United States Patent

Hawkins

[15] **3,668,298**

[45] **June 6, 1972**

[54] **MULTICONDUCTOR COMMUNICATIONS CABLE**

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[22] Filed: **Dec. 10, 1969**

[21] Appl. No.: **883,973**

[52] **U.S. Cl.** ....**174/23 C,** 174/113

[51] **Int. Cl.** **H02g 15/20**

[58] **Field of Search**..................260/45.9, 95; 174/116, 23 R, 174/23 C, 113

[56] **References Cited**

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[57] **ABSTRACT**

A multiconductor communications cable includes a hydrophobic material filling the space between primary insulated conductors. Compatible filler-insulation materials designed for long-life stabilization are described. Insulation materials include various ingredients which stabilize the insulation and resist extraction by the filler.

1 Claims, 2 Drawing Figures

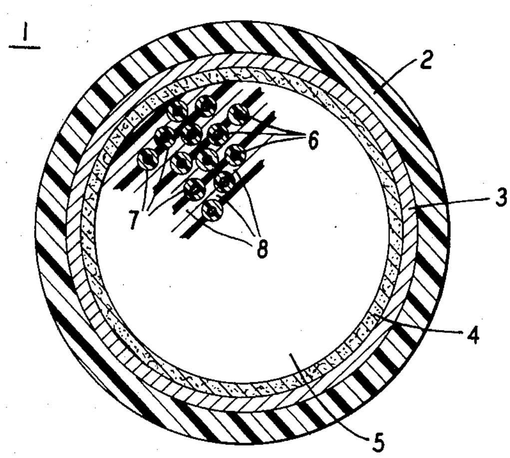


FIG. 1

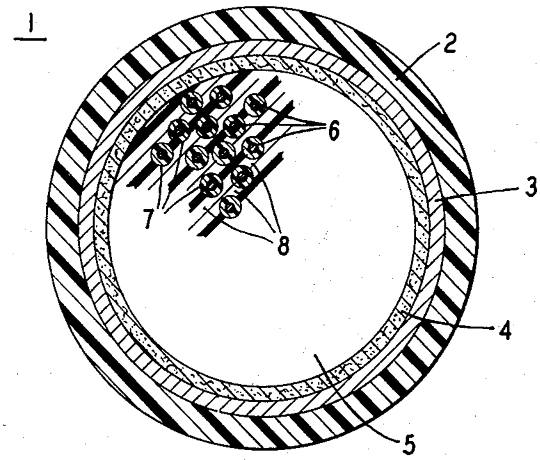
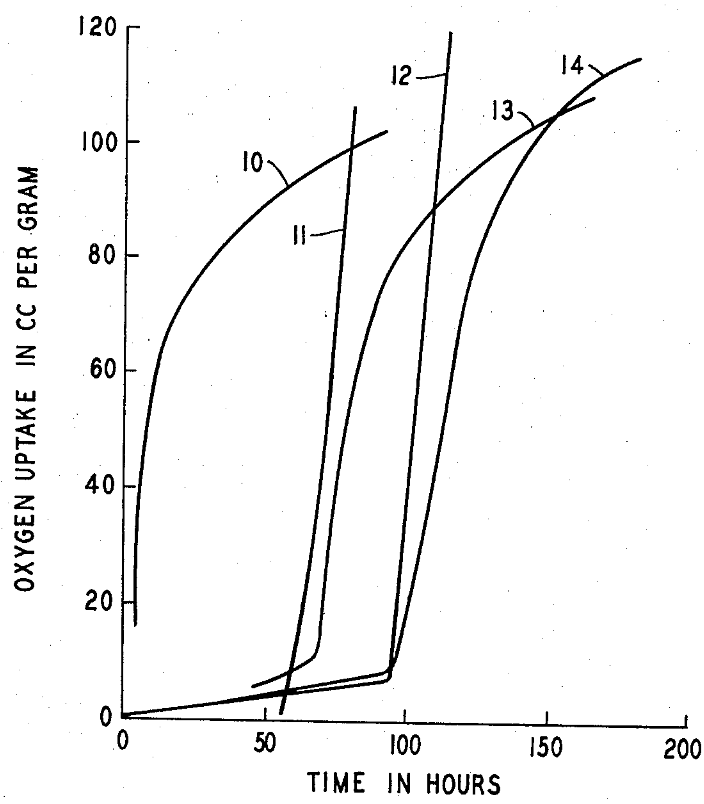


FIG. 2



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MULTICONDUCTOR COMMUNICATIONS CABLE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is concerned with multiconductor communication cables in which water penetration is minimized by inclusion of a hydrophobic material filling the space between insulated conductors.

