

1458281

PATENT SPECIFICATION

(11) 1458281

- (21) Application No. 3937/74 (22) Filed 28 Jan. 1974
 (31) Convention Application No. 11377/73 (32) Filed 26 Jan. 1973 in (19)
 (33) Japan (JA)
 (44) Complete Specification published 15 Dec. 1976
 (51) INT CL³ H01B 7/00 B05D 1/36 5/12 H01B 3/30
 (52) Index at acceptance
 B2E 179 19Y 20Y 339 410 416 443 444 446 44Y 462
 463 467 46Y 477 498 653 656 65Y 693 707 708
 70Y 71X 724 804 80Y
 H1A 2E3D2 2E5



(54) SOLDERABLE AND THERMOSTABLE INSULATED WIRE

(71) We, SUMITOMO ELECTRIC INDUSTRIES, LTD., a Japanese Company, of No. 15, Kitahama 5-Chome, Higashi-Ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to solderable and thermostable insulated wire.

In recent years, there has been a growing tendency for electrical machines, such as motors or transformers, to be constructed in smaller sizes and lighter weights, and it is obviously desirable to increase the reliability of these machines. In order for the electrical machines to be smaller in size, it is necessary to attenuate the insulated wires. Accordingly, thinner and higher performance insulated wires or magnet wires used in these electrical machines have been sought. It is not sufficient, however, to use known insulating materials as, even when the machinery is reduced in size, there is required of it the same performance as, or a higher performance than, that required of conventional machinery, and a higher load is exerted on the attenuated insulated wires. Accordingly, the insulating material must have a higher performance. With such a background, highly thermostable materials have been developed for use in producing thermostable insulated wires. Moreover, for use under severe conditions, an increase in the reliability of insulated wires is desired, and development of materials having superior chemical-resistance, e.g., resistance to alkali, resistance to solvents or resistance to hydrolysis, is in progress. An important point to be borne in mind during the following discussion is that, of the thermostable insulating materials now available, those having good thermal-stability also have good chemical-resistance.

On the other hand, electrical machinery manufacturers have developed automation and assembly line techniques in order to minimize the cost of production. One such development is the removal of insulation on an assembly line: magnet wires are wound on, for example, a motor, transformer and the insulation must be removed from the coil ends or lead wires to allow soldering.

Methods for removal of insulation include (1) mechanical removal (the insulation is cut off mechanically, using, for example, a wire brush or a knife); (2) removal by heat decomposition (the insulation is decomposed at high temperatures using a flame, for example); (3) chemical removal (the insulation is decomposed with a chemical such as an alkali), and (4) removal by solder (the insulation is decomposed in a molten solder bath). All these methods have their own disadvantages.

With method (1), large quantities of insulation can be simultaneously removed and also the conductors tend to be damaged. Thus, in the case of thin wires, breakage frequently occurs rendering them unsuitable for use, and this method does not accord with the trend toward attenuation of wires. With method (2), that part of the insulating material which is adjacent that to be removed at the end of a coil tends to be decomposed as well because of the heat applied. Particularly in the case of thin wires, not only the insulating material but also the conductor is melted resulting in a breakage of the wires or a crease in the conductor diameter. Thus, this method is not feasible for practical applications, and again does not accord with the trend toward attenuation. Method (3) makes it possible to remove a large number of insulations simultaneously but, since a certain period of time is required, problems arise when applying the method to continuous operation. Moreover, this method is more time-consuming for insulation having good chemical resistance.

Method (4) enables a large number of insulations to be removed within a short period of time, and no problem arises even when the removal is conducted on a continuous assembly line. Furthermore, since solder is adhered to the conductors after removal of the insulation, the conductors are easily solderable. When it is desired to solder insulated wires to each other, this method can be advantageously used since by twisting insulated wires having coatings of wire enamel and dipping the twisted strands of wire in molten solder, the removal of the insulation and soldering are performed at the same time: the removal of the insulation can therefore be simply and precisely performed even with thin wires. However, when the coatings of wire enamel are not decomposable with molten solder, this method is useless.

Of these methods for insulation removal, method (3) (chemical removal) and method (4) (removal with solder) have process advantages in that they permit the processing of a large number of wires at one time and can be automated and performed on an assembly line. Method (4) is considered the most useful because solder adheres to the conductors at the time of the removal of the insulation, and the removal of the insulation and the soldering of the wires can be simultaneously accomplished. This capability of being removed by solder is called solderability, and is one of the characteristics which is desired of insulated wire by electrical machinery manufacturers.

As has been stated hereinabove, insulated wires desirably should be not only attenuated and have improved thermal- and chemical-resistance, but should also be processable on an assembly line for the removal of the insulation. However, improvement in thermal-resistance and chemical-resistance is quite inconsistent with the removability of the insulation on an assembly line. Methods for attaining removability of insulation on an assembly line are method (3) (chemical removal) and method (4) (removal by solder). However, the higher the chemical-resistance of the insulation, the more stable is the insulation to chemicals, making it difficult to remove the insulation with chemicals. Furthermore, when wires are made thermally resistant, the insulation becomes thermally stable, and cannot be completely decomposed in molten solder, but remain carbonized, in which case the soldering of the wires becomes difficult. With solderable wires, the insulation is usually easily decomposed and separated when the molten solder is at a temperature of about 360 to 400°C, and solder is adhered to the conductors. However, with thermally stable wires, the insulation is not completely decomposed even when the temperature of the molten solder is increased to a temperature as high as 500°C, with the result that the insulation is carbonized and covers the conductors. To decompose the insulation by further increasing the temperature of the molten solder would not only be dangerous, but would also cause the copper of the conductors to diffuse into the solder and thus make the conductors thinner. Consequently, the conductors tend to break at the soldered joint or, with thin wires, the conductors would be lost entirely.

The time during which the insulated wires are dipped in a molten solder bath is preferably as short as possible. If this treatment is carried out for a long period of time, it causes troubles during continuous production, and there is a bad effect upon the insulation near the solder bath because of heat conducted through the conductor. Moreover, the copper of the conductor gradually diffuses into the solder bath and the conductor becomes thin and easily broken. Accordingly, it is preferable that the temperature of the solder is lower and the period of dipping in the solder is shorter.

Thus, when soldering thermostable magnet wires having a diameter of 1 mm, it is preferable to use a bath temperature of below 450°C and an immersion time of less than 10 seconds and preferably of less than 5 seconds.

Some makers of electrical apparatus allow soldering at a high temperature for a long period of time because of the ease of soldering, but a treatment at a high temperature for a long period of time naturally has limitations. For example, in the case of soldering a conductor having a diameter of 1 mm at a temperature of 480°C, the period of time available for soldering is at most 30 seconds, because soldering at 480°C poses difficulties in continuous production, if the treatment period is longer than 30 seconds. Furthermore, as mentioned above, at this temperature heat conducted through the conductor has a bad effect upon the insulation near the solder bath, and, most importantly, the copper of the conductor diffuses into the solder and the conductor becomes thin and is easily broken. Thus, satisfactory joints cannot be obtained.

On the other hand, it is impossible not only to solder thermostable magnet wire known at present at less than 450°C for less than 10 seconds, but also at less than 480°C for less than 30 seconds.

Such being the case, improvements in thermal-resistance and chemical-resis-

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tance are in direct opposition to the removal of the insulation on an assembly line. Thus, when it is strongly desired to improve the thermal-resistance and chemical-resistance of insulated wires, the insulation must be removed by a mechanical method or a heat-decomposition method, and no attempt to perform either of these removal operations on an assembly line can be made. Since mechanical removal of the insulation of thin wires is difficult, it has been necessary to rely on the heat-decomposition method in spite of the possible adverse effects on portions of the wires other than the coil ends. Conversely, when it is desired to perform the removal of the insulation on an assembly line, the thermal-resistance and chemical-resistance of the wires cannot but be sacrificed. In recent years, however, attenuation of wires and cables has been attempted to a greater extent, and because of the demand for automation, there has been a strong desire for thermostable insulated wires having solderability. More recently, as a result of fires in colour television sets in the USA, fire retardancy of the wires has become increasingly desirable.

Examples of thermostable materials now in widespread use are polyimides, polyamide-imides, and isocyanurated polyesterimide materials. When these materials are used for insulated wires, they have superior cut-through resistance and heat-resistance as well as good fire-retardance and chemical-resistance. However, these superior properties make the removal of the insulation even more troublesome and time-consuming. When these materials are dipped in chemicals, they are not decomposed within a short period of time, and when immersed in a solder bath at a temperature as high as 500°C, they are carbonized and adhere to the conductor, making it impossible for the solder also to adhere to the conductor. This is clearly demonstrated, for example, by Comparative Examples 1, 2, 3 and 5 to be given hereinafter. Accordingly, the removal of insulation can at present be performed only by mechanical cutting of the insulation or burning it away with a flame, and this is a great drawback to the performance of this operation on an assembly line. In addition, as stated previously, the above methods are substantially useless for treating thin wires, and do not comply with the current trend for attenuating insulated wires. Accordingly, these materials are used mainly for wires of medium to large sizes, and only in applications which require high thermal-resistance.

One of the insulating materials which have recently come into widespread use is a thermosetting polyester, but this material has low thermal stability and does not exhibit satisfactory fire-retardancy, a property which has been of greater concern lately. An attempt to enhance the thermal properties of the polyester by increasing the amount of cross-linking improves the thermal properties that are effective over a short period of time (such as cut-through resistance), but makes, because of its chemical structure, only a limited improvement in the thermal properties that are effective over a long period of time (such as dielectric breakdown after heat degradation). This material can be decomposed with an alkali, but those thermosetting polyesters which have improved thermal stability take a longer time to decompose. Generally, polyesters have poor solderability, and even when they are immersed in a solder bath for prolonged periods of time, the carbonized insulation frequently remains attached to the conductors. This will be clear from Comparative Example 4 to be given hereinafter. Accordingly, polyesters are not completely satisfactory as insulating materials in application which require both solderability and thermal stability.

Polyurethanes are well known as insulating materials having solderability, and are popular among electrical machinery manufacturers because they are solderable at a relatively low temperature of 360 to 400°C and can be easily processed on an assembly line. However, polyurethanes have poor thermal-resistance which is classified at best as Class B (a thermal rating according to the criterion given in JIS C-4003, corresponding to IEC Publication 85). Furthermore, since they are combustible, they do not meet the requirements for modern insulating materials. However, polyurethane insulating materials are still popular among manufacturers, because they permit easy insulation removal on an assembly line, and this advantage is especially great with attenuated wires. In other words, polyurethane insulating materials have process advantages and are readily available especially in the case of attenuated wires, and a demand to render them thermally stable and fire-retardant has arisen.

