal surface the plastic mass contacts or between contiguous particles.

The conductive plastic seal of this invention has all the advantages of the plastic-form. It can be soft, flexible and resilient and will comply with flange surfaces without scaring them. Properly designed molded forms of the seal can be quite abuse-resistant. While having the advantage of a plastic-form seal, however, it also has the quality of an electrical seal customarily made from rigid metal.

To make an effective electrical seal with a metal-filled plastic the resistance offered by three types of films must be overcome:

(1) any insulating films such as oxides on the metal particles themselves
(2) insulating films of the plastic matrix that may exist between the particles themselves, or between the particles and the metal surface contacting the plastic mass
(3) any insulating films on the metal surfaces which the plastic mass contacts

Conductivity of a plastic mass filled with a conductive metal powder depends upon the particle-to-particle contact between the metal particles. Electric current must be able to flow from particle-to-particle with desirably the lowest amount of contact resistance between particles as possible. The noble metals have been used in the past as the conductive metal powders in plastics because insulating oxide coatings do not form on the particles as is the case with other metal particles such as copper and aluminum. With the non-noble metals the oxide coating that forms on the particles, while perhaps only a few atoms thick, has a relatively high resistivity and may prevent the ready flow of current between contiguous particles.

In the present invention metal powders having an outer surface of a non-noble metal that are not inherently conductive metal powders have been used to load the plastics and make them electrically conductive. Examples of suitable metals are nickel, lead, zinc, cadmium and copper. Suitable alloys can, of course, be used such as a tin-lead solder or a brass. Generally speaking, the non-noble metals are electrically conductive only under the proper pressural situation in a flange. The pressure on the loaded plastic mass overcomes the insulating films of oxide on the particles and of the plastic between particles particularly when coarse particles are used, and high point contact pressures are obtained. Thus the current can flow between particles.

Because of the oxide coating problem, it is preferred to use particles that have an outer surface at least of a noble metal and are inherently conductive when in particle-to-particle contact. The particles can be solid noble metal praticles or non-noble metal particles overcoated with a protective noble metal coating such as silver or gold. It is much preferred in the present case to use the coated powders because they are less expensive.

One test for the conductivity of metallic powders is to test them in free-form unmixed with any plastic matrix. If probes from a volt-ohm meter indicate that the conductive metallic powder is suitably conductive in free-form, it will impart adequate conductivity to any plastic when properly incorporated therein. The stability of the metallc powder can be checked by heat treating it for at least 24 hours at 400° F. in air. If it still retains within 50% of its initial conductivity in free-form after this temperature treatment there is little danger that it will degrade when it is incorporated in a plastic binder.

The preparations of the two types of the preferred non-noble metal powders coated with a noble metal are described in copending cases "Inexpensive Conductive Metal Filler," Ser. No. 227,756, filed Oct. 2, 1962, and "Iron Based Conductive Filler for Plastics," Ser. No. 227,755, filed Oct. 2, 1962, by the present inventors.

The metal powders used in the practice of this invention have a select particle size, surface area and shape. Coarse particles of low surface area present a relatively low number of sites for contact between the particles. The effect of any pressure externally applied to the plastic is thus greatly enhanced, i.e. the pressure of contact between any two particles is many times higher than that obtained with finely divided particles with high surface areas. Coarse particles readily overcome the insulating oxide and plastic films between the particles and even modest externally applied pressures will drive the particles into good electrical particle-to-particle contact. Spherical or generally spherical particles are also advantageous in this connection. Flat or platelet forms of powders tend to align themselves in the plastic mass and are exceedingly difficult to force into particle-to-particle contact because of intervening films of the plastic matrix. A spherical particle, however, has essentially point contact with its neighbor and very high unit contact pressurces can be enjoyed.

