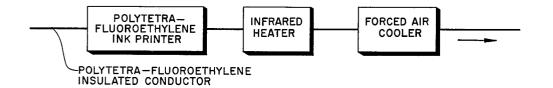
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METHOD OF PERMANENTLY MARKING POLYTETRAFLUOROETHYLENE Filed Feb. 24, 1960



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3,085,912 METHOD OF PERMANENTLY MARKING POLYTETRAFLUOROETHYLENE Charles L. Friese, Towson Township, Harford County, 5 Md., assignor to Martin-Marietta Corporation, a corporation of Maryland Filed Feb. 24, 1960, Ser. No. 10,580 5 Claims. (Cl. 117-212)

Teflon or polytetrafluoroethylene has a wax-like surface 10 texture which cannot be permanently marked with conventional marking inks in a satisfactory manner. Hotstamping produces a permanent mark but causes the Teflon to break down, which is highly undesirable in cases where the Teflon is used as an electrical insulation 15 since the stamping process reduces the insulating capacity of the Tefion. Heretofore, Tefion-coated electrical conductors have been marked in a non-permanent manner, such that the markings may be rubbed off easily or become illegible during use. It has been considered neces- 20 sary in many instances to admix an identifying color with the Teflon prior to polymerization so that the different types of wire might be identified by the distinctive coloring in the Teflon. This method of identification has proven unsatisfactory, however, because it requires a 25 large inventory of wires of different colors to be maintained in stock. Another method of marking Teflon wire comprises placing ink striping on the surface of the Teflon insulation and then passing the inked Teflon wire through a gas heated oven to dry the ink. The dried 30 striping, however, is not permanently affixed to the Teflon and may be readily rubbed off.

It is a purpose of this invention to provide a method of identifying Teflon wire by permanently marking same the Teflon are not materially impaired. It has been discovered, in fact, that the present marking method actually improves certain electrical qualities of the Teflon coating on commercial Teflon wires.

In outline, as shown on the drawing, the present meth- 40 od comprises impressing Teflon ink on the Teflon wire and then rapidly heating the surface of the impressed Teflon wire with radiant energy to fix the ink marking permanently. The markings so produced are extremely durable and cannot be removed except by destroying the 45 underlying Teflon.

This method differs essentially from all prior marking methods in that the Teflon insulation is heated by means of radiant energy, whereas, heretofore, the Tefion has been heated by means of convection or conduction. The 50 conduction method is exemplified by hot stamping, which, as noted above, materially decreases the electrical insulating capacity of Teflon. Convection heating, utilized in applying striping to Teflon, cannot be performed at a temperature which would cause the ink to bond perma- 55 identifying symbol by pressing Teflon ink on/or into the manently to the Teflon insulation because the temperature of the wire conductor would be raised to excessive values, such that the individual strands of conductor are caused to stick together, thereby seriously reducing the flexibility of the Teflon wire. For example, when striping is dried in a gas heated oven at about 850° F., the silver plated individual conductor strands become joined.

In the present process, heat is transferred to the outer surface of the Teflon insulation at a high rate for a short period of time, the rate at which heat is absorbed 65 at the outer surface of the Teflon insulation being much greater in magnitude than the rate at which heat is conducted from the outer surface to the wire conductor. In

this manner, a steep temperature gradient is established radially in the Teflon insulation during the heating step. Before an excessive amount of heat is able to build up in the interior of the Teflon wire, the wire is cooled. Depending on the radiant energy heat flux, the time of exposure and the physical dimensions of the Teflon wire, cooling may be effected by either allowing the processed wire to stand in air or by cooling the wire with a forced draft of air or by other suitable accelerated cooling means.

For the purposes of the present invention, the term "Teflon" encompasses not only the homopolymer of tetrafluoroethylene but also substances wherein an organic material is admixed with or copolymerized with tetrafluoroethylene in such proportion and in such manner that the resulting admixture or polymeric product partakes of the properties of tetrafluoroethylene. The organic additive may constitute up to about 25% of the admixture or copolymeric product and may, for example, be a material like polyisobutylene; butyl rubber including the elastomeric copolymers of isobutylene and diolefins such as butadiene; polyacrylates and polyalkylacrylates including polymethylacrylate, polymethyl methacrylate, polyethylacrylate, polyethyl methacrylate and the like; butadiene-acrylic copolymers including butadiene-acrylate, butadiene-acrylonitrile, and butadiene-acrylamide; butadiene-styrene copolymer; plasticized polystyrene; polyvinyl halides and polyvinylidene halides including polyvinyl chloride, polyvinyl fluoride, polyvinylidene chloride, and polyvinylidene fluoride; and alkyl-acrylate copolymers including copolymers of 90% methyl methacrylate-10% methylacrylate, 90% methyl methacrylate-10% ethylacrylate and the like. The term "Teflon wire," therefore, is to be understood as a metal conductor having with ink in such a manner that the electrical qualities of 35 a sheath of the homopolymer of tetrafluoroethylene or a sheath of any one or more of the admixtures or copolymeric products hereinbefore enumerated. "Teflon ink," in an analogous fashion refers to liquid suspensions or thermoplastic materials comprising a suitable pigment or colored filler admixed with particles of tetrafluoroethylene or particles of any one or more of the aforesaid admixtures or copolymeric products. Specifically, the composition of such ink includes (1) a polytetrafluoroethylene dispersion; (2) a ceramic oxide pigment; (3) a binder (or thickener); (4) a distilled water carrier; and (5) a fluorocarbon wetting agent. Ink in accordance with this specification is commercially available from the Hi-Temp Wire Company as Black Marking Fluid, Code 913A. This invention, however, is not directed to the particular materials used; but, rather, to the method by which Teflon wires of the type described may be permanently marked with Teflon ink.