To use other insulating materials, the course of the manufacturing process must be changed and the consequent increase in the number of process steps requires an increase in manpower or equipment. It is for this reason that the change

to thermally stable materials has not been made, and even now, polyurethane materials are in widespread use.

Thus, none of the known insulating materials have a combination of solderability, thermal stability and fire retardance, and there has been an increasing demand for these materials in recent years.

On the other hand, the performance requirements for magnet wire have recently become more and more severe and complex. For example, now that the makers of electrical apparatus intend to introduce high speed automatic winding apparatus, it is desirable that the wires can endure the mechanical stress imposed by automatic winding at a high speed. Furthermore, insulated wire for use in refrigerant of a refrigerator or a cooler is required to have a refrigerant-resisting property; insulated wire for use in a steam atmosphere is required to have moisture-proof thermostability; insulated wire which is to be subjected to a rapid thermal load is required to have heat-shock resistance and over-load resistance; and insulated wire which is to be in contact with solvents is required to have an anti-crazing property; also of course, thermostability, that is thermal life, is always required. Polyimide insulated and polyamide-imide insulated wire have sufficient thermostability and other properties to meet the above-described requirements.

However, as is known, polyimide-insulated and polyamide-imide insulated wire are very expensive and meet the above-described requirements unnecessarily well. Accordingly, it is not necessary to use polyimide-insulated or polyamide-imide insulated wire.

Recently, insulated wires have been developed that satisfy the above-described requirements without being too good for the purpose and are not so expensive: these are multi-layer wires composed of a combination of insulating materials which provide the characteristics of each insulating material.

As multi-layer magnet wires which have good properties and are widely used, there are those that have an under insulating layer formed on a conductor and an over insulating layer formed thereon, said under insulating layer being formed by applying a polyimide wire enamel or a polyamide imide wire enamel to the conductor and baking, and said over insulating layer being formed by applying another wire enamel (e.g., polyester wire enamel or polyester-imide wire enamel) and baking; and insulated wires which comprise a polyimide insulating layer or a polyamide-imide insulating layer as an over layer and another insulating layer as an under layer (e.g., a polyester insulating layer or polyester-imide insulating layer). These insulated wires have a characteristic that the inferior properties of the polyester insulating layer or the polyester-imide insulating layer are compensated by the excellent thermal, electrical, mechanical and chemical properties of the polyimide insulating layer or the polyamide-imide insulating layer. Furthermore, since a sufficient effect is obtained even if the polyimide insulating layer or the polyamide-imide insulating layer is thin, the wires are not expensive as compared with the polyimide insulated wires or the polyamide-imide insulated wires. However, the cost thereof is of course slightly higher than that of wire insulated with only one insulating material (e.g., polyester or polyester-imide). The characteristics of these multi-layer insulated wires will now be described in greater detail.

The polyimides or the polyamide-imides which are known as thermostable insulating materials are effective for improvement of thermal properties. For examples, with respect to heat-shock resistance, although polyester insulated wires exhibit cracking when heated at a temperature of 150°C for 2 hours when wound at 3-fold diameter, insulated wires having a polyamide-imide insulating layer or a polyimide insulating layer on a polyester insulating layer do not exhibit cracking even at 180°C under otherwise the same conditions. Furthermore, an improved over-load resistance and thermal life are observable in insulated wire having a multi-layer structure. With respect to mechanical properties, although the life of polyester insulated wire, subjected to repeated scrape abrasion, is 40 cycles or so, that of insulated wire having a multi-layer insulation comprising a polyamide-imide insulating layer as the over layer is 80 cycles or more. With respect to chemical properties, a polyester is easily hydrolyzed if used in a moist atmosphere because it has ester bonds, and thus has an inferior moisture-proof thermostability. Furthermore, a polyester-imide exhibits crazing by varnish solvents if it is brought into contact with a varnish.

These faults can be overcome by combining a polyimide or a polyamide-imide so as to form a multi-layer structure. Accordingly, it is possible remarkably to improve the properties by forming a multi-layer structure using a polyimide or a polyamide-imide and recently these multi-layer magnet wires have been widely used.

Such magnet wires however have the fault that it is difficult to remove the

polyimide or polyamide-imide insulation: chemical removal is substantially impossible to carry out because the polyimides or the polyamide-imide are stable to chemicals; and the solder removal method is also impossible to carry out on such multi-layer insulated wires which incorporate a thermostable polyimide or polyamide-imide.

Accordingly, there has been required a method of easily and continuously removing from multi-layer insulated wires insulation that is composed for reasons of properties and cost of a combination of a polyimide insulating material or a polyamide-imide insulating material and another insulating material (e.g. polyester or polyester-imide).

As the result of many studies on meeting these requirements, we have arrived at the present invention according to which there is provided a solderable and thermostable insulated wire which comprises a conductor having an insulating under layer formed by applying thereto a coating of a polyester-imide wire enamel (which may include polyester-imide or polyesteramide-imide) and baking the applied coating, said polyester-imide wire enamel having 5-membered imide rings and ester bonds in the molecule and comprising the reaction product of A) a dibasic carboxylic acid free of 5-membered imide ring, a derivative thereof or a mixture thereof, B) a dibasic carboxylic acid which has at least one 5-membered imide ring, a derivative thereof or a mixture thereof, C) a tri- and/or higher polyhydric aliphatic alcohol and D) a dihydric alcohol, and an insulating over layer formed by applying a polyimide wire enamel or a polyamide-imide wire enamel to said under layer and baking.

Such polyester-imide wire enamels for use in the present invention are described and claimed in our co-pending Application No. 60312/74.

The present invention will now be discussed in greater detail. Since insulated wire according to the present invention has a multi-layer structure comprising a combination of a layer of a polyester-imide insulating material and of a polyimide insulating material or polyamide-imide insulating material, it has excellent thermal, mechanical, electrical and chemical properties as well as excellent solderability. Polyester-imides are, of course, fire-retardant thermostable materials belonging to Class F. As described above, it was previously believed that solderability was incompatible with thermostability because they are opposed properties. Accordingly, it was supposed that it would be impossible to solder wire coated with polyester-imide which is in Class F and which has higher thermostability than that of thermosetting polyester which is only in Class B and wire coated with which cannot be soldered.

Moreover, it has not previously been considered possible to impart solderability to a multi-layer insulated wire having a polyamide or polyamide-imide insulation layer on account of the excellent thermostability of these materials and indeed there is not multi-layer insulated wire having excellent thermostability and which can be soldered. Accordingly, improvement of the solderability of such multi-layer insulated wire has not been attempted and only methods of continuously treating the insulation in order to remove it have been studied and many such studies have been made. For example, removal agents for decomposing the insulating film have been examined. However, since the polyimide and polyamide-imides are stable to chemicals, viable removal agents have not been found. If such removal agents should be developed, the handling thereof will be attended with danger and the conductor will suffer from chemical changes. Furthermore, fusion has been attempted with a view to causing heat decomposition of the insulating film at a high temperature. However, this method is not only dangerous, but also has a deleterious effect upon the insulating layers.

However, we have discovered a viable method for removal of the insulation from insulated wire, the insulation having a multi-layer structure and being composed of a combination of a polyester-imide insulating material and a polyimide or a polyamide-imide insulating material, which is in fact a method of imparting solderability which has previously been believed to be impossible and investigation of which has therefore been disregarded.

In the insulated wire according to the present invention, the characteristics of the polyester imide insulating material forming the insulating under layer are effectively utilized by combining it with a polyimide or polyamide-imide insulating over layer which compensates for defects of the polyester-imide under layer. Consequently, the insulated wire of the present invention has excellent thermal properties e.g., heat deterioration life, over-load resistance, heat-shock resistance and cut-through resistance; excellent mechanical properties e.g., abrasion-resistance and windability;

excellent chemical properties e.g., alkali-resistance, anticrazing property, refrigerant-resisting property and moisture-proofing thermostability; and excellent electrical properties, while retaining non-flammability. Especially, the poor anti-crazing property which is a significant defect of polyester-imide insulating materials is effectively improved. Further, the windability is remarkably improved. A characteristic of the present invention is therefore to impart solderability while displaying the above-described excellent thermal, mechanical, chemical and electrical properties.

In the present invention, the solderability is imparted by, and is entirely dependent on the presence of, the polyester-imide insulating layer.

In multi-layer insulated wire, the materials of the over layer and under layer are chosen according to the characteristics desired, and in many cases the material of the over layer can be interchanged with that of the under layer. However, in the present invention, the polyester-imide insulating layer must constitute the under layer and the polyimide or polyamide-imide must constitute the over layer. In the reverse case, the solderability is lost although the other properties do not deteriorate. This is because the solderability depends upon the kind of insulating material forming an interface with the conductor. By forming a solderable polyester-imide insulating layer as the under layer, it becomes possible to carry out soldering even if a non-solderable polyimide or polyamide-imide insulating layer is present as an overlayer, because the under layer is decomposed and removed from the conductor during soldering and thus the over layer is also removed.

In the reverse case, although a solderable polyester-imide insulating layer present as an over layer is decomposed and removed during soldering, a non-solderable polyimide or polyamide-imide insulating layer as the under layer does not decompose or, if decomposed, is carbonized. Thus it is impossible to carry out soldering, because the non-decomposed layer or carbonized material adheres to the conductor and cannot be removed therefrom.

Solderable and thermostable insulated wire for general use falls within the scope of the present invention, however, a preferred range of components A), B), C) and D) can be selected within the scope of the present invention so as to satisfy the many characteristics required of magnet wire.

For magnet wire, it is preferred to use polyester-imide wire enamel which mainly comprises the reaction product of the components when the equivalent proportion of component A) is from 5 to 55 equivalent %, of B) from 10 to 60 equivalent %, and of C) from 35 to 55 equivalent %, based on the sum of A), B) and C), in order to produce the insulating under layer. The equivalent proportion of component D) fulfils the condition: $\text{Equivalent \% D)} \geq \text{Equivalent \% (A+B+C)}$. This preferred range of equivalent proportions is represented in the ternary composition diagram shown in the accompanying drawing by the area E—F—G—H—E.

If the proportion of component A) is less than 5 equivalent %, difficulties occur in the synthesis of the wire enamel and in the production of insulated wire; if the proportion of component B) is less than 10 equivalent %, the heat-shock resistance becomes inferior; if the proportion of component C) is less than 35 equivalent %, the cut through resistance becomes inferior; and if the proportion of the component C) exceeds 55 equivalent %, the flexibility is somewhat impaired. These disadvantages do not occur when the components A), B), C) and D) are present in the above-described range.