The surface area to volume ratio of the fillers used is in the range of 450 to 200,000 square feet/cubic foot. The maximum particle size is about 100 mils, and preferably does not exceed 40 mils. In the case of powders presenting a surface of a noble metal, the minimum particle size used is 0.5 mil. With other types of powders where the resistance of an oxide film on the particles must be overcome the minimum particle size used is about 5 mils so that high unit contact pressures between particles will result. In this connection, it is preferred to work with "soft" metals or metals that are deformable when these particles have a non-noble metal surface because the deformation of the particles when external pressure is applied causes the insualting oxide films to break and better electrical particle-to-particle contact results. The Brinell hardness of the solid metal content of such particles is preferably 100 or less.

The plastic matrix should be fairly highly filled to pretty well assure that there is no "excess" plastic available to encapsulate and insulate the metal particles. The loading with a coarse spherical filler that a plastic will accept and still remain workable is considerably higher than loading level possible with finely divided high surface area fillers. The loading used will normally be in the range of 45 to 80 volume percent.

The metal surfaces with which the conductive plastic is to form an electrical seal should, of course, be free of insulating paint or oil films, and should be reasonably clean. Some oxide films such as aluminum oxide are difficult to penetrate. The coarse nature of the metal powder used in this invention has the additional advantage of imparting a grittiness to the plastic mass. The gritty particles break through any insulating films on the surface of metal to be contacted much more readily than a platelet form will, and good electrical contact is secured.

The plastic matrix used should be compressible or responsive to externally applied pressure so that the metal particles will feel the effects of such pressure. With elastomers or other form-stable plastic binders, the durometer of the plastic (unfilled) should be less than 99 Shore A (ASTM D695) and the compression modules at 1000 p.s.i. should preferably result in a deflection of at least 10 percent. With caulking compounds, the plastic matrix should not be so viscous as not to be capable of undergoing plastic flow under the conditions of use. Rigid binders such as a diallyl phthalate do not permit the effects of externally applied pressures to be felt by the metal particles. Another preferred property of the plastic matrix is that it forms good adhesion bonds with the filler to minimize powder shedding.

The plastic matrix used is preferably but not required to be one that shrinks slightly during curing or drying. This places the plastic under tension which helps to assure that good particle-to-particle contact is maintained.

A soft material if subjected to tension tends to allow the metal particles to separate with a loss in conductivity. It is desirable therefore to design for compression type forces in the sealing application when using the present type of conductive plastics.

The drawings attached to and forming a part of this specification illustrate various forms of the conductive plastic seals of this invention, as described in the following examples.

EXAMPLE I

A highly electrically conductive gasket (see FIG. 1) for sealing a microwave flange was made as follows. A silver coated copper powder was prepared in accordance with the example of the above referred to copending application Ser. No. 227,756. Coarse copper powder (Metals Disintegrating M.D. 103A) was first cleaned with an acetic acid wash and then replacement plated with silver from a silver cyanide solution containing an abnormally high amount of cyanide ions. Nine weight percent silver was laid down in the above manner to give an electrically adherent coating. The particles had a particle diameter of 2–3 mils and were generally spherical.

About 89 weight percent of the silver-coated copper powder was incorporated into a polyvinyl chloride plastisol having a curing temperature of 330° F. and a viscosity at room temperature in the uncured state of 160,000 cps. (Dewey and Almy Chemical Division, W. R. Grace & Company, Daxene A–60). The heavy paste obtained was spread into a 30 mesh-10 mil aluminum wire screen (Newark Wire Cloth Co.). The filled screen was cured in an oven at 330° F. for 8 minutes. The reinforced sheet obtained and a thickness of about 22 mils. It had a weight of 1.18 grams per inch. About 17 weight percent of the sheet consisted of the wire screen and 83 weight percent consist of the conductive metal-filled plastic.

The cured sheet was rolled (2 passes) in a rolling mill, one customarily used to roll steel sheets, at an average rolling pressure of 850/lbs./in. of width. The reduction obtained was 30%, i.e. the final thickness of the sheet was 17 mils. This rolling impressed the screen somewhat into the sheet so that the wire of the screen was not at the surface of the sheet. It is preferred in this method of manufacturing to decrease the thickness of the screen at least 5% by rolling.