In accordance with the present invention, the Teflon wire or other Teflon article is marked with the desired Teflon surface. For this purpose, any conventional printing machine may be used. A particular machine which has been employed successfully for marking Teflon wire is the Dual Printer made by Duncan M. Gillies Co., Inc., West Bozleston, Massachusetts, which impresses the 60 Teflon wire by opposed printing discs through which the wire is fed. Each disc is provided on its periphery with a plurality of raised symbols and is made to pass through a bath of Teflon ink whereby the raised symbols become coated therewith.

The Teflon wire is subjected on its marked surface to a predetermined flux of radiant energy, the principal wavelengths of which are in infrared region, which is 3

absorbed by and heats the outer surface of the Teflon wire. Heating is continued for a length of time sufficient to permanently bond the ink to the Teflon, whereupon heating is discontinued to prevent an undue buildup of heat in the interior of the wire as would adversely affect the Teflon insulation or the wire conductor.

The source of infrared energy may be a resistance element, a quartz infrared lamp or other conventional device. In the preferred embodiment of the present invention radiant energy is supplied by a metal resistance element of cylindrical configuration through which the wire to be heated is passed. The resistance element is suitably insulated by means of a refractory material so as to form an open ended furnace.

After processing all samples were subjected to the insulation resistance test, the dielectric strength test, the cold bend test and the heat resistance test as detailed in National Aircraft Standard 703. An unprinted sample which had not been heated was included as a control specimen for comparison.

The dielectric strength test calls for the application of 3000 volts, to Class "A" insulation for a period of five minutes without breakdown. In order to obtain a figure of relative merit for these specimens, the standard dielectric strength test was followed immediately by a dielectric breakdown test.

Results of these tests on 16 ga. Class "A" Teflon wire are listed in Table I.

| Table | IResults of | Infrared | Irradiation | of | "Class | A" |
|-------|-----------------|----------|--------------|-----|--------|----|
| | Wire at Indicat | ed Tempe | rature of 18 | 00° | , F. | |

| Sample No. | Fced Rate (ft./sec.) | Durability | Insulation Resistance | Diele | etric | Cold J | Bend | Heat Re | lleat Resistance | |
|----------------------------------|---|---|---|--------------------------------|--|--|---|----------------------------------|---|--|
| | | of Printing | (Megs./50 ft.) | Strength | bkdn., (kv.) | Strength | bkdn., (kv.) | Strength | bkdn., (kv.) | |
| | | | | | | | | | | |
| A B C D E Control | $\begin{array}{c} 0.7\\ 0.6\\ 0.5\\ 0.4\\ 0.3\end{array}$ | Fair Good do Excelient Fair | $\begin{array}{c} 320,000\\ 250,000\\ 2,000,000\\ 2,000,000\\ 2,000,000\\ 2,000,000\\ 260,000\end{array}$ | Passed do do do do | 12.3 10.5 10.1 10.1 10.8 11.8 | Passeddo do do do do do do | $14.3 \\ 15.0 \\ 12.3 \\ 11.3 \\ 12.5 \\ 9.8$ | Passeddo do do do do | 13.5 8.8 8.8 8.4 11.8 12.0 | |

In order to provide a better understanding of the present invention, reference is made to the following specific examples, wherein the source of infrared energy was a heated Nichrome screen, 30 x 30 mesh, made of 0.014 inch wire. The screen was formed into a tube 3 inches in diameter by 3 feet long, and insulated by a wrapping of Thermoflex, an asbestos sheet manufactured by Johns-35 Mansville Co., Chicago, Illinois.

The screen temperature was monitored with a 22 ga. Chromel-Alumel thermocouple placed between the Nichrome screen and the insulation midway of the tube. The particular Teflon ink used in the following examples $_{40}$ was Black Marking Fluid, Code 913–A produced by Hi-Temp, Inc., Chicago, Illinois.

EXAMPLE I

Five 100 foot samples (A thru E) of #16 ga. Teflon insulated wire, satisfying military standard MIL W 16878, were printed with Hi-Temp black marking fluid (Code 913A), a Teflon ink, and sintered at speeds between 0.3 and 0.7 ft. per second.