In recent years, many different properties have been required of magnet wire and this tendency will continue in the future and this is true generally of solderable and thermostable insulated wire. For example, with regard to thermostability, it is assumed at present that it would be sufficient if soldering could be carried out within 30 seconds at 480°C in the case of a wire having a diameter of 1 mm, because no solderable and thermostable wire now exists to meet these requirements. However, more exacting requirements for shortening the period of soldering time, and decreasing the soldering temperature, as much as possible will soon appear in the field of electrical apparatus. Furthermore, with regard to the heat-shock resistance, it is usually sufficient if wire wound at 3-fold diameter withstands 200°C for 2 hours, since magnet wire is not wound on articles having so small a diameter and the temperature obtaining in the apparatus is not as high. Nevertheless better resistance will be required. Again, with respect to the heat-resisting life, it will be thought desirable to meet the conditions of Class F comfortably and the same will be true of other properties.

There will now be described the most preferred range of components A), B), C) and D), by use of which many properties required of magnet wire, such as better solderability, better thermostability and low cost, are obtained: The polyester-imide

wire enamel used for forming the under insulating layer most preferably comprises the reaction product of components A), B), C) and D) when the equivalent proportion of component A) is from 10 to 40 equivalent %, of B) is from 20 to 50 equivalent %, and of C) is from 40 to 55 equivalent %, based on the sum of A), B) and C) and the equivalent proportion of D) fulfils the above condition, as represented by the area I—J—K—L—I, in the composition diagram shown in the accompanying drawing.

If the proportion of component A) is less than 10 equivalent %, component B) is of course present in a larger proportion. Consequently the cost of the product rises, because component B) is expensive, and the resultant product lacks flexibility.

If the proportion of component B) is less than 20 equivalent %, the product cannot be expected to have good heat-shock resistance or good solderability: although it is possible to obtain good results at 200°C for 2 hours for wire wound at three times its diameter, it is not possible to obtain good results under these conditions for wire wound at its own diameter. Furthermore, although soldering can be carried out at 480°C within 30 seconds in the case of a conductor having a diameter of 1 mm, it cannot be carried out at 450°C within 10 seconds.

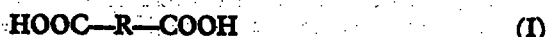
When the proportion of the component C) is less than 40 equivalent %, there is the disadvantage that dielectric breakdown tends to occur after heat aging; and when the proportion of the component C) exceeds 55 equivalent %, the resulting product is lacking in plasticity.

Accordingly, the most preferred range is that described above.

In the following, the polyester-imide wire enamel of the present invention will be illustrated.

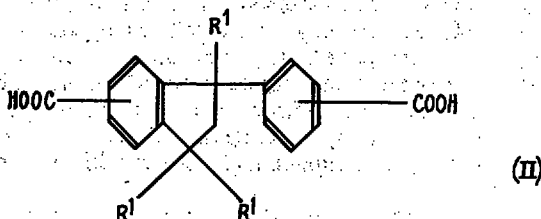
The components A), B), C) and D) do not necessarily represent the starting materials *per se* used in producing the insulation coating, but rather represent the essential nature of constituents that exert effects on the characteristics of the insulated wire. Accordingly, the components A) and B) are characterized as carboxylic acids or their derivatives or mixtures thereof, and the components C) and D) are characterized as alcohols. However, the reaction product may be used in various ways, for example, by using the reaction product of each by using a product obtained by decomposing this reaction product, by using materials before forming the reaction product or by using a precursor thereof.

With respect to component A), the divalent carboxylic acid may be an aromatic, aliphatic or alicyclic dicarboxylic acid, with an aromatic dicarboxylic acid being preferred. The class of dicarboxylic acid may be expressed by the general formula



in which R is a divalent group containing at least two carbon atoms. Examples of aromatic dicarboxylic acids are isophthalic acid, terephthalic acid, 1,2-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 1,7-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, diphenyl-2,2'-dicarboxylic acid, diphenyl-2,3'-dicarboxylic acid, diphenyl-2,4'-dicarboxylic acid, diphenyl-3,3'-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, diphenylmethane-2,2'-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylethane-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, and diphenyl-2,2-propane-4,4'-dicarboxylic acid.

The alicyclic dicarboxylic acids which are suitable also include those expressed by the following general formula (II):



wherein R¹ is a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, preferred examples of which are given hereinafter. Examples of alicyclic dicarboxylic acids of formula (II) are 3-(4-carboxyphenyl)-5-indanecarboxylic acid, 3-(3-carboxyphenyl)-5-indanecarboxylic acid, 3-(3-carboxyphenyl)-1,1,3-triethyl-6-

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indanecarboxylic acid, 3-(4-carboxyphenyl)-1-methyl-1,3-dipropyl-5-indanecarboxylic acid of 3-(4-carboxyphenyl)-1-methyl-1,3-diethyl-6-indanecarboxylic acid. Examples of aliphatic dicarboxylic acids are adipic acid, succinic acid, maleic acid, sebacic acid, isosebacic acid and dimerized unsaturated fatty acid.

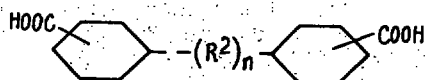
Alicyclic dicarboxylic acids of the general formula



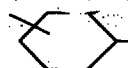
in which



is a cyclohexyl group or



in which



is a cyclohexyl group, R^2 is $-O-$, $-CH_2-$, $-(CH_2)_2-$, $-C(CH_3)_2-$, $-SO_2-$, $-Si(CH_3)_2-$ or



and n is a positive integer may also be used. Examples of these dicarboxylic acids are hexahydroisophthalic acid (*cis*- and *trans*- or a mixture thereof), hexahydroterephthalic acid (*cis*- and *trans*- or a mixture thereof), and bicyclo[2,2,2]octane-1,4-dicarboxylic acid.

The derivative may be an ester, such as a lower dialkyl ester of the above carboxylic acid, for example, dimethyl terephthalate, diethyl terephthalate, dipropyl terephthalate, dibutyl terephthalate, diamyl terephthalate, dihexyl terephthalate or dioctyl terephthalate, when the carboxylic acid is terephthalic acid. A half-ester of such a carboxylic acid such as monomethyl terephthalate is also suitable. Other derivatives include the dihalides of the above carboxylic acids, such as the carboxylic acid dichlorides, and the acid anhydrides of these carboxylic acids, such as phthalic anhydride. These carboxylic acids and their derivatives may be used either alone or as a mixture.

Terephthalic acid, isophthalic acid, or their derivatives, or those derived by replacing a portion of these by another carboxylic acid or its derivative are especially preferred as component (A).

As long as the effects of the present invention are not reduced, component (A) may be replaced in part by a polybasic carboxylic acid which is tribasic or higher or by its derivatives. Examples of such a polybasic carboxylic acid or its derivative are trimellitic acid, trimellitic anhydride, hemimellitic acid, hemimellitic anhydride, trimesic acid and trimesic anhydride.

Component (B) is a dibasic carboxylic acid containing a five-membered imide ring or a mixture thereof, but as long as the effects of the present invention are not reduced, a portion of component (B) can be replaced by a polybasic carboxylic acid containing a five-membered imide ring which is tribasic or higher, or its derivative or its mixture. The dibasic or higher carboxylic acid containing a five-membered imide is obtained by reacting a compound (1) below with a compound (2) below, or by reacting a compound (1) below with a compound (3) below.

(1) An aromatic carboxylic anhydride containing a five-membered cyclic carboxylic anhydride group and at least one reactive group, which can be a carboxyl group or a carboxylic anhydride group. Instead of the cyclic carboxylic anhydride group, two carboxyl groups bonded to adjacent carbon atoms or esters or half-esters thereof, or as long as an imide group can be formed, half-amides with a primary amine described in (2) below, can also be used.

(2) A primary amine containing a primary amino group and at least one other reactive group, which can be a carboxyl group or a primary amino group. Instead of the primary amine, a salt of the amine, an amide, a lactam or a polyamide may be used so long as the primary amino group bonded can contribute to the formation of an imide.

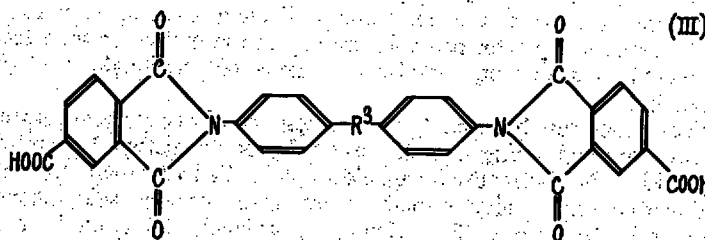
(3) A polyisocyanate compound.

Examples of the compound (1), which contains a cyclic carboxylic anhydride group and another functional group, are tricarboxylic acid anhydrides such as trimellitic anhydride, hemimellitic anhydride, 1,2,5-naphthalenetetracarboxylic anhydride, 2,3,6-naphthalenetetracarboxylic anhydride, 1,8,4-naphthalenetetracarboxylic anhydride, 3,4,4'-diphenyltricarboxylic anhydride, 3,4,4'-diphenylmethanetetracarboxylic anhydride, 3,4,4'-diphenylethertricarboxylic anhydride or 3,4,4'-benzophenonetetracarboxylic anhydride; and tetracarboxylic dianhydrides such as pyromellitic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,8,4,5-naphthalenetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 3,3',4,4'-diphenyltetracarboxylic dianhydride, 2,2',3,3'-diphenyltetracarboxylic dianhydride, 3,3',4,4'-diphenylethertetracarboxylic dianhydride, 3,3',4,4'-diphenylmethanetetracarboxylic dianhydride or 3,3',4,4'-benzophenonetetracarboxylic dianhydride. Trimellitic anhydride is especially preferred.

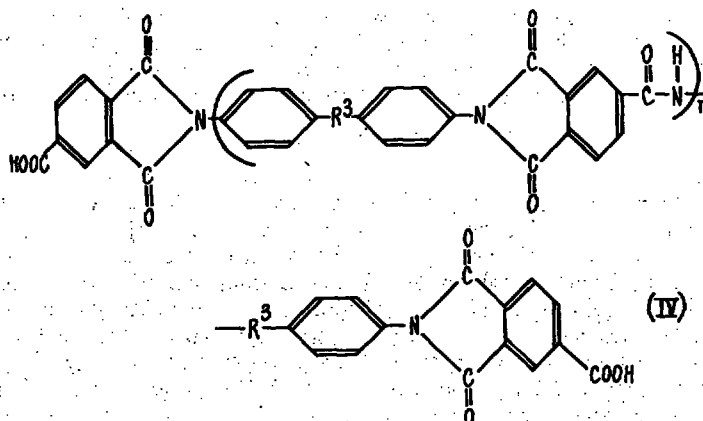
Examples of the compound (2) which contains a primary amino group and other functional groups are primary diamines such as 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl, 1,4-diaminonaphthalene, *m*-phenylene diamine, *p*-phenylene diamine, α,ω -nonamethylene diamine, 1,7-dimethylheptamethylene diamine, 4,4'-diaminodiphenyl ketone, bis-(4-aminophenyl)- α,α' -*p*-xylene, tolylene diamine, xylylene diamine, hexamethylene diamine, ethylene diamine, 4,4'-dicyclohexylmethane diamine or diaminodiphenylsulfone; and amino carboxylic acid such as glycoglycol (glycine), aminopropionic acid, aminocaproic acid or aminobenzoic acid.

