TECHNICAL REPORT

AN EVALUATION OF HEAT STABILIZED, FLAME-RETARDED, CROSS-LINKED POLYOLEFINS FOR ELECTRONIC WIRE AND CABLE APPLICATIONS

by

PAUL M. COOK

RICHARD W. MUCHMORE

HOWARD RAPP

For presentation at
8th ANNUAL SYMPOSIUM
COMMUNICATION WIRE AND CABLE
Asbury Park, New Jersey
December 1, 2 and 3, 1959

RAYCHEM CORPORATION

FORMERLY RAYTHERM CORPORATION

OAKSIDE AT NORTHSIDE, REDWOOD CITY, CALIFORNIA

ABSTRACT

Polyolefins, although important insulations for power and telephone wire and cable, have only recently been considered for electronic hookup wire and cable. Four properties of the polyolefins have limited this application in spite of otherwise almost ideal characteristics. These limitations have been (1) flammability, (2) low softening temperature, (3) poor oxidation resistance at elevated temperatures and (4) poor load deformation properties.

The polyolefins have been made attractive for hookup wire and cable applications by the development of a flame-retarded, cross-linked, heat-stabilized insulation. The addition of a newly developed flame-retardant provides self-extinguishing properties without sacrifice in color stability, corrosiveness, strength and other properties normally associated with the use of the conventional antimony trioxide, chlorinated paraffin flame-retarding system. Radiation cross-linking changes the thermoplastic into a three dimensional network exhibiting rubber-like elasticity at temperatures above the crystalline melting range. To permit operation at elevated temperatures however, it has been necessary to strengthen the three dimensional gel so that the insulation has sufficient strength to withstand physical abuse. Protection against oxidation is accomplished by the addition of low-volatility heat stabilizers.

Hookup wire and cable product evaluations are reported with emphasis on those properties previously found limiting. Detailed testing of the properties of the wire and cable constructions at elevated temperature for both long and short life periods have led to conservative life ratings. Heat aging, while under severe stress, is found to be the most limiting property of this high temperature insulation, and a test based upon this observation is recommended for proper product control.

INTRODUCTION

Although polyethylene has become an important insulation for power, telephone and high frequency wire and cable, several limitations have precluded its use for low voltage, thin wall hookup wire. The major limitations have been: 1) low softening temperature, 2) flammability, 3) poor oxidation resistance at elevated temperatures, and 4) poor load deformation properties. An intensive research and development program has resulted in the introduction of a new flame-retarded, heat stabilized, cross-linked polyolefin wire which surmounts these limitations.

The evaluation of a hookup wire intended for use over a wide temperature range must be preceded by an understanding of the insulation material. It is the purpose of this report to describe the nature of the insulation and evaluate its properties, particularly with respect to the above mentioned limitations of a polyethylene insulated thin wall hookup wire.

NATURE OF THE MATERIAL

The cross-linking of polyethylene has been successfully accomplished by both chemical and radiation techniques. The oxidative stabilization of a cross-linked polyethylene is difficult, however, because the most effective antioxidants interfere with the peroxides in chemical cross-linking and act as antirads in a radiation cross-linking process. Successful stabilization of a radiation cross-linked polyolefin system has now provided remarkably long time oxidation resistance at elevated temperatures. This accomplishment has led to the adoption of the radiation technique to obtain substantial cross-linking and the resultant high elastomeric strength at elevated temperatures.

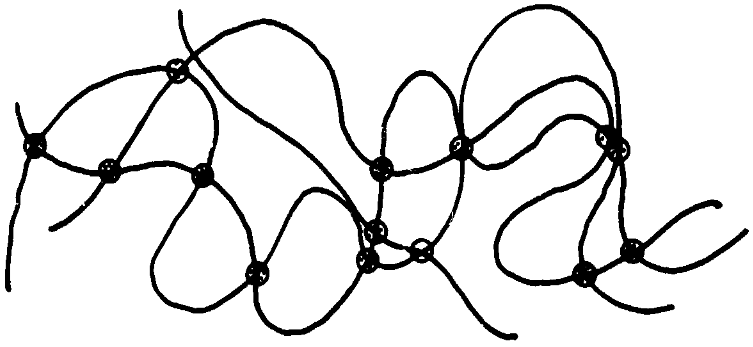
Polyethylene is commonly flame retarded by the addition of antimony trioxide and chlorinated hydrocarbons. This system is completely unsatisfactory for use in an insulation to be radiation cross-linked and used at elevated temperatures because of the instability of the carbon-chlorine bond to both radiation and heat. A new inorganic flame retardant system has provided a heat stable non-corrosive insulation.