A gasket for a 8.6 kilomegacycle (X-band) RG51/U waveguide flange was die-cut from the sheet stock at an angle of 45° from the warp of the screen. When tested at an internal air pressure of 25 lb. per sq. inch at 2.5 megawatt peak load and a 2.5 kilowatt average load, the insertion loss for the gasket was 0.005 lb. This was considerably better than the performance obtained from a commercial machined metal-molded O-ring composite seal tested in the same apparatus. In this case, the peak power that could be obtained was only 1.6 megawatts.

The isolation afforded by the gasket was in excess of 85 decibels.

In additional tests, a gasket of the same type was able to withstand a continuous load of 6 kilowatts without arcing in a continuous wave X-band testing unit.

EXAMPLE II

A silver-copper coated iron powder is prepared in the manner described in copending application Ser. No. 227,755. The base iron powder has a surface area of 70 square feet per pound, and an average particle diameter of 3 mils. It is first replacement coated with 18 mole percent copper from a copper sulphate solution and then 12 mole percent of the copper is replaced with silver from a silver cyanide solution. The silver-coated powder in loose form has a volume resistivity under 0.5 ohm per centimeter as measured by probes from a volt-ohm meter.

The plastisol of Example I is filled with 80 weight percent of the coated powder and cast into a ring 2½ inches O.D., 2¼ inches I.D. and 3/16 of an inch thick. (See FIG. 2.) It has a resistivity of about 0.05 ohm-cm. and a permeability of 5 to 10. It is used to seal the base of a kylstron tube (JAN 2K–25).

The use of the polyvinyl chloride plastisol binder of Examples I and II represents a particularly preferred embodiment of this invention. There are only a few binders available that are liquids before curing and permit direct incorporation of the conductive metal filler by simple mixing. With other types of binders the metal filler may have to be incorporated by milling or through the use of solvents. Silicones and urethanes are additional examples of plastics that are liquids before curing but both rely on a catalyst for curing which may be effected by the metal particles. A PVC plastisol however is a one component system of indefinite pot life and is unaffected by the presence of metal particles.

EXAMPLE III

9.6 parts by weight of a silicone resin (Dow Corning 601) is loaded with 90 parts by weight of the silver-plated particles of Example I. The filled resin cures in 7 minutes at 300° F. upon the addition of 0.4 part by weight of a catalyst (Dow Corning 601 Catalyst). The catalyst is added to the silver loaded resin and the mixture is cast into an unreinforced 90-mil thick sheet stock using a heated platen press. Five by six inch sections are cut from this sheet stock and placed within the lid of a shielded container having several interior compartments that must be electrically sealed from each other.

The use of the coarse, low surface area conductive fillers of this invention is particularly advantageous with the silicone resins. The conventional finely-divided silver flakes and powders have very high surface areas per unit volume and the catalysts used to cure the silicone resin

appear to be rapidly poisoned by the filler such that a cure cannot be obtained, or can be obtained only with poor results. The coarse fillers of this invention, however, present a much lower level of metal surface to the catalyst such that the rate of poisoning is greatly reduced, sufficiently so as to permit the ingredients to be mixed together and properly cured, either at elevated temperatures or a room temperature depending on which silicone resin system is used.

EXAMPLE IV

A reinforced microwave flange gasket was prepared as in Example I with the exception being that the M.D. 103A powder was used per se, i.e. it was not replacement plated. The plastic sheet was initially conductive when tested with the probes of a volt-ohm meter. When tested for insertion loss in the same equipment its performance was about the same as that of the reinforced gasket of Example I.

EXAMPLE V

A reinforced microwave flange gasket was prepared as in Example I with the exception being that a spherical nickel powder (Foote Mineral Nickel C) was used as the filler. This gasket performed adequately when tested in the X-band unit.

EXAMPLE VI

A gasket was made up using the same resin and conductive powder as in Example I, but not the screen reinforcing. A 60-mil sheet of the resin filled with 86 weight percent of the powder was cast by means of a heated platen press. A gasket whose outside dimensions were 4″ x 4″ and inside dimensions were 3″ x 3″ was cut from the sheet stock. The conductivity of this gasket versus sealing pressure was tested by inserting it between two metal plates in a press and measuring the resistance. Its volume conductivity with 0.3 pound per square inch pressure was about 0.01 ohm-cm., and dropped to under 0.00002 ohm-cm. at a sealing pressure of 700 pounds per square inch.