Examples of the polyisocyanate compound (3) are mononuclear polyisocyanates such as *m*-phenylene diisocyanate, 2,4-tolylene diisocyanate or 2,6-tolylene diisocyanate; aromatic polyisocyanates having a number of rings or a fused ring, such as diphenyl ether-4,4'-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, diphenylsulfone-4,4'-diisocyanate, diphenylthioether-4,4'-diisocyanate or naphthalenediisocyanate; polymethylenepolyphenylene polyisocyanate, hexamethylene diisocyanate xylylene diisocyanate; and blocked isocyanates obtained by stabilizing the isocyanate groups of these polyisocyanates with, for example, a phenolic hydroxyl group.

The most preferred dibasic carboxylic acids containing a five-membered imide ring are those of the following general formula (III):



wherein R^3 is $-\text{CH}_2-$, $-\text{O}-$ or $-\text{SO}_2-$, which are obtained from 2 mols of trimellitic anhydride and 1 mol of either 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl ether, diphenylmethane-4,4'-diisocyanate, diphenylether-4,4'-diisocyanate or diphenylsulfone-4,4'-diisocyanate; and those of the following general formula (IV):



wherein R is $-\text{CH}_2-$, $-\text{O}-$ or $-\text{SO}_2-$, and n on average is preferably greater than 0 but not more than 4, which are obtained from 2 mols of trimellitic anhydride and 1 to 2 mols of either 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, diphenylmethane-4,4'-diisocyanate, diphenylether-4,4'-diisocyanate or diphenylsulfone-4,4'-diisocyanate.

In the compound (1) above, a part of the aromatic carboxylic anhydride may be replaced by a dicarboxylic acid to form an amide bond. Furthermore, it is possible to react 1 mol of a dicarboxylic acid or its derivative (e.g., the acid halide) with 0.5 to 1 mol of a diamine to form a diamine having a terminal amino group and use the product as (2). Alternatively, it is possible to use a diamine having an amide group in the molecule as (2). The dicarboxylic acid, referred to herein, is, for example, terephthalic acid, isophthalic acid or a phenylindanedicarboxylic acid of the general formula (II) such as 3-(4-carboxyphenyl)-5-indanecarboxylic acid, 3-(3-carboxyphenyl)-5-indane carboxylic acid, 3-(3-carboxyphenyl)-1,1,3-triethyl-6-indanecarboxylic acid, 3-(4-carboxyphenyl)-1-methyl-1,3-dipropyl-5-indanecarboxylic acid or 3-(4-carboxyphenyl)-1-methyl-1,3-diethyl-6-indanecarboxylic acid; phthalic acid; phthalic anhydride; hexahydroterephthalic acid; hexahydroisophthalic acid; adipic acid; succinic acid; maleic acid; sebacic acid; isosebacic acid; dimeric acid; tetrachlorophthalic acid; hexachloroendomethylene tetrahydrophthalic acid; 4,4'-dicarboxy-diphenylmethane; 4,4'-dicarboxy-diphenylpropane; and benzophenonedicarboxylic acid. The derivative thereof can be the acid dihalides of these dicarboxylic acids, such as the acid dichloride.

These polycarboxylic acids containing a five-membered imide ring can be obtained by reacting a compound (1) with a compound (2) or by reacting a compound (1) with a compound (3) in the presence or absence of a solvent. In the reaction of the compound (1) with the compound (3), a small amount of a solvent as exemplified below is used and if desired, a small amount of an isocyanate activating catalyst is added; and the reaction is performed substantially in the molten or solid state although it can be effected in a solvent, thereby to form a polycarboxylic acid containing a five-membered imide.

The solvent that can be used for preparing the above polycarboxylic acid containing a five-membered imide can, for example, be N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, N,N-diethylformamide, N,N-diethylacetamide, dimethyl sulfoxide, N-methylcaprolactam, cresolic acid, phenol, o-cresol, m-cresol, p-cresol, 2,3-xyleneol, 2,5-xyleneol, 2,6-xyleneol, 3,4-xyleneol or 3,5-xyleneol. An aliphatic hydrocarbon, an aromatic hydrocarbon, a halogenated hydrocarbon, an ether, a ketone and an ester can also be used; specific examples of these include benzene, toluene, xylene, ethylbenzene, diethylbenzene, isopropylbenzene, petroleum naphtha, coal tar naphtha, solvent naphtha, acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl acetate and ethyl acetate.

These solvents can be used either alone or as a mixture.

The derivatives of the above polycarboxylic acids containing a five-membered imide ring are, for example, their esters or acid halides. As component (B) not only one of the above-exemplified polycarboxylic acids or the derivatives thereof, but also a mixture of these, can be used.

The aliphatic polyhydric alcohol which is trihydric or higher used as component (C) is an alcohol having neither an aromatic nor a heterocyclic ring at any position of the molecule. Examples of such polyhydric alcohols are glycerol, pentaerythritol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane sorbitol, mannitol, dipentaerythritol, diglycerol and 1,2,6-hexanetriol.

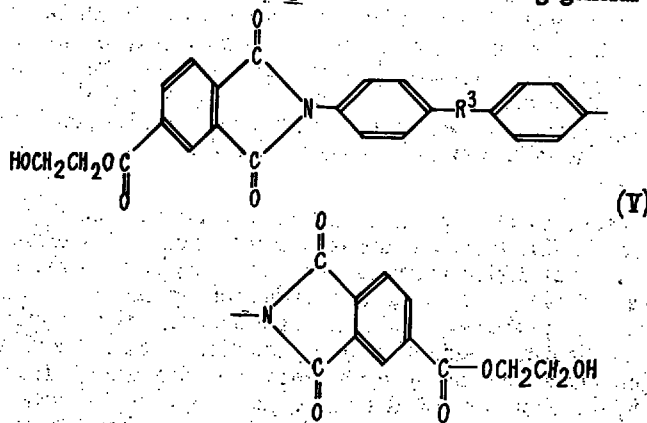
As long as the effects of the present invention are not reduced, a portion of the aliphatic polyhydric alcohol as component (C) may be replaced by an alcohol containing an aromatic ring or heterocyclic ring which is trihydric or higher. Examples of these other alcohols are tris-(β -hydroxyethyl)isocyanurate, and tris-(β -hydroxypropyl)isocyanurate. However, since this aromatic or heterocyclic polyhydric alcohol remarkably reduces the solderability of the insulated wire, it is not preferred to replace a portion of component (C) by it. Even if this replacement is made, only a small portion of component (C) should be replaced, and it is preferred that component (C) be composed substantially solely of the aliphatic polyhydric alcohol described above.

Examples of dihydric alcohols suitable as component (D) are ethylene glycol, diethyleneglycol, triethylene glycol, 1,2-propylene glycol, 1,3-propanediol, butanediol-1,3 or 1,4, pentanediol-1,5, hexanediol-1,6, butene-2-diol-1,4 or 2,2-dimethylpropanediol-1,3; 2-ethyl-2-butyl-propanediol-1,8; 1,4-dimethylolcyclohexane; butenediol-1,4; hydrogenated bisphenols (for example, hydrogenated *p,p'*-dihydroxydiphenylpropane or its homologues), cyclic glycols such as 2,2,4,4-tetramethyl-1,3-cyclobutanediol, hydroquinone-di- β -hydroxyethyl-ether, 1,4-cyclohexanedimethanol, 1,4-cyclohexane diethanol diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, trimethylene glycol, hexylene glycol or octylene glycol.

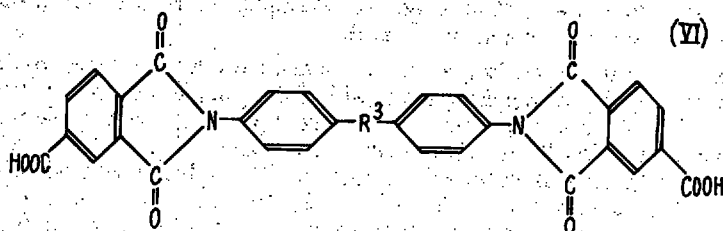
As previously described, these components (A), (B), (C) and (D) are the most basic forms of the constituent starting materials that affect the characteristics of the insulating wire. Accordingly, in the manufacture of wire enamels, the materials can be used in various forms, such as in the form of the reaction products thereof, products obtained by the decomposition of the reaction products, the starting materials before the formation of such components or the precursors of such.

Some examples will be given hereinafter as to the form of the starting materials. One example of using a reaction product is to use a reaction product between components (A) and (D), such as bis-(hydroxyethyl) isophthalate or bis-(hydroxyethyl) terephthalate. The bis-(hydroxyethyl) terephthalate is sometimes used as a material for the production of a wire enamel. However, in the present invention, this is considered to be composed of components (A) and (D) as the dihydric alcohol (D) only. In this case, for example, component (A) is terephthalic acid and component (D) is ethylene glycol.

It is also possible to use a compound of the following general formula (V):



wherein R^3 is $-\text{CH}_2-$, $-\text{O}-$ or $-\text{SO}_2-$, which is a reaction product of components (B) and (D). Like the first example set forth, this may also be considered as a dihydric alcohol from a structural viewpoint, but for the purposes of the present invention, it is considered to be composed of the components (B) and (D), and not as the dihydric alcohol (D) only. In this case, component (B) is expressed, for example, by the following general formula (VI):



and component (D) is ethylene glycol.

Exemplary of the case of using a decomposed reaction product is the use of a product obtained by decomposing a reaction product of (A) and (D). A high-molecular-weight linear polyester or a decomposition product thereof can also be used. The high-molecular-weight straight-chain polyester may be, for example, polyethylene terephthalate, polyethylene isophthalate, polyethylene isophthalate-terephthalate co-ester, polytetramethylene isophthalate, polytetramethylene terephthalate, polyethylene adipate, poly(1,4-cyclohexanedicarbinyl terephthalate), poly(1,4-cyclohexanedicarbinyl isophthalate) or polyethylene terephthalatephenylindanedicarboxylate co-ester. These linear polyesters are produced on a large commercial scale as resins for fabricating fibres or films and are readily available. The wastes which occur during the manufacture or processing of these polyesters can also be used. The use of such a material is very effective and advantageous from a commercial standpoint.

