Sept. 25, 1962 P. H. RHODES 3,055,778

METHOD FOR APPLYING A MIXTURE OF A VINYL HALIDE POLYMER AND AN EPOXIDIZED TRIGLYCERIDE ON A WIRE AND THE RESULTING ARTICLE

Filed March 23, 1960

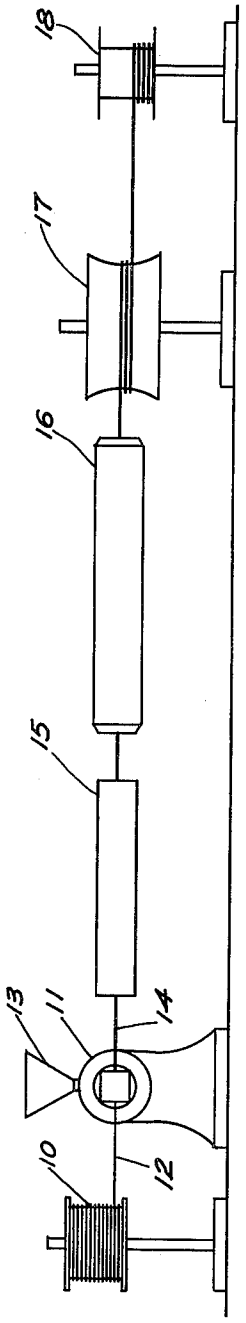


Fig. 1

INVENTOR.
PHILIP H. RHODES

BY

Roy G. Story

United States Patent Office 3,055,778 Patented Sept. 25, 1962

3,055,778

METHOD FOR APPLYING A MIXTURE OF A VINYL HALIDE POLYMER AND AN EPOXIDIZED TRIGLYCERIDE ON A WIRE AND THE RESULTING ARTICLE

Philip H. Rhodes, Cincinnati, Ohio, assignor to Swift & Company, Chicago, Ill., a corporation of Illinois

Filed Mar. 23, 1960, Ser. No. 16,936
6 Claims. (Cl. 117—232)

This invention relates to the coating of metallic conductors with a plastic substance and to the coated conductor thereby produced. More particularly the invention relates to the extrusion coating of metallic cores with a heat hardenable thermosetting composition.

Various methods of manufacture have been employed in the past in the production of insulated metallic conductors, the diverse techniques for the most part being dictated by limitations inherent in the physical and chemical characteristics of the insulating material. In those cases where the nature of the insulating material permits, extrusion is a favored method for forming a sheath of the insulation around the core. Crosshead extrusion is a particularly desirable method since this technique provides a rapid and economic production means. Crosshead extrusion involves passing the wire conductor through a crosshead die and enveloping the conductor with the fluid coating composition followed by passage of the coated wire through a constricting die which presses the coating into close adherence with the conductor. Finally the coated conductor is passed to a cooling zone where the semifluid coating is set.

Rubber compounds including mixtures of rubber compositions with resins such as polyethylene and vinyl halide resins have been employed in the insulation of wire in the past but such compositions possess shortcomings principally in high temperature resistance, chemical resistance, poor aging characteristics, low dielectric strength or poor flexibility. High temperature resistance is most important since the insulating composition is exposed to temperatures in excess of 400° F. in formulating and extruding and to much greater temperatures in actual use.

Moreover the insulated conductor should be capable of withstanding elevated temperatures without flowing. The use of polyvinyl chloride resin compositions for this purpose has been restricted to comparatively low temperature use since such compositions tend to flow and break down with increasing temperature resulting in a decrease in dielectric properties. Utlimately as sufficiently high temperatures are reached the insulation flows away from the conductor causing shorts in the electrical system.

Thermosetting materials can be employed to avoid this high temperature softening or flow but thermosetting compositions do not provide the ease of handling of thermoplastics. Where thermosetting materials are employed as insulators extrusion cannot be employed as the coating technique since the temperatures required in the extruder for liquifying the resin cause a thermosetting material to set up in the extruder. The dip and draw method is employed for the application of thermosetting materials to conductors usually from a solution of the resin. Obviously only thin coatings can be applied by the dip and draw method as distinguished from the thicker coatings provided by extrusion.