EXAMPLE VII

An O-ring seal for UG–40B/U choke flange was molded from the 87 weight percent loaded polyvinyl chloride plastisol described in Example I. The O-ring had an internal diameter of 1.338 inches and the rim had a diameter of 0.092 inch in cross-section.

EXAMPLE VIII

The strip seal illustrated in FIG. 3 was designed to replace the woven wire seals customarily used in the construction of shielded containers and enclosures. The metal powder used was a coarse copper shot having an average particle size of 14 mils (Metals Disintegrating M.D. 46HP). The plastic matrix used with the plastisol of Example I. The strip seal was formed using a cavity having the shape and being positioned as shown in FIG. 3*a*. The plastisol was deliberately underfilled (40 weight percent loading) such that during the heat fluxing of the plastisol the heavy metal particles settled in the position shown. The gasket had a thickness of 0.20 inch and a maximum width of 0.75 inch. The beveled edge made a 45° angle with the longest side.

This arrangement was developed because highly loading a plastic with the amount of the coarse metal particles required to assure good electrical conductivity reduce the compressibility of the plastic mass. The undercutting of the conductive plastic layer with the unfilled plastic makes the strip seal much more resilient when the two sealing surfaces are placed in a flange or closure shown by the arrows in FIG. 3*b*. The conductive layer is able to make good electrical contact with the two flange faces while the unfilled portion of the strip seal makes a good pressure and weather-tight seal.

EXAMPLE IX

An R.F.I. (radio frequency interference) caulking compound useful for sealing the seams of shielded enclosures such as shielded rooms and electronic equipment cabinets as illustrated in FIG. 4 was prepared by admixing 288 parts of the silver-plated powder of Example I with a solution consisting of 34 parts toluene, 34 parts ethanol and 32 parts of a polyamide resin (Side Seam Cement 8304, Dewey and Almy Chemical Division, W. R. Grace and Company). This mixture is a heavy, non-settling paste having a gritty nature. It sets or dries to a vibration resistant adhesive having moderate tack. The volume resistivity of the dried adhesive is less than 0.01 ohm-cm. In another version, the 288 parts of the silver-plated powder can be replaced with 288 parts of the coarse copper shot described in Example XIII to make an inherently less expensive compound.

When using a very coarse powder as a filler in a flexible or elastomeric binder, conductivity along the longitudinal axis of the shape may readily be lost by bending or stretching. This does not mean, however, that the shape is not suitable for some purposes. For example in a R.F. shielding application where it is desired for an electrical connection to be made between two conductive surfaces, such as between two metal flange faces, and conductivity along the axis of the space defined by the surfaces is not required, a gasket based on a coarse filler can be used. Even if the particles had separated somewhat because of flexing or relaxation of the plastic binder, the exerting of even a modest amount of compressive force on the filled plastic will bring the metal particles into electrical particle-to-particle contact in the direction transverse to the surfaces so that electric current can flow therebetween. Very coarse particles get a good "bite" into the surface in this situation which assures that a good electrical connection is obtained. As an illustration, the resin of Example I was loaded with 90 weight percent of an atomized copper powder having an average particle size of 14 mils, and cast as a sheet ⅛ inch thick. The sheet initially was highly conductive along its major axis, but this conductivity was quickly lost with moderate flexing. However, by exerting a slight pressure on the flat surfaces conductivity could be regained.

The term "plastic" is intended to include resins and elastomers (rubbers) and other conventional plastics that are compressible. The plastic matrix used can be thermosetting or thermoplastic, depending upon the use to which the gasket is to be put. Asphalts, polyurethanes, polyamides and natural rubber are additional examples of suitable matrices.

The term "matrix" means "something holding or capable of holding embedded within it another object to which it gives shape or form." (The Winston Dictionary: College Edition, The John C. Winston Company, Philadelphia, Penn. 1946).