In this case also, the material used is considered to be composed of components (A) and (D). For example, even when both end groups of the polyethylene terephthalate are hydroxyl groups, it is not considered to be a dihydric alcohol (D) only but to be composed of components (A) and (D). In this case, component (A) is, for example, terephthalic acid and component (D) is ethyleneglycol.

As an example of using the materials before the formation of components (A), (B), (C) and (D), there may be cited the use of compounds (1) and (2) or (1) and (3) in a solvent or in the absence of a solvent, as described above with respect to the component (B). These materials may be used in the form that exists before the formation of a five-membered imide by reacting compounds (1) and (2), that is in the form of an amido acid as a precursor.

Thus, each of the components can be used in various forms, and one or more than one compound in admixture can be used as each of these components. The reaction sequence employed is also optional.

The resin obtained by reacting components (A), (B), (C) and (D) is dissolved in a solvent to form wire enamel. Examples of suitable solvents are solvents containing a phenolic hydroxyl group such as phenol, *o*-cresol, *m*-cresol, *p*-cresol, *o*-ethylphenyl, *m*-ethylphenol, *p*-ethylphenol, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 2,6-xyleneol, 3,4-xyleneol, 3,5-xyleneol, *o*-*n*-propylphenol, 2,4,6-trimethylphenol, 2,3,5-trimethylphenol, 2,4,5-trimethylphenol, 4-ethyl-2-methylphenol, 5-ethyl-2-methylphenol, and cresolic acid; and polar solvents such as *N,N*-dimethylacetamide or *N*-methyl-2-pyrrolidone. As a diluent, an aliphatic hydrocarbon, an aromatic hydrocarbon or a halogenated hydrocarbon, an ether, an acetal, a ketone or an ester may be used. Examples of aliphatic hydrocarbons and aromatic hydrocarbons are *n*-heptane, *n*-octane, cyclohexane, decalin, dipentene, pinene, *p*-menthane, decane, dodecane, tetradecane, benzene, toluene, xylene, ethylbenzene, diethylbenzene, isopropylbenzene, amylbenzene, *p*-cymene, tetralin, mixtures of these, petroleum naphtha, coal tar naphtha and solvent naphtha.

The wire enamel so obtained is coated on a conductor and baked to produce an insulated wire. At this time, the use of a small amount of a metal drying agent is useful. Such a metal drying agent can be, for example, an octoate, naphthenate, resinate or linolate of zinc, calcium, lead or cadmium. Specific examples include zinc octoate, cadmium naphthenate, calcium naphthenate, zinc naphthenate, lead naphthenate, lead linolate, calcium linolate, cadmium resinate, and zinc resinate. Manganese naphthenate and cobalt naphthenate are also useful. Instead of, or in conjunction with, the above-described metal dryer, a tetraalkyl titanate or its derivative (a tetraalkyl titanium chelate or tetraalkyl titanium acylate) may effectively be used.

Typical examples of tetraalkyl titanates are tetraisopropyl titanate, tetrabutyl titanate, tetrahexyl titanate, tetramethyl titanate, tetrapropyl titanate and tetraoctyl titanate. Examples of tetraalkyl titanium chelates are the products obtained by reacting tetraalkyl titanates with octylene glycol, triethanolamine or an acetoacetic acid ester. The tetraalkyl titanium acylate may, for example, be a reaction product formed between a tetraalkyl titanate and stearic acid.

A polyisocyanate or an isocyanate regenerated product obtained by blocking the isocyanate group of the polyisocyanate with for example phenol or cresol may be used as a curing agent or cross-linking agent. Examples of the curing agent are 4,4',4''-triphenylmethane triisocyanate (Desmodur R, a trade name of Bayer AG), a cyclic trimer of 2,6-tolylene diisocyanate, a trimer of 4,4'-diphenylmethane diisocyanate, a reaction product obtained from 3 mols of 2,4-tolylene diisocyanate and 1 mol of trimethylol propane, a reaction product formed from 3 mols of 2,6-tolylene diisocyanate and 1 mol of trimethylol propane, a reaction product formed from 3 mols of

2,4-tolylene diisocyanate and 1 mol of trimethylol ethane and the products obtained by blocking the isocyanate group of these isocyanates with phenol or cresol.

As long as the effects of the present invention are not reduced, a polyamide resin, a phenolic resin, a melamine-formaldehyde resin, an epoxy resin, a urea resin or a silicone resin may be used in conjunction with the above-described titanium compound or polyisocyanate (or its derivative).

The term "polyimide wire enamel" in the present specification means those containing polyimide resins (which include imidazopyrrolone) or polyimide precursor resins (which include imidazopyrrolone) as main components. A portion of these resins may be modified by resins commonly used in wire enamels such as epoxy resins, phenolic resins, polyisocyanates or stabilized polyisocyanates. Processes for producing the polyimide resins (including imidazopyrrolone), solutions thereof, polyimide precursor resins (including imidazopyrrolone) and solutions thereof have been described in U.S. Patent Specification No. 3,377,043 and U.S. Patent Specification No. 3,666,709.

An example of a typical process comprises reacting at least one tetracarboxylic dianhydride with at least one polyamine. Examples of the tetracarboxylic acid dianhydride which may be used include pyromellitic acid anhydride and benzophenone tetracarboxylic acid dianhydride. As the polyamine, a diamine, triamine or tetramine is usually used. Preferred triamines are those wherein two amino groups in three amino groups are in positions ortho to each other. Examples of the diamines include 4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenylmethane; examples of the triamines include 3,4,4'-triaminodiphenyl ether and 3-amino-benzidine; and examples of the tetramines include 3,3',4,4'-tetra-aminodiphenyl ether and 3,3'-diaminobenzidine.

The term "polyamide-imide wire enamels" in the present specification means those which contain polyamide-imide resin or polyamide-imide precursor resin as main components. A portion of these resins may be substituted by resins commonly used in wire enamels such as epoxy resins, phenolic resins, polyisocyanates or stabilized polyisocyanates. Processes for producing the polyamide-imide resins, solutions thereof, polyamide imide precursor resins and solutions thereof have been described in U.S. Patent Specifications Nos. 3,355,427; 3,448,068; 3,562,217; and 3,518,230. An example of a typical process comprises reacting at least one acid chloride of tricarboxylic anhydride with at least one diamine. A portion of the acid chloride of tricarboxylic acid anhydride may be substituted by at least one dicarboxylic acid dichloride, at least one tetracarboxylic acid dianhydride or at least one dicarboxylic acid dichloride and at least one tetracarboxylic acid dianhydride. A portion of the above diamine may also be substituted by at least one triamine or at least one tetramine. An example of an acid chloride of tricarboxylic acid anhydride is tetrachloride of trimellitic acid anhydride. Examples of the dichloride of dicarboxylic acid include terephthalic acid dichloride, isophthalic acid dichloride and adipic acid dichloride. Examples of diamines include 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether and *m*-phenylenediamine; an example of the triamine is 3,4,4'-triaminodiphenyl ether; and an example of the tetramine is 3,3',4,4'-tetraaminodiphenyl ether.

Another example of a typical process comprises reacting at least one tricarboxylic acid anhydride with at least one diisocyanate. In this case, a portion of the tricarboxylic acid anhydride may be substituted by at least one dicarboxylic acid, at least one tetracarboxylic acid dihydride, or at least one dicarboxylic acid and at least one tetracarboxylic acid dianhydride. Furthermore, a portion of the diisocyanate may be substituted by at least one tri- or more valent polyisocyanate. An example of the tricarboxylic acid anhydride is trimellitic acid anhydride; examples of the dicarboxylic acids include isophthalic acid, terephthalic acid and adipic acid; examples of the tetracarboxylic acid dianhydride include pyromellitic acid dianhydride and benzophenone tetracarboxylic acid dianhydride; examples of the diisocyanates include diphenylmethane-4,4'-diisocyanate, diphenyl ether-4,4'-diisocyanate, tolylene-diisocyanate, xylylenediisocyanate and hexamethylenediisocyanate; and an example of the polyisocyanate is polymethylene-polyphenylene-polyisocyanate.

One or more of silicones, fluoride type surface active agents and lower molecule weight polyethylenes are preferably added to the polyimide wire enamels or the polyamide-imide wire enamels used for forming the insulating over layer; by addition of these materials, windability can be improved because the friction factor of the insulated wire is decreased.

It is preferred to produce self-bonding magnet wire by forming a self-bonding layer on the insulated magnet wire of the present invention as previously described. Magnet wire customarily fixed by impregnating with a varnish so that the wire is

not released after winding. However, the impregnation treatment requires much time and labour and gives off an offensive smell caused by solvents of the varnish. Therefore, self-bonding magnet wire has recently been developed; the self-bonding magnet wire is bonded by heating the wound wire. Consequently, there is no difficulty with impregnation and no offensive smell because an impregnation treatment is not employed.

Accordingly, by forming a self-bonding layer on the basic insulated wire of the present invention, there can be produced thermostable insulated wire which does not require impregnation before use and from which the insulation may be removed. Examples of self-bonding layers include those produced from polyvinyl butyral, phenoxy resins, polyamides and polysulphones.

The present invention will now be illustrated in greater detail by the following Examples, Reference Examples and Comparison Examples.

Reference 1

Trimellitic anhydride (1921 g, 10 moles) was dispersed in 6000 g. of cresol. A solution of 991 g (5 moles) of 4,4'-diaminodiphenylmethane in 3000 g. of cresol was slowly added dropwise thereto. The temperature was elevated to 150°C over 3 hours and reaction was carried out at that temperature for 3 hours. After cooling, fine light yellow crystals were precipitated which were washed with acetone a few times and then separated by filtration to produce diimide-dicarboxylic acid.

Reference 2

Diimide dicarboxylic acid was produced by the same procedure as an Reference 1 by reacting 1921 g (10 moles) of trimellitic anhydride with 1001 g (5 moles) of 4,4'-diamino-diphenyl ether in cresol.

Reference 3

Imide dicarboxylic acid was produced by the same procedure as in Reference 1 by reacting 1921 g (10 moles) of trimellitic anhydride with 1371 g (10 moles) of *p*-aminobenzoic acid in cresol.

Reference 4

Diimide dicarboxylic acid was produced by the same procedure as in Reference 1 by reacting 1091 g (5 moles) of pyromellitic acid anhydride with 1371 g (10 moles) of *p*-aminobenzoic acid in cresol.