The screen temperature was manually controlled at a $_{50}$ temperature of 1800° F. $\pm 20^{\circ}$.

The following procedure was followed in bringing the furnace to operating temperature. Four hundred amperes at 10 volts were supplied to the Nichrome screen until the temperature indicated at the thermocouple was 55 1550° F., at which point current was reduced to 300 amperes. When the indicated temperature reached 1800° F., the current was further reduced to 250 amperes. A

The optimum wire feed rate through the 36 inch furnace at 1800° F. was 0.4 ft. per second.

Generally, the processed specimens exhibited marked improvements in breakdown voltage following the cold bend test and in insulation resistance. However, the processed samples showed slightly lower resistance to dielectric breakdown after having been subjected to the dielectric strength test and the heat resistance test.

In all instances it was impossible to remove the markings after irradiation except by destroying the underlying Teflon.

EXAMPLE II

One hundred foot samples of #22 ga. Teflon insulated wire satisfying military standard MIL W 16878 were printed with Hi-Temp Black Marking Fluid, Code 913A.

Three samples were processed at 1800° F. at speeds of 0.40, 0.35, and 0.30 ft. per second, respectively, which are within the range of speeds at which optimum results were obtained with the #16 ga. Tefion insulated "Class A" wire of Example I. The marking on one of these samples had poor durability, and the insulation on the other two samples separated and burned. These failures apparently were caused by overheating.

Three additional samples were then processed at the same temperature, 1800° F., but at higher feed rates, viz., 0.5, 0.6 and 0.7 ft. per second, respectively. The markings after processing proved to be of fair to good durability. The temperature of the Nichrome screen was then raised to an indicated 1950° F. Results are listed in Table II.

Table II.—Results of Infrared Irradiation of "Class C" Wire at Indicated Temperature of 1950° F.

| Sample No. | Feed Rate (ft./sec.) | Durability | Insulation Resistance | Dieleo | etric | Cold Bend | | Heat Re | sistance |
|----------------------------------|---------------------------------|---------------------------------|---|--------------------------|---|---------------------------|------------------------------|--------------------------|---------------------------------------|
| | | of Printing | (Megs./50 ft.) | Strength | bkdn., (kv.) | Strength | bkdn., (kv.) | Strength | bkdn., (kv.) |
| | | | | | | | | | |
| A B C D E Control | 0.9 0.8 0.7 0.6 0.5 | N.G. Excellent do Fair | 2,000,000 2,000,000 2,000,000 2,000,000 2,000,000 | Passed do do do | $ \begin{array}{r} 10.9 \\ 9.0 \\ 11.7 \\ 13.5 \\ 12.8 \\ \end{array} $ | Passed dodo Cracked | 12.5 12.6 12.0 11.2 | Passed do do do | $11.3 \\ 11.4 \\ 13.8 \\ 8.0 \\ 14.3$ |

forced-air cooler placed at the exit end of the furnace was then turned on, and the printed Teflon was fed through the furnace substantially coincident with the lon-75 gitudinal axis thereof.

Specimens A through E of Example II provide a complete spectrum of processing speeds with results ranging from failure due to insufficient heating (at 0.9 ft./sec.) to unsatisfactory results, which were caused by excessive heating (at 0.5 ft./sec.) and consequent decomposition of the Teflon. Any speed between 0.6 and 0.8 ft. per sec. yielded excellent durability at this furance temperature.

Decomposition of the Teflon was indicated by the color of the processed specimen, namely, an oyster white 5 coloration.

Results of the tests performed on the #22 ga. Teflon insulated wire followed the trend observed in Example I.

Although the invention has been described with particular reference to specific embodiments thereof, it will be understood that it is susceptible of embodiment in many other forms, such as will appear to one skilled in the art in view of the foregoing teachings, without departing from the scope of the invention as set forth in the following claims:

What is claimed is:

1. A method of marking articles of homopolymers and copolymers of tetrafluoroethylene comprising the steps of printing the surface of such an article with ink in the desired pattern, said ink comprising a pigment admixed with particles of polytetrafluoroethylene, and irradiating said surface with infrared radiation so as to cause said ink to become permanently bonded to said surface.

2. A method of marking polytetrafluoroethylene coated wire comprising the steps of impressing ink onto the surface of said wire, said ink comprising a pigment admixed with particles of polytetrafluoroethylene, and ir-

radiating said surface with infrared radiation so as to bond said ink permanently to said surface.

3. The method of claim 2, wherein said polytetrafluoroethylene coated wire is cooled after the irradiating step.

4. In the method of marking polytetrafluoroethylene coated wire wherein the surface of said wire is coated with ink so as to form an identifying symbol thereon, said ink comprising a colored filler admixed with particles of a copolymer of tetrafluoroethylene, the improvement comprising irradiating said surface with infrared radiation so as to cause said ink to become permanently bonded to said surface.

5. The improvement of claim 4 wherein said polytet-15 rafluoroethylene coated wire is cooled after the irradiating step.

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