2. Description of the Prior Art

In Vol. 47, Bell Laboratories Record, p.70 (Mar. 1969), there is described a cable structure in which water penetration is minimized by use of a filler material in the interstices between primary insulated conductors. As indicated in that article, conventional cable structures in which interstices are occupied by air or other gases, while suitable for many purposes, are subject to various types of malfunction due to water penetration. This water penetration which is most significant in underground installations, while not particularly significant when present locally, may, through capillary action, fill exceedingly long lengths of cable. The ultimate effect is somewhat dependent upon the frequency of which the cable operates. In high frequency operation, the mere presence of the water between unbroken insulated sections adversely modifies the dielectric properties of the cable. In ordinary voice frequency installations, significant difficulty is ordinarily encountered only upon actual penetration of the water through the insulation. This, however, is not an unusual occurrence in long insulation lengths. Punctures may be due to manufacturing defects or to mishandling, particularly in the very thin layers (10 mils) in prevalent use.

Recognizing this difficulty, there has been a widespread effort directed toward alleviation of the problem. A significant development which shows some promise involves the use of a water-repellent material filling the air spaces between insulated conductors. The cited reference outlines this approach. In accordance with the article, the hydrophobic filler material, which may include petroleum jelly as a primary ingredient, is introduced in a heated fluid form. Upon cooling, the filler becomes sufficiently rigid so as to be retained in position.

Such filler materials, while eminently satisfactory for water exclusion have introduced concomitant difficulties. For example, where utilized with ordinary polyethylene primary insulation, the filler has produced swelling and also stabilizer extraction. Attempts to overcome this difficulty have included substitutions of polypropylene insulator compositions. While this substitution has largely avoided the swelling problem, it is observed that stabilizer impairment is still present. This difficulty is the more pronounced due to the inherent instability of polypropylene which, as is well known, has required larger concentrations of oxidation inhibitors for given life expectancy. In fact, it is this known susceptibility to oxidation which has limited the use of polypropylene for many long-term applications.

SUMMARY OF THE INVENTION

In accordance with the invention, a long-life cable structure of the type described in the preceding section utilizes critical specified primary insulation compositions which remain satisfactorily stabilized in contact with filler. As in some preceding structures, the base polymer contains at least 75 percent of polypropylene which may be present as a constituent in a blend or as an equivalent amount of homopolymer based on the initial amount of monomer in a copolymer.

The advantage of the inventive structure resides primarily in the nature of the constituents which are designed to protect against oxidative degradation. It is convenient to consider stabilization against oxidation degradation in terms of three categories, and ordinarily compositions utilized in accordance with the invention contain at least one ingredient for protection in each category. In one embodiment, however, a single ingredient serves simultaneously in each of two categories.

The first stabilizing ingredient is sometimes thought of as a chain terminator. This is characteristically a labile hydrogen donor which contributes its hydrogen to terminate an oxidative chain.

The second category is concerned with the hydroperoxides which are intermediate decomposition products. These intermediate products, if not inactivated, take part in further autocatalytic oxidation of the polymer. It is the function of stabilizers in this category to decompose such peroxides and thereby render them inert.

The third category is designed to inhibit the catalytic effect that certain metals, such as copper, are known to have on oxidation processes.

In accordance with the invention, ingredients in each category are so selected that their extraction by normal hydrophobic filler materials is minimal. Selection of appropriate ingredients in each category is extremely critical and, accordingly, acceptable categories are set forth with considerable specificity.

In addition to the stabilizing ingredients which are of primary concern, usual design objectives required certain additional ingredients. In general, selection of such additional ingredients has not posed a problem aggravated by use of a hydrophobic filler. Such additional ingredients include pigments for color code identification, and processing aids, serving mainly as lubricants during extrusion.