Reference 5

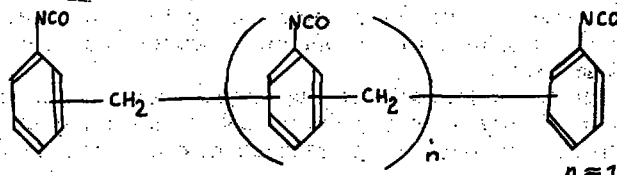
Trimellitic anhydride (384 g, 2 moles) and 250 g (1 mole) of diphenylmethane-4,4'-diisocyanate were mixed with 150 g of solvent naphtha (boiling point: 165—175°C). The mixture was allowed to react at 140°C for 1 hour and at 150°C for 3 hours. As the reaction proceeded, the trimellitic anhydride was dissolved to become a light yellow transparent solution. With further progress of the reaction the solution bubbled and solidified. The resultant solid was milled to produce a dibasic carboxylic acid containing 5-membered imide rings.

Reference 6

N-methyl-2-pyrrolidone (2 g) was added to a mixture of 384 g (2 moles) of trimellitic anhydride and 252 g (1 mole) of diphenyl ether-4,4'-diisocyanate. The mixture was reacted at 120°C for 1 hour and at 140°C for another 1 hour. The resultant homogeneous transparent light yellow solution bubbled gradually and solidified. Then 150 g of solvent naphtha (boiling point: 165—175°C) were added thereto and the mixture was heated at 150°C for 1 hours. The reaction product was milled to produce a dibasic carboxylic acid having 5-membered imide rings.

Reference 7

Solvent naphtha (200 g, boiling point: 150—190°C) was added to a mixture of 384.2 g of trimellitic anhydride and 266 g of polymethylene polyphenylene isocyanate (PAPI, produced by Sumitomo Chemical Co., isocyanate value: 133.5 and having the following formula):



The mixture was reacted at 140°C for 3 hours and at 150°C for 2 hours to produce a dark brown material. This was milled to produce a polycarboxylic acid having 5-membered imide rings.

Reference 8

4,4'-Diaminodiphenyl ether (200.2 g, 1.0 mole) was dissolved in 1500 g of N-methyl-2-pyrrolidone and the solution was cooled by ice. Then 218.1 g (1.0 mole) of pyromellitic anhydride were slowly added thereto while cooling the reaction container to produce a viscous polymer solution. This solution was diluted by adding 500 g of N,N-dimethylacetamide to produce a polyimide wire enamel.

Reference 9

Trimellitic anhydride (192 g, 1.0 mole) and 250 g (1.0 mole) of diphenylmethane-4,4'-diisocyanate were added to a mixture of 630 g N-methyl-2-pyrrolidone and 270 g of solvent naphtha (Swasol No. 1000, produced by Maruzen Petro-Chemical Co.). After reacting at 80°C for 3 hours, the mixture was heated up to 165°C over 6 hours. The reaction was carried out at that temperature for 2 hours to produce a polyamide-imide wire enamel.

Reference 10

Dimethyl terephthalate (486 g, 5.0 equivalents), 154 g (5.0 equivalents) of glycerine, 155 g (5.0 equivalents) of ethylene glycol, 0.3 g of cadmium acetate and 300 g of xylene were mixed with stirring. The mixture was reacted at 130–140°C for 5 hours while removing distillates having a lower boiling point and the temperature was then gradually elevated up to 240°C while continuing to remove the distillate having a lower boiling point. When the reaction product became viscous, cresol was added in an amount of 40% of the solid content. To this solution, 4% by weight based on the whole solid resin content of tetrabutyl titanate was added, and the mixture was stirred to produce a wire enamel.

Reference 11

Dimethyl terephthalate (243 g, 2.5 equivalents), 155 g (5.0 equivalents) of ethylene glycol, 436 g (5.0 equivalents) of tris-(2-hydroxyethyl)-isocyanate, 0.2 g of litharge and 250 g of xylene were mixed with stirring. The mixture was reacted by heating to 140–170°C and the temperature was elevated to 180°C while removing distillate having a lower boiling point. Then 683 g (2.5 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of Reference 5 were slowly added thereto. The temperature was kept to 200°C and after the dibasic carboxylic acid having 5-membered imide rings was completely absorbed in the reaction system, the temperature was gradually elevated to 230°C. When the mixture became viscous, cresol in an amount of 35% of the solid resin content to produce a solution. To this solution, 2% by weight based on the whole solid resin content of tetrabutyl titanate was added with stirring to produce a wire enamel.

Reference 12

Dimethyl terephthalate (340 g, 3.5 equivalents), 155 g (5.0 equivalents) of ethylene glycol, 154 g (5.0 equivalents) of glycerine, 0.4 g of litharge and 300 g of xylene were mixed with stirring. The mixture was reacted for 5 hours by heating to 140–170°C and then the temperature was gradually elevated to 180°C. Next 410 g (1.5 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of Reference 5 was added slowly thereto, while keeping the temperature to 200°C. After the dibasic carboxylic acid having 5-membered imide rings was completely absorbed in the reaction system, the temperature was gradually elevated to 240°C. When the mixture became sufficiently viscous, cresol was added so as to produce a solution having a 40% solid resin content. Further, solvent naphtha (Swasol No. 1000, produced by Maruzen Petro-Chemical Co.) was added thereto to produce a solution having a 35% solid content.

To this solution 3% by weight, based on the whole solid resin content, of tetrabutyl titanate was added to produce a wire enamel.

Reference 13

Polyethylene terephthalate (240 g, Mylar (registered Trade Mark) film, produced by Du Pont Co.), 154 g (5.0 equivalents) of glycerine and 0.5 g of litharge were reacted at 250°C. After the polyethylene terephthalate was completely dissolved, the temperature was reduced to 180°C and after adding 155 g (5.0 equivalents) of ethylene

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glycol thereto, 683 g (2.5 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of Reference 5 were gradually added. The reaction was carried out at 200°C. After the dibasic carboxylic acid having 5-membered imide rings was dissolved, the temperature was elevated up to 240°C while removing distillate under vacuum. When the mixture became sufficiently viscous, cresol was added to produce a solution having a 35% solid resin content. Then 4% by weight of tetrabutyl titanate based on the whole solid resin content was added thereto to produce a wire enamel. During the reaction the distillate having a lower boiling point was removed, if desired.

Reference 14

A wire enamel was produced by the same procedure as in Reference 12 but using 291 g (3.0 equivalents) of dimethyl terephthalate, 171 g (5.5 equivalents) of ethylene glycol, 138 g (4.5 equivalents) of glycerine, 0.2 g of litharge, 250 g of xylene and 683 g (2.5 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of reference 5.

Reference 15

A wire enamel was produced by the same procedure as in Reference 13 but using 192 g of polyethylene terephthalate (Tetoron (registered Trade Mark) fibers, produced by Teijin Limited), 154 g of glycerine (5.0 equivalents), 0.2 g of cadmium acetate, 155 g of ethylene glycol (5.0 equivalents) and 819 g (3.0 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of Reference 5.

Reference 16

Dimethyl terephthalate (243 g, 2.5 equivalents), 171 g (5.5 equivalents) of ethylene glycol, 138 g (4.5 equivalents) of glycerine, 576 g of trimellitic acid anhydride, 297 g of 4,4'-diaminodiphenylmethane, 1500 g of cresol, 300 g of xylene and 0.5 g of cadmium acetate were mixed. The mixture was gradually heated while removing materials having a low boiling point. When the temperature reached 210°C, it was kept for 5 hours and the temperature was then elevated to 240°C to remove cresol in vacuum. When the mixture became sufficiently viscous, cresol was added to produce a solution having a 35% solid content. Then 2% by weight of tetrabutyl titanate based on the whole solid resin content was added thereto to produce a wire enamel.

Reference 17

A wire enamel was produced by the same procedure as in Reference 12 but using 146 g (1.5 equivalents) of dimethyl terephthalate, 155 g (5.0 equivalents) of ethylene glycol, 154 g (5.0 equivalents) of glycerine, 0.2 g of litharge, 250 g of xylene and 956 g (3.5 equivalents) of the diimide dicarboxylic acid of Reference 1.

Reference 18

A wire enamel was produced by the same procedure as in Reference 13 but using 192 g of polyethylene terephthalate (Lumirror (registered Trade Mark) film, produced by Toray Industries, Inc.), 138 g (4.5 equivalents) of glycerine, 0.7 g of litharge, 171 g (5.5 equivalents) of ethylene glycol and 959 g (3.5 equivalents) of the diimide dicarboxylic acid of reference 2.

Reference 19

A wire enamel was produced by the same procedure as in Reference 12 but using 146 g (1.5 equivalents) of dimethyl terephthalate, 171 g (5.5 equivalents) of ethylene glycol, 138 g (4.5 equivalents) of glycerine, 0.4 g of litharge, 300 g of xylene and 1092 g (4.0 equivalents) of the dibasic carboxylic acid containing 5-membered imide rings of Reference 5.

Reference 20

Ethylene glycol (310 g, 10.0 equivalents), 154 g (5.0 equivalents) of glycerine and 0.2 g of litharge were mixed and heated to 180°C with stirring. Then 1365 g (5.0 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of Reference 5 were slowly added thereto, while the temperature was elevated gradually to 220°C and stirring was continued at that temperature. After the dibasic carboxylic acid having 5-membered imide rings was completely absorbed in the reaction system, the temperature was elevated to 240°C and when the mixture became sufficiently viscous, cresol was added thereto to produce a solution having a 35% solid resin content. Then 2% by weight of tetrabutyl titanate, based on the whole solid resin content was added thereto with stirring to produce a wire enamel.

Reference 21

A wire enamel was produced by the same procedure as in Reference 12 but using 340 g (3.5 equivalents) of dimethyl terephthalate, 217 g (7.0 equivalents) of ethylene glycol, 92 g (3.0 equivalents) of glycerine, 0.5 g of litharge, 300 g of xylene and 956 g (3.5 equivalents) of the dibasic carboxylic acid having 5-membered imide rings of Reference 5.

Reference 22

A wire enamel was produced by the same procedure as in Reference 12 but using 437 g (4.5 equivalents) of dimethyl terephthalate, 279 g (9.0 equivalents) of ethylene glycol, 31 g (1.0 equivalent) of glycerine, 0.5 g of litharge, 300 g of xylene and 1229 g (4.5 equivalents) of the dibasic carboxylic acid containing 5-membered imide rings of Reference 5.

Comparison 1

The polyimide wire enamel produced by Reference 8 was applied to a copper wire having a diameter of 1.0 mm by a conventional method and baked. This treatment was repeated several times to form a film having a thickness of 0.040 mm. The properties of the resultant polyimide insulated wire are shown in Table 1.

Comparisons 2—11

Wires having the structure shown in the following table were produced by the same procedure as in Comparison 1:

	Wire enamel used	Thickness of film (mm)	Chemical structure of insulating layer
Comparison 2	Reference 8	0.035	polyimide
Comparison 3	Reference 9	0.038	Polyamide-imide
Comparison 4	Reference 10	0.039	Polyester
Comparison 5	Reference 11	0.041	Polyester-imide
Comparison 6	Reference 12	0.035	Polyester-imide
Comparison 7	Reference 15	0.042	Polyester-imide
Comparison 8	Reference 16	0.039	Polyester-imide
Comparison 9	Reference 20	0.038	Polyester imide
Comparison 10	Reference 21	0.043	Polyester-imide
Comparison 11	Reference 21	0.040	Polyester-imide

The properties of the insulated wires produced in the Comparison Examples 2—11 are also shown in Table 1.