It is therefore an object of this invention to provide an insulated filamentous electrical conductor having an improved resistance to flow at high temperatures.

A further object of the invention is the provision of a method for coating electrical conductors by extrusion of a thermoplastic composition on said conductor to provide an insulated conductor exhibiting desirable dielectric properties at high temperatures.

Additional objects, if not specifically set forth herein, will be readily apparent to those skilled in the art from the detailed description of the invention which follows.

Generally this invention contemplates the deposition of a resinous insulating composition in the form of a sheath by extrusion on a filamentous metallic conductor and treating the coated conductor to harden the coating and provide a coating having a greatly increased resistance to the effect of elevated temperatures. Inasmuch as the insulating composition is thermoplastic and thus flowable at formulating and extrusion temperatures, yet does not set up at these temperatures, substantial benefits are provided in high production speeds and efficiency and uniformity of coating. Wide variations in size of the wire coated and thickness in coatings are possible. Additionally high temperature curing produces a tough yet flexible adherent insulation possessing a greatly increased resistance to softening and flow when the cured coating is exposed to elevated temperatures. Also the coating shows a greatly improved resistance to chemicals and solvents, has good impact strength, and good resistance to abrasion.

The FIGURE illustrates equipment which may be utilized in carrying out the method of the invention.

The insulating compositions of this invention are fluid thermoplastic resins which remain fluid at extrusion temperatures but can be cured to a thermosetting form by a short-time, high-temperature treatment. These compositions comprise vinyl halide resins and oxirane containing fatty acyl derivatives such as epoxidized linseed oil, epoxidized safflower oil, epoxidized fish oils or epoxidized perilla oil wherein the unsaturation present in the fatty acyl radicals of the naturally occurring oil is substantially converted to oxirane groups providing a high oxirane triglyceride. The epoxidized oils are very low viscosity fluids having a residual iodine value of not more than 10. The oxirane containing fatty acyl derivative must contain several three-membered epoxy groups in internal open-chained portions of the molecule to provide an average epoxy content greater than about 8.5% and preferably about 8.8–9.5%. Esters of high oxirane fatty acids with lower mono-, di-, and polyhydric alcohols are particularly desirable. These esters are characterized as high oxirane fatty materials containing oxirane rings (epoxy groups) at those points in the fatty acyl radical which are normally occupied by double bonds in the original non-epoxidized fatty acid or ester. The di-, tri-, tetra-, penta-, and hexahydric alcohol esters of oxirane containing fatty acids of 10–30 carbons containing more than 8.5% oxirane oxygen are preferred. Best results are obtained if these compositions have been subjected to alkali refining as is disclosed in copending application Serial Number 807,985, filed April 22, 1959, and also deodorized. Refining insures that by-products such as peroxides and hydroxyl groups are reduced to a minimum while deodorization removes volatiles which might cause gassing in the resin coating.

The vinyl halide resin component should contain a predominant portion, i.e., greater than 50% vinyl halide and lesser amounts of other monoolefinic monomers. This includes polymers prepared from 50–95% of vinyl halide units such as co-polymers and interpolymers of vinyl chloride with vinylidene chloride, vinyl esters, such as vinyl acetate, vinyl butyrate, and the like, and acrylic and alkyl-acrylic acid esters. Particularly preferred thermoplastic resins are those having 70–99% vinyl chloride units and smaller amounts, up to about 30% vinylidene chloride and vinyl esters. A preferred example is a thermoplastic resin containing 90–95% polyvinyl chloride units. Very suitable vinyl halide resins are the high molecular weight polyvinyl chloride resins having a molecular weight above about 20,000 and preferably around 100,000–200,000.