A significant additional ingredient is concerned with economics and contemplates dilution of the primary insulation with a cheaper material. Ingredients serving this function by introduction of gas include nucleating agents for providing bubble sites and blowing agents for providing the gaseous expander.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a cross-sectional view of a cable containing a hydrophobic filler and utilizing a primary insulation composition in accordance with the invention; and

FIG. 2, on coordinates of oxygen uptake in cubic centimeters per gram and time in hours, is a plot including several curves representative of accelerated test data for compositions of the invention. Also included is a commercial composition for comparison purposes.

DETAILED DESCRIPTION

1. Drawing

The cable structure **1**, depicted in FIG. **1**, is composed of an outer sheathing **2** which is ordinarily predominantly polyethylene and which encloses a metallic layer **3**. This metallic layer, which may be aluminum, is designed to lend structural rigidity, lightning protection and a means of dissipating heat which may be generated locally. Region **4** is a core wrap. This generally takes the form of an overlapping spiral wrapping of a suitable material. Region **5**, contained within wrap **4**, includes the primary conductors **6** which may be of copper or other suitable metal, each of which is electrically insulated by primary insulation **7**. Interstitial positions **8**, shown in shaded cross section, are, in the concerned structure, filled with a hydrophobic filler material.

The structure depicted is merely illustrative and may take other forms. Under specific environmental conditions, there may be additional metallic layers to protect against animal life as well as additional plastic sheathing layers. Other forms may be designed for high frequency use and, to this end, may contain one or more conductor pairs of coaxial configuration.

2. Concerned Compositions

a. The Primary Insulation

The nature of the primary insulation, as unmodified, has been briefly discussed. Since the problem to which the invention is addressed concerns extraction of modifying ingredients from polypropylene, it is required that the primary insulation contain a sufficient amount of this polymer for the extraction problem to be significant. It has been stated that the equivalent amount of polypropylene in the primary insulation, at least at the surface exposed to the hydrophobic filler, must be a minimum of 75 percent by weight polypropylene. Since both simple blends and copolymers are contemplated, the 75 percent figure has reference either to a distinguishable amount of polypropylene or to the amount of propylene monomer required to produce a copolymer within the specified composition range.

Additional ingredients may be polymers or monomers of ethylene, vinyl monomers such as vinyl acetate, butene-1, acrylic acid, methacrylic acid, and their corresponding esters as well as similar vinyl monomers.

b. Insulation Modifiers

The first category of modifiers is conventional. These include colorants, processing aids, blowing agents, etc. While some colorants are subject to extraction by the hydrophobic filler, materials now in use do not appear to suffer significantly from this problem. Extraction of processing aids and of blowing agents is of little concern since they are intended to serve no function in the completed product.

In the main, disadvantages in earlier structures have been concerned with the stabilizer systems, and systems considered appropriate in accordance with the invention are now discussed in some detail under the three categories noted above.

Chain Terminators

This ingredient is ordinarily included in the amount of from 0.1 to 1.0 percent by weight. Chain termination is dependent upon one or more functional hydroxyl groups. However, while there is a large category of materials which owe their effectiveness to this grouping, only a selected few have been shown to be appropriately included in the inventive structure. The basic chain terminators found suitable are classified as thiobis phenols. Typical examples include:

4,4′ thiobis(2 tert. butyl-5 methyl phenol);

2,2′ thiobis(6 tert. butyl-4 methyl phenol); and thiobis beta naphthol.

Isomers of any of the above materials as well as modifications in which cyclic moieties contain additional hydrocarbon or other substituents are also effective. Generally, hydrocarbon substituents, where present in the named examples or where added in any modification, should result in a total of no more than about 10 carbons in each moiety, it being observed that further increase results in a significant loss in protection.