Comparison 12

The polyamide-imide wire enamel produced by the procedure of reference 9 was applied to a copper wire having a diameter of 1.0 mm and baked. This treatment was repeated several times to form a film having a thickness of 0.008 mm. Then, the polyester wire enamel produced by Reference 10 was applied to the coated wire and baked, this treatment being repeated several times to form a film having a thickness of 0.032 mm. The total thickness of the wire was 0.040 mm.

When solderability of the resulted insulated wire was examined at 420°C, 450°C and 480°C, it was impossible in each case to carry out soldering even with an immersion time of 60 seconds.

Comparisons 13—21

Insulated wires having the structure shown in the following table were produced by the same procedure as in Comparison 12. The insulated wires in Comparisons 13—21 had a polyimide or polyamide-imide insulating layer as an under layer and a polyester-imide insulating layer as an over layer.

	Polyimide or polyamide-imide under insulating layer		Polyester-imide over insulating layer		Total thickness
	Wire enamel used	Thickness (mm)	Wire enamel used	Thickness (mm)	(mm)
Comparison 13	Reference 9	0.005	Reference 11	0.031	0.036
Comparison 14	Reference 8	0.032	Reference 12	0.008	0.040
Comparison 15	Reference 8	0.008	Reference 13	0.033	0.041
Comparison 16	Reference 9	0.012	Reference 14	0.025	0.037
Comparison 17	Reference 9	0.025	Reference 17	0.012	0.037
Comparison 18	Reference 8	0.031	Reference 19	0.007	0.038
Comparison 19	Reference 9	0.032	Reference 20	0.008	0.040
Comparison 20	Reference 9	0.024	Reference 21	0.011	0.035
Comparison 21	Reference 8	0.010	Reference 22	0.030	0.040

Examinations of the solderability of the insulated wires of each Comparison Example solder bath temperatures of 420°C, 450°C and 480°C, showed that it was impossible in each case to carry out soldering even with an immersion time of 60 seconds.

Comparison 22

The polyester wire enamel produced by Reference 10 was applied to a copper wire having a diameter of 1.0 mm and baked. This treatment was repeated several times to form a film having a thickness of 0.034 mm. Then the polyamide-imide wire enamel produced by Reference 9 was applied thereto and baked, this treatment being repeated several times to form a film having a thickness of 0.006 mm. The total thickness of the films was 0.040 mm.

The properties of the resultant insulated wire are shown in Table 2.

Comparison 23

The polyester-imide wire enamel produced by Reference 11 was applied to a copper wire having a diameter of 1.0 mm and baked, this treatment being repeated several times to form a film having a thickness of 0.035 mm. Then, the polyimide wire enamel produced by Reference 8 was applied thereto and baked, this treatment being repeated to form a film having a thickness of 0.006 mm. The total thickness of the films was 0.041 mm.

The properties of the resultant insulated wire are shown in Table 2.

EXAMPLE 1

The polyester-imide wire enamel produced by Reference 12 was applied to a copper wire having a diameter of 1.0 mm. and baked, this treatment being repeated several times to form a film having a thickness of 0.031 mm. Then, the polyimide wire enamel produced by Reference 9 was applied thereto and baked, this treatment being repeated several times to form a film having a thickness of 0.007 mm. The total thickness of the films was 0.038 mm.

The properties of the resultant insulated wire are shown in Table 2.

EXAMPLES 2-11

Insulated wires having a polyester-imide insulating layer as an under layer and a polyimide or polyamide-imide insulating layer as an over layer where produced by the same procedure as in Example 1 but using the following combinations.

	Polyester-imide under insulating layer		Polyimide or poly- amide-imide over insulating layer		Total thick- ness (mm)
	Wire enamel used	Thick- ness (mm)	Wire enamel used	Thick- ness (mm)	
Example 2	Reference 13	0.031	Reference 8	0.008	0.039
Example 3	Reference 14	0.036	Reference 9	0.006	0.042
Example 4	Reference 15	0.030	Reference 8	0.010	0.040
Example 5	Reference 16	0.032	Reference 9	0.008	0.040
Example 6	Reference 17	0.029	Reference 8	0.007	0.036
Example 7	Reference 18	0.030	Reference 9	0.006	0.036
Example 8	Reference 19	0.025	Reference 8	0.008	0.033
Example 9	Reference 20	0.033	Reference 8	0.009	0.042
Example 10	Reference 21	0.032	Reference 9	0.008	0.040
Example 11	Reference 22	0.025	Reference 8	0.012	0.037

The properties of the resultant insulated wires are shown in Table 2.

TABLE 1

Solderability (second)
Temperature of solder

		420°C	450°C	480°C	
5	Comparison 1	more than 60	more than 60	more than 60	5
	Comparison 2	more than 60	more than 60	more than 60	
	Comparison 3	more than 60	more than 60	more than 60	
	Comparison 4	more than 60	more than 60	more than 60	
	Comparison 5	more than 60	more than 60	more than 60	
10	Comparison 6	more than 60	55	28	10
	Comparison 7	10	5	3	
	Comparison 8	8	4	3	
	Comparison 9	12	5	4	
	Comparison 10	5	3	3	
15	Comparison 11	5	3	2	15

TABLE 2

Solderability
Temperature of solder

		420°C	450°C	480°C	Heat-shock resistance	
20	Comparison 22	more than 60	more than 60	more than 60	4d	20
	Comparison 23	more than 60	more than 60	more than 60	1d	
	Example 1	more than 60	55	30	2d	
	Example 2	12	5	4	1d	
	Example 3	12	5	4	1d	
25	Example 4	15	6	4	1d	25
	Example 5	10	5	3	1d	
	Example 6	11	5	4	1d	
	Example 7	9	5	3	1d	
	Example 8	10	5	4	1d	
30	Example 9	11	5	4	2d	30
	Example 10	9	4	3	1d	
	Example 11	9	4	3	1d	

Wound diameter needed to withstand heating at 200°C for 2 hours.

EXAMPLE 12

35 Phenoxy (PKHH, produced by Union Carbide Corp., 100 parts by weight) were dissolved in 400 g of m-cresol to produce a bondable enamel. This bondable enamel was applied to the insulated wire produced by the procedure of Example 2 and baked to form a self-bonding layer having a thickness of 15 u. 35

40 The resultant self-bonding magnet wire was wound to form a helical coil having an inside diameter of 6 mm and bound at 600 g load at 170°C for 20 minutes. When determined by ASTM D 2519, the bond strength at normal temperature was 20 kg. The solderability of the self-bonding magnet wire produced in this Example was 14 seconds at a solder temperature of 420°C, 7 seconds at 450°C and 6 seconds at 480°C. 40

WHAT WE CLAIM IS:—

45 1. Solderable and thermostable insulated wire which comprises a conductor, an insulating under layer formed thereon by applying thereto a polyester-imide wire enamel (which may include polyester-imide or polyesteramide-imide) and baking the applied enamel, said polyester-imide wire enamel having 5-membered imide groups and ester bonds in the molecule and comprising the reaction product of A) 50 a dibasic carboxylic acid free of 5-membered imide ring, and/or a derivative thereof, B) a dibasic carboxylic acid containing at least one 5-membered imide ring and/or a derivative thereof, C) a tri- and/or high-hydric aliphatic alcohol and D) a dihydric aliphatic alcohol and an insulating over layer formed by applying a poly-imide wire enamel or a polyamide-imide wire enamel to said under layer and baking. 55

2. Wire as claimed in Claim 1, in which the polyester-imide wire enamel comprises the reaction product of from 5 to 55 equivalent % of component A), from 10 to 60 equivalent % of component B) and from 35 to 55 equivalent % of component C), based on the sum of the equivalents of A, B and C, the equivalent % of D being not less than the sum of the equivalent percentages of A and B less that 60 of C. 60



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TABLE 1

Solderability (second)
Temperature of solder

		420°C	450°C	480°C	
5	Comparison 1	more than 60	more than 60	more than 60	5
	Comparison 2	more than 60	more than 60	more than 60	
	Comparison 3	more than 60	more than 60	more than 60	
	Comparison 4	more than 60	more than 60	more than 60	
	Comparison 5	more than 60	more than 60	more than 60	
10	Comparison 6	more than 60	55	28	10
	Comparison 7	10	5	3	
	Comparison 8	8	4	3	
	Comparison 9	12	5	4	
	Comparison 10	5	3	3	
15	Comparison 11	5	3	2	15

TABLE 2

Solderability
Temperature of solderHeat-shock
resistance

		420°C	450°C	480°C	
20	Comparison 22	more than 60	more than 60	more than 60	20
	Comparison 23	more than 60	more than 60	more than 60	
	Example 1	more than 60	55	30	
	Example 2	12	5	4	
	Example 3	12	5	4	
25	Example 4	15	6	4	25
	Example 5	10	5	3	
	Example 6	11	5	4	
	Example 7	9	5	3	
	Example 8	10	5	4	
30	Example 9	11	5	4	30
	Example 10	9	4	3	
	Example 11	9	4	3	

Wound diameter needed to withstand heating at 200°C for 2 hours.

EXAMPLE 12

Phenoxy (PKHH, produced by Union Carbide Corp., 100 parts by weight) were dissolved in 400 g of m-cresol to produce a bondable enamel. This bondable enamel was applied to the insulated wire produced by the procedure of Example 2 and baked to form a self-bonding layer having a thickness of 15 u.

The resultant self-bonding magnet wire was wound to form a helical coil having an inside diameter of 6 mm and bound at 600 g load at 170°C for 20 minutes. When determined by ASTM D 2519, the bond strength at normal temperature was 20 kg. The solderability of the self-bonding magnet wire produced in this Example was 14 seconds at a solder temperature of 420°C, 7 seconds at 450°C and 6 seconds at 480°C.

WHAT WE CLAIM IS:—

1. Solderable and thermostable insulated wire which comprises a conductor, an insulating under layer formed thereon by applying thereto a polyester-imide wire enamel (which may include polyester-imide or polyesteramide-imide) and baking the applied enamel, said polyester-imide wire enamel having 5-membered imide groups and ester bonds in the molecule and comprising the reaction product of A) a dibasic carboxylic acid free of 5-membered imide ring, and/or a derivative thereof, B) a dibasic carboxylic acid containing at least one 5-membered imide ring and/or a derivative thereof, C) a tri- and/or high-hydric aliphatic alcohol and D) a dihydric aliphatic alcohol and an insulating over layer formed by applying a polyester-imide wire enamel or a polyamide-imide wire enamel to said under layer and baking.
2. Wire as claimed in Claim 1, in which the polyester-imide wire enamel comprises the reaction product of from 5 to 55 equivalent % of component A), from 10 to 60 equivalent % of component B) and from 35 to 55 equivalent % of component C), based on the sum of the equivalents of A, B and C, the equivalent % of D being not less than the sum of the equivalent percentages of A and B less that of C.