The term "conductive metal powder" means a particulate powder having an outer surface of a noble metal, such as solid gold powder or the silver coated powder of Example I, which is so inherently conductive when maintained in particle-to-particle contact in loose form (i.e. in the absence of plastic matrix) as to have a volume resistivity of less than 10 ohm-cm. as measured by the probes of a volt-ohm meter, particularly after having been maintained in an oven at 400° F. for 24 hours in the presence of a circulating air atmosphere.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

That which is claimed is:

1. In an electromagnetic energy shield in the form of a gasket or caulking compound having a volume resistivity to be effective as an electromagnetic energy shield

comprising a resin matrix loaded with particles coated with silver in an amount of about 40 to 80 volume percent, the improvement being that the silver coated particles are of a maximum size in the range of from 0.5 to 40 mils and wherein the resin is compressible.

2. In a shield according to claim **1** in which said resin is an elastomer.

3. In a shield according to claim **1** in which said resin is silicone resin.

4. In a shield according to claim **1** in which said particles are spherical or generally spherically shaped.

5. In a shield according to claim **4** in which the resin is an elastomer.

6. In a shield according to claim **5** in which the resin is silicone resin.

7. In a shield according to claim **1** in which the exposed surface area of the silver coating the particles is in the range of 450 to 200,000 square feet per cubic foot.

8. In a shield according to claim **7** in which the particles when coated are spherical or generally spherically shaped.

9. An electromagnetic energy shield in the form of a gasket having a volume resistivity to be effective as an electromagnetic energy shield comprising a compressible resin matrix loaded with substantially spherical particles coated with a layer of silver and ranging in size from 0.5 to 40 mils.

10. An electromagnetic energy shield according to claim **9** in which the coated particles comprise about 40 to 80 volume percent of the shield and in which the particles have a total exposed silver surface area of 450 to 200,000 square feet per cubic foot.

11. A shield according to claim **10** in which the resin is an elastomer.

12. In an electromagnetic energy shield having a volume resistivity to be effective as an electromagnetic shield comprising a resin matrix loaded with particles coated with silver in an amount of about 40 to 80 volume percent, the improvement being that the silver coated particles are of a maximum size in the range of from 0.5 to 40 mils and wherein the resin is compressible.

13. In a shield according to claim **12** in the form of a coating.

14. In a shield according to claim **13** in which the resin is an elastomer.

15. In a shield according to claim **13** in which the resin is silicone resin.

16. In a shield according to claim **14** in which the particles are spherical or generally spherical.

17. In a shield according to claim **14** in which the exposed surface area of the silver coating the particles is in the range of 450 to 200,000 square feet per cubic foot.

18. In a shield according to claim **17** in which the particles are spherical or generally spherical.

19. In a shield according to claim **18** in which the resin is an elastomer.

20. In a shield acocrding to claim **18** in which the resin is silicone resin.

21. In a shield according to claim **1** in which the resin matrix is loaded with particles coated with silver in an amount of about 45 to 80 volume percent.

22. In a shield according to claim **21** in which the resin is an elastomer and the shield is in the form of a gasket.

23. In a shield according to claim **22** in which said particles are spherical or generally spherically shaped.

24. In a shield according to claim **23** in which the resin is silicone resin.

25. An electromagnetic shield according to claim **10** in which the coated particles comprise about 45 to 80 volume percent of the shield.

26. In an electromagnetic shield according to claim **24** in which the particles coated with silver are in an amount from about 45 to 80 volume percent.

27. In an electromagnetic shield according to claim **26** in which the particles are spherical or generally spherical.

28. In an electromagnetic shield according to claim 27 in which the resin is an elastomer.

29. An electromagnetic shield according to claim 26 in which the resin is an elastomer.

30. In a shield according to claim 1 in which the particles are solid metal.

31. An electromagnetic energy shield according to claim 2 in which the particles are solid metal.

32. An electromagnetic energy shield according to claim 10 in which the particles are solid metal.

33. In a shield according to claim 21 in which the particles are solid metal.

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