The preparation of the curable insulating composition involves techniques which are for the most part well known

in the art. The thermoplastic resin may be dispersed in the epoxidized fatty material and the two components may be blended and compounded in a Banbury mixer or on a two-roll mill or other suitable compounding equipment. Usually about 20–80 parts of the epoxide for each 100 parts of the resin will provide a desirable coating depending upon the flexibility and strength required for a given instance. A preferred example is 40–80 parts based on the vinyl halide resin of epoxidized linseed oil. Fillers, stabilizers, pigments, and lubricants may also be incorporated in the mix. The components may first be mixed in the Banbury mixer for about 10 minutes more or less at a temperature of around 200–300° F. followed by sheeting at about 240–260° F. on a mill. The sheets may then be granulated and fed to an extruder which is heated at around 300–400° F. and then extruded on the core. It can be seen that the mix must be fluid and remain fluid when exposed to elevated temperatures during the handling time. Although setting up of the composition is not a problem with heat stable thermoplastic materials, such exposure to heat during handling and compounding obviously is not possible with thermosetting compositions.

The following examples which are intended to be illustrative only show the preparation of coated conductors and the physical characteristics thereof.

Example I

A mixture of 100 parts of polyvinyl chloride resin (Geon–103) [1] and 40 parts of alkali refined, deodorized epoxidized linseed oil (oxirane content 9.02) containing 50 parts of satintone clay, 2 parts of pigment, and ½ part of zinc stearate lubricant is blended and compounded in a Banbury mixer at a temperature in the range 350–405° F. The mix is then sheeted on a two-roll mill and hot strip fed to an extruder directly from the two-roll mill. The heated screw type extruder is equipped with an appropriate crosshead wire coating die. The resin composition is liquefied by the heat of the extruder and the flowable resinous mixture enters the center of the die while the wire enters from one side of the die. The coated wire emerges from the opposite side of the die and is passed directly to a curing oven where the coated conductor is subjected to a high temperature (about 500–550° F.) and a treating time of approximately 2–20 seconds. The physical characteristics of the cured coating are as follows:

1. Tensile strength p.s.i.	6500
2. Percent elongation	10
3. Trichloroethylene extraction (24 hrs. at 100° F.) ——percent—	0.2
4. Soapy water extraction (24 hrs. at 100° F.) ——do——	0.05
5. Tensile strength p.s.i. after aging 7 days at 100° C.	6600

Similar results are obtained when epoxidized safflower oil, epoxidized perilla oil, or purified epoxidized fish oils are employed as the source of the fluid epoxide.

The coating from a similarly coated conductor having conventionally plasticized polyvinyl chloride as the coating possessed the following physical characteristics.

1. Tensile strength p.s.i.	3200
2. Percent elongation	120
3. Trichloroethylene extraction (24 hrs. at 100° F.) ——percent—	19.5
4. Soapy water extraction (24 hrs. at 100° F.) ——do——	3.5
5. Tensile strength p.s.i. after aging 7 days at 100° C	3300

In the drawing an unwind reel **10** contains the wire source **12** which which is fed into an extruder **11** which is equipped with a standard crosshead die. The resin coating material comprising the mixture of vinyl halide resin and oxirane-substituted ester is introduced into the extruder through hopper **13**. The coated wire **14** is then passed through curing tunnel **15** where the coated wire is subjected to high temperature to render the coating thermosetting. The wire having the hard protective coating is then passed through cooling bath **16** and wound around capstan **17**. Rewind reel **18** is provided for use in preparing rolls of the coated conductor for storage and shipment.

The apparatus employed in the coating operations described herein comprises an NRM 1½" extruder with a standard wire coating crosshead. The die employed produces .030" insulation on an 18 gauge copper wire, the finished wire being .100" in diameter. Usually the thickness of the coating is about 60–100% of the thickness of the core. Following the extruder in the line is a tunnel type curing oven. The oven is constructed so as to provide temperatures up to about 1100° F. From the curing oven the cured coated conductor is conveyed through a cooling water tank and then wound on reels.

The curing temperature as in all curing cycles is adjusted to and dependent upon the time of exposure of the coating within the curing zone. Increases in the rate of passage of the coated wire through the heat treating zone requires that the temperature of the zone be increased to insure that a cure will be realized in the shorter residence time within the zone. Correlation of curing temperatures with curing times to obtain a desired degree of cure is well within the ability of the skilled artisan. For the purpose of the present examples, cures are effected at 550° F. with an average residence time within the curing zone of 2 seconds. Curing time can be accelerated by use of one of the conventional epoxy curing agents in the composition. Dibasic acids, polybasic acids and the anhydrides thereof are particularly dsirable for this purpose. Such known epoxy curing agents as isophthalic acid, Nadic anhydride, pyromellitic dianhydride, phthalic acid, terephthalic acid, phthalic anhydride, and trimellitic anhydride are particularly desirable for this purpose. Also the strong Lewis acids such as boron trifluoride and boron trifluoride complexes can be used.