Peroxide Decomposers

Peroxide decomposers are all dependent upon either free sulfur or compounds containing two or more bonded sulfurs. Interestingly, most monosulfides have been determined to be ineffective for this use in a long-life product. Exemplary disulfides are listed:

1. Tetramethyl thiuram disulfide
2. Tetraethyl thiuram disulfide
3. Dinaphthyl disulfide

Several variations are permitted. For example, any of the listed compounds may contain simple alkalyl substituents although, again, where such substituents are present on a cyclic moiety, the total number of carbons in the substituents should not exceed 10. Other substituents either on cyclic or aliphatic compounds may include elements known to be harmless to the polymer. These include nitro groups, halogens, carboxyls and various esters. Generally, the aliphatics have been found to be of decreasing effectiveness as the chain length of substituents increases and, for this purpose, a limit of 8 carbons is imposed. Substituents may also be cyclic and the basic cyclic grouping in the moiety may be heterocyclic as well as hydrocarbon. An example is morpholine disulfide. An additional class of materials useful in this category is the polymers including repeating units of which meet the requirements set forth. An example is the polymer formed from 1, 10 dimercapto-decane. Permissible amounts of peroxide decomposers are, again, in the range of from 0.1 to 1.0 percent by weight based on total composition.

Elemental sulfur may serve both as a chain terminator and peroxide decomposer and, if unsupplemented in either function, may be included in amounts of up to 2 percent by weight.

Copper Deactivators

The preferred material in this category is oxanilide (diphenyl oxamide) although other oxamide derivatives may be substituted. Such derivatives include:

Di-2-pyridyl oxamide
Di-p-tolyl oxamide
Di-o-chlorophenyl oxamide
Di-p-ethoxyphenyl oxamide
Dibenzyl oxamide
Dimethyl oxamide
Di-p-chlorophenyl oxamide
Di-allyl oxamide
Di-n-hexyl oxamide

Inclusion is within the range of from 0.1 to 1.0 weight percent.

c. The Hydrophobic Filler

Filler materials must fulfill certain physical requirements. For example, they must have significantly low viscosity to fill the interstices at extrusion temperatures which are ordinarily in the range of from 165° to 250° C, and must be sufficiently rigid at operating temperatures to be retained in position. It has been previously determined that a composition suited to this end consists of a blend of 80–89 percent petroleum jelly, remainder a polyolefin having a molecular weight of the order of 20,000 or greater. Suitable alternatives include blends of higher molecular weight polymers which may contain lesser amounts of high molecular additives, and also low molecular weight polymers such as, for example, polyethylene having a molecular weight of less than 5,000.

3. Test Data

An extensive series of tests has been conducted to determine the effectiveness of the inventive compositions. The basic accelerated procedure is now well established and has been in use for many years. It involves heating the sample under test in an oxygen-containing atmosphere and measuring oxygen uptake per unit volume of sample. The trend of such data as represented on rectilinear coordinates of oxygen uptake and time is familiar. Representative curves may be regarded as being made up of two essentially straight line portions, the first commencing at the origin and of small slope while the second and subsequent section is of substantially steeper slope. As for typical antioxidant protected plastics, the break in slope represents the commencement of autocatalytic breakdown; and for many purposes, this point (at which the slop changes) is considered to represent the termination of useful life of the plastic. For usual purposes, the precise value considered is that of the intercept of the autocatalytic portion of the curve with the abscissa. The period from the origin to the time so defined is commonly referred to as the "induction period." Curves on FIG. 2 corresponding with inventive compositions show this general form. While precise equivalent operating temperature lifetime under real conditions corresponding with the test data presented cannot be specified due in part to the variation in conditions under which cables operate, the induction periods for all inventive compositions represented on FIG. 2 and for all compositions otherwise defined in the specification correspond with minimum useful life of the order of 20 years or greater. For most purposes, this is considered adequate. The commercial sample, in accordance with the data presented, does not result in a sufficiently long protected life to be useful in accordance with most cable standards.

The test procedure is presented:

Test compositions were milled in an atmosphere of nitrogen. The antioxidant mixtures were added to 35 grams of unprotected polypropylene with mixing at 180° to 190° C for 5 minutes at a speed of 50 rpm. Copper dust was then added to the concentration of 1.4 percent and mixing was continued for 5 minutes. The composition was then removed and 10 mil sheets were molded on an electric press. Test samples were cut from these sheets.

Test samples weighing between 0.6 and 0.9 grams were covered with an equal weight of the filler mixture by smearing over one surface. The samples, in contact with filler, were then heated at 70° C for 40 hours. After removal from the oven, the filler was wiped off with paper towels, and samples were cut from the treated material for oxygen-uptake measurements.