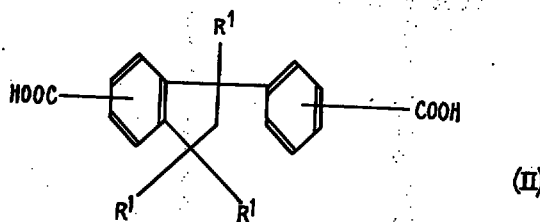
3. Wire as claimed in Claim 2, in which the polyester-imide wire enamel comprises the reaction product of from 10 to 40 equivalent % of component A), from 20 to 50 equivalent % of component B) and from 40 to 55 equivalent % of said component C, on the same basis as defined in Claim 2, and the equivalent percentage of D also being as defined in Claim 2.

4. Wire as claimed in any preceding Claim, in which said polyester-imide wire enamel comprises a reaction product in which the dicarboxylic acid of component (A) is an alicyclic or an aliphatic dicarboxylic acid.

5. Wire as claimed in any of Claims 1 to 3, in which polyester-imide wire enamel comprises a reaction product in which the dicarboxylic acid of component (A) is an aromatic dicarboxylic acid.

6. Wire as claimed in Claim 5, in which said aromatic dicarboxylic acid is isophthalic acid, terephthalic acid, 1,2-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 1,7-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, diphenyl-2,2'-dicarboxylic acid, diphenyl-2,3'-dicarboxylic acid, diphenyl-2,4'-dicarboxylic acid, diphenyl-3,3'-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, diphenylmethane-2,2'-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylethane-4,4'-dicarboxylic acid, diphenylsulphone-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid or diphenyl-2,2-propane-4,4'-dicarboxylic acid.

7. Wire as claimed in Claim 4, in which said alicyclic dicarboxylic acid of component (A) has the following general formula (II):



wherein R^1 is a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms.

8. Wire as claimed in Claim 7, in which said alicyclic dicarboxylic acid is 3-(4-carboxyphenyl)-5-indanecarboxylic acid, 3-(3-carboxyphenyl)-5-indanecarboxylic acid, 3-(3-carboxyphenyl)-1,1,3-triethyl-6-indanecarboxylic acid, 3-(4-carboxyphenyl)-1-methyl-1,3-diethyl-6-indanecarboxylic acid or 3-(4-carboxyphenyl)-1-methyl-1,3-diethyl-6-indanecarboxylic acid.

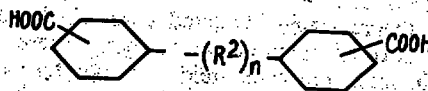
9. Wire as claimed in Claim 4, in which said alicyclic dicarboxylic acid has the general formula



in which



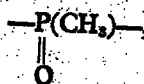
is a cyclohexyl group or



in which



is a cyclohexyl group, R^2 is $-O-$, $-CH_2-$, $-(CH_2)_2-$, $-C(CH_3)_2-$, $-SO_2-$, $-Si(CH_3)_2-$ or



and n is a positive integer.



10. Wire as claimed in Claim 9, in which said alicyclic dicarboxylic acid is hexahydroisophthalic acid, hexahydroterephthalic acid or bicyclo[2,2,2]octane-1,4-dicarboxylic acid.

11. Wire as claimed in Claim 4, in which aliphatic acid is adipic acid, succinic acid, maleic acid, sebacic acid, isosebacic acid or a dimerized unsaturated fatty acid.

12. Wire as claimed in any preceding Claim, in which said polyester-imide wire enamel comprises a reaction product in which the dicarboxylic acid containing a five-membered imide ring of component (B) comprises the reaction product of an aromatic carboxylic anhydride containing a five-membered cyclic carboxylic anhydride group and at least one other reactive group and a primary amine containing a primary amino group and at least one other reactive group or is the reaction product of an aromatic carboxylic anhydride containing a five-membered cyclic carboxylic anhydride group and at least one other reactive group and a polyisocyanate compound.

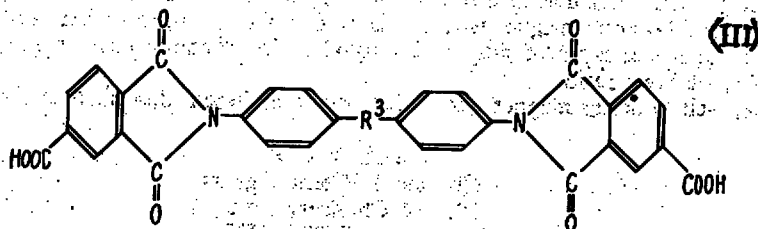
13. Wire as claimed in Claim 12, in which said aromatic carboxylic anhydride is a tricarboxylic acid anhydride or a tetracarboxylic dianhydride.

14. Wire as claimed in Claim 13, in which said aromatic carboxylic anhydride is trimellitic anhydride, hemi-trimellitic anhydride, 1,2,5-naphthalenetetracarboxylic anhydride, 2,3,6-naphthalenetetracarboxylic anhydride, 1,8,4-naphthalenetetracarboxylic anhydride, 3,4,4'-diphenyltricarboxylic anhydride, 3,4,4'-diphenylmethanetricarboxylic anhydride, 3,4,4'-diphenylethertricarboxylic anhydride, 3,4,4'-benzophenonetetracarboxylic anhydride, pyromellitic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,8,4,5-naphthalenetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 3,3',4,4'-diphenyltetracarboxylic dianhydride, 2,2',3,3'-diphenyltetracarboxylic dianhydride, 3,3',4,4'-diphenylethertetracarboxylic dianhydride, 3,3',4,4'-diphenylmethanetetracarboxylic dianhydride or 3,3',4,4'-benzophenonetetracarboxylic dianhydride.

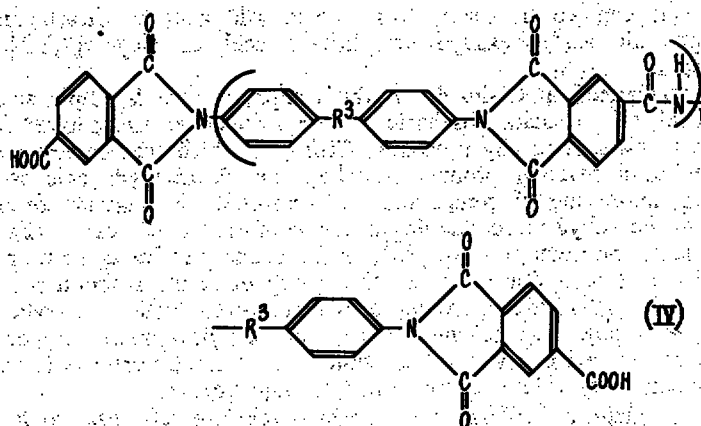
15. Wire as claimed in Claim 12, 13 or 14, in which said compound containing said primary amino group is 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl, 1,4-diaminonaphthalene, *m*-phenylene diamine, *p*-phenylene diamine, *o,o'*-nonamethylene diamine, 1,7-dimethylheptamethylene diamine, 4,4'-diaminodiphenyl ketone, bis-(4-aminophenyl)-*o,o'*-*p*-xylene, tolylene diamine, xylylene diamine, hexamethylene diamine, ethylene diamine, 4,4'-dicyclohexylmethane diamine or diaminodiphenyl sulphone benzoguanamine.

16. Wire as claimed in any one of Claims 12 to 15, in which said polyisocyanate compound is *m*-phenyl diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, diphenylether-4,4'-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, diphenylthioether-4,4'-diisocyanate, naphthalenediisocyanate, polymethylenepolyphenylene polyisocyanate, hexamethylene diisocyanate or xylene diisocyanate; or a stabilized isocyanate obtained by stabilizing the isocyanate groups of one of the foregoing polyisocyanates with a phenolic hydroxyl group.

17. Wire as claimed in any one of Claims 1 to 11, in which said polyester-imide wire enamel comprises a reaction product in which the dicarboxylic acid containing a five-membered imide ring of component (B) has the following general formula (III):



or the following general formula (IV):



wherein R^3 is $-\text{CH}_2-$, $-\text{O}-$ or $-\text{SO}_2-$, and n is on average greater than 0 but not more than 4.

18. Wire as claimed in any one of Claims 1 to 11, in which said polyester-imide wire enamel comprises a reaction product in which component (B) is a product, the preparation of which is described in any one of Referential Examples 5 to 7.

19. Wire as claimed in any preceding Claim, in which said polyester-imide wire enamel comprises a reaction product in which the aliphatic polyhydric alcohol component (C) is glycerol, pentaerythritol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, sorbitol, mannitol, dipentaerythritol, diglycerol or 1,2,6-hexanetriol.

20. Wire as claimed in any preceding Claim, in which said polyester-imide wire enamel comprises a reaction product in which the divalent alcohol of said component (D) is ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propanediol, butanediol-1,3, butanediol-1,4, pentanediol-1,5, hexanediol-1,6, butane-2,3-diol-1,4, 2,2-dimethylpropanediol-1,3, 2-ethyl-2-butyl-propanediol-1,8, 1,4-dimethylcyclohexane, butenediol-1,4, a hydrogenated bisphenol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, hydroquinone-di- β -hydroxyethyl-ether, 1,4-cyclohexanedi-methanol, 1,4-cyclohexane diethanol diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, trimethylene glycol, hexylene glycol or octylene glycol.

21. Wire as claimed in any preceding claim in which said polyester-imide wire enamel additionally comprises a metal drying agent.

22. Wire as claimed in Claim 1, in which said polyester-imide wire enamel is substantially as described in any one of Reference Examples 8 to 22 herein.

23. Wire as claimed in Claim 1 and substantially as hereinbefore described.

24. Wire substantially as hereinbefore described with reference to the accompanying drawing.

25. Wire substantially as hereinbefore described in any one of the foregoing Examples 1 to 11.

26. Self-bonding magnet wire comprising insulated wire as claimed in any preceding Claim and having a self-bonding layer formed on said insulating over layer.

27. Self-bonding magnet wire as claimed in Claim 26, in which said self-bonding layer comprises a layer of polyvinyl butyral resin, phenoxy resin, a polyamide resin or a polysulphone resin.

28. Self-bonding magnet wire substantially as herein described in Example 12.

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