Electrical conductors made in accordance with the method hereinbefore disclosed have significant physical and electrical advantages over conductors heretofore known. Since the coating exhibits good dielectric properties, a greater resistance to deterioration on aging, good flexibility, heat resistance, and abrasion resistance, it is adapted to a wide area of diverse uses. The coating exhibits excellent adherence to the core when cured, has good pigmenting properties and high impact strength. Important advantages in handling result from the face that the coating composition is fluid and easily handled without objectionable degradation at extrusion temperatures but cures easily to a tough, hard, heat and chemical resistant thermoset form.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations are to be imposed as are indicated in the appended claims.

I claim:

1. An electrical conductor provided with a heat resistant tough adherent coating of high dielectric strength comprising: a filamentous metallic conductor continuously coated with a cured mixture of a polyvinyl halide polymer containing at least 50% vinyl halide units and an epoxidized triglyceride having an oxirane content in excess of 8.8%.

2. A method of coating an electrical conductor with a thermoplastic composition which may be rendered thermosetting by heat comprising: conveying a filamentous metal strip through an extrusion zone; enveloping said metal strip with a heated fluid mixture of a vinyl halide polymer containing at least 50% vinyl halide units and epoxidized triglyceride having an oxirane content

[1] B. F. Goodrich & Co., Cleveland 15, Ohio.

in excess of 8.8%; continuously removing said coated conductor from said extruding zone; passing said conductor through a heat curing zone whereby to harden the coating of said polymer on said metal strip and increase the adherence of said coating to said metal strip and passing said coated conductor through a cooling zone.

3. A method of manufacturing an insulated conductor having an improved resistance to breakdown at high temperatures comprising: passing a filamentous metal conductor through an extrusion zone; continuously extruding a polymeric vinyl halide coating composition at a temperature above its fusion point around said conductor to form a sheath of the polymer around the conductor; passing the sheathed conductor through a constriction zone to compress said sheath around said conductor; passing said sheathed conductor through a curing zone maintained at a temperature above about 500° F. to effect curing of said sheath; and cooling said conductor with said insulation continuously coated thereon.

4. A method for manufacturing an insulated electrical conductor comprising: passing a filamentous metal core through an extrusion zone; extruding a thermoplastic polymer around said conductor, said polymer comprising a mixture of a vinyl halide resin containing at least 50% vinyl halide units and 40–80 parts based on said vinyl halide resin of epoxidized linseed oil having an oxirane content greater than 8.5% and an iodine value not greater than 10.

5. An insulated electrical conductor of improved flexibility and resistance to softening and flow upon exposure

to elevated temperatures comprising: a filamentous metallic core continuously coated with a thermoplastic resin mixture of polyvinyl chloride and epoxidized linseed oil, said polyvinyl chloride containing 90–95% polyvinyl chloride units, said epoxidized linseed oil containing more than about 8.5% oxirane oxygen, the thickness of said coating being about 60–100% of the thickness of said core.

6. An electrical conductor provided with a heat-resistant, tough, adherent coating of high dielectric strength comprising: a filamentous metallic conductor continuously coated with a cured mixture of a polyvinyl halide polymer containing at least 50% polymerized vinyl halide units and about 40–80 parts based on the weight of said polymer of an epoxidized triglyceride having an oxirane content in excess of 8.8%.

References Cited in the file of this patent

UNITED STATES PATENTS

2,528,523	Kent	Nov. 7, 1950
2,559,177	Terry et al.	July 3, 1951
2,569,502	Swern et al.	Oct. 2, 1951
2,795,565	Newey	June 11, 1957
2,810,733	Greenspan	Oct. 22, 1957
2,836,605	Rowland et al.	May 27, 1958
2,889,338	Dazzi	June 2, 1959

FOREIGN PATENTS

762,856	Germany	Mar. 23, 1953
512,026	Canada	Apr. 19, 1955