Samples weighing approximately 0.1 grams were oxidized in an atmosphere of pure oxygen at 120° C. The oxidations were carried out in an aluminum block with duplicate samples for each composition. The rate of reaction with oxygen was measured through the period of autocatalysis, and the steady-state rate of oxidation was extrapolated back to the time axis in the conventional method for determining the induction period.

4. FIG. 2

Each of the curves represents oxygen uptake data conducted in accordance with the generalized procedure set forth above. Conditions for each set of data were identical. Based on prior experience, it has been determined that the stabilizer most significantly impaired by extraction is the peroxide decomposer. The data in FIG. 2 shows a variation in the character and amount of this particular ingredient. Five curves are presented.

Curve **10**

Curve **10** corresponds with an undesignated proprietary composition prepared by a commercial compounder specifically for use in the filled structure which is the subject for this application. The stabilizer system is known to contain at least three and possibly four members, and it is considered as the best commercially available composition for this purpose. From curve **10**, it is seen that the induction period after exposure to filler is of the order of 2 hours.

The following curves, for comparison purposes, utilize 4,4′ thiobis (2 tert. butyl-5 methyl phenol) which at this time is probably the most prevalently used chain terminator for communications cable insulation. The metal deactivator, probably the least affected of the stabilizer ingredients, is oxanilide. For the purpose of this figure, experimental data utilizing three peroxide decomposers was used. Additionally, composition variations within one particular system are represented.

Curve **11**

The peroxide decomposer is tetramethyl thiuram disulfide. The amounts by weight of each of the three stabilizer ingredients is 0.5 percent. The induction period is approximately 70 hours.

Curve **12**

Again, utilizing 0.5 percent by weight of each of the three stabilizer ingredients, however, substituting elemental sulfur as the peroxide decomposer, it is seen that the induction period is now 94 hours.

Curve **13**

The peroxide decomposer is dinaphthyl disulfide. Amounts of the three members are 0.8 percent of peroxide decomposer, 0.2 percent of chain terminator, and 0.5 percent of metal deactivator. The induction period is 60 hours.

Curve **14**

Still utilizing dinaphthyl disulfide as the peroxide decomposer but with a sample containing 0.8 percent of the peroxide decomposer and 0.2 percent of the chain terminator, it is seen that the induction period has risen to 100 hours. While the difference in induction periods is experimentally significant and while data represented by curve **14** is certainly definitive of a preferred embodiment, all induction periods for curves **11** through **14** are considered adequate for commercial installation. The preferred embodiment represented by data of which curve **14** is exemplary may be represented in terms of the preferred peroxide decomposer to chain terminator ratio of from 1:1 to 5:1.

What is claimed is:

1. In a communications cable comprising a plurality of insulating conductors, said conductors including, as primary insulation, a plastic composition consisting essentially of a polymer at least 75 percent of which may be considered as having been polymerized from propylene, the interstices of which are substantially filled by a hydrophobic substantially hydrocarbon filler which includes petroleum jelly as a primary ingredient, said primary insulation contains at least one modifier each from the groups of chain terminators, peroxide decomposers and metal deactivators, the chain terminator being selected from the group consisting of elemental sulfur, 4,4′ thiobis(2 tert. butyl-5 methyl phenol), 2,2′ thiobis(6 tert. butyl-4 methyl phenol), thiobis beta naphthol; the peroxide decomposer being selected from the group consisting of dinaphthyl disulfide, tetramethyl thiuram sulfide and elemental sulfur and polymers containing repeating units meeting the foregoing requirements; and the metal deactivator being selected from the group consisting of Di-2-pyridyl oxamide, Di-p-tolyl oxamide, Di-o-chlorophenyl oxamide, Di-p-ethoxyphenyl oxamide, Dibenzyl oxamide, Dimethyl oxamide, Di-p-chlorophenyl oxamide, Di-allyl oxamide and Di-n-hexyl oxamide, in which each of the said modifiers is contained in an amount of from 0.1 percent to 1.0 percent by weight of the total composition and in which the ratio of peroxide decomposer to chain terminator is from 1:1 to 4:1.

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