A blend of various commercial polyolefins has provided a rugged insulation which will withstand the abuse coincident with commercial fabrication and assembly procedures.

To understand the nature of a cross-linked polyolefin insulation, a visualization of the molecular structure is of assistance. Since polyethylene constitutes a significant portion of the polyolefins used and for simplification, the explanation is based upon polyethylene molecules. For visual clarity some liberties are taken with respect to dimensions and molecular configurations but functional considerations are accurate.

The structure of polyethylene consists of long molecules (macromolecules) in a random arrangement. Crystals form where the molecules come close together in an ordered arrangement. Figure 1 is a visual representation of the molecular structure of polyethylene.

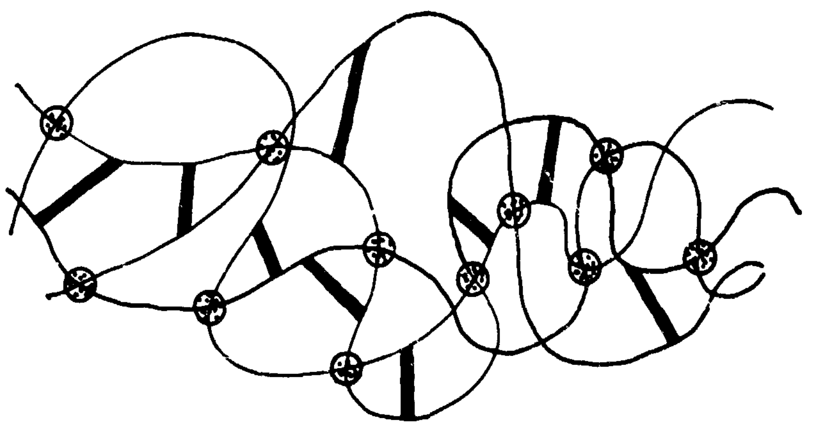
①



Exposure of polyethylene to high energy penetrating radiation causes a chemical change to take place. This results in the joining together or cross-linking of the molecules into a three dimensional structure.

Figure 2 is a representation of the molecular structure of such a system after exposure to radiation with the cross-links shown in heavy black lines.

②

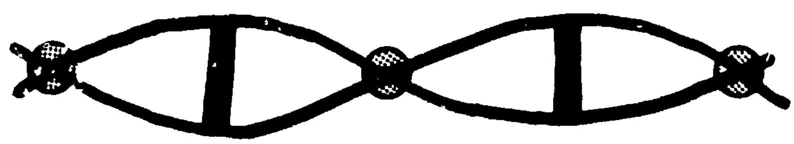


The properties of cross-linked polyethylene at temperatures below the crystalline melting range are determined primarily by the crystallinity and the length and branching of the molecules. These factors are controlled by the original polymer manufacturer and are well documented and understood. Literally hundreds of varieties of polyethylene are available and proper selection is made on the basis of the product to be fabricated.

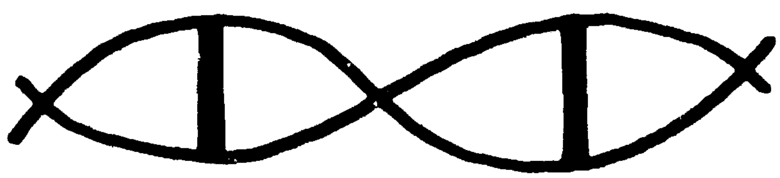
When cross-linked polyethylene is heated above the temperature where the crystals melt, the material becomes a gel exhibiting perfect elasticity. In other words, the material acts like a rubber band. Any force will cause it to deform. Release of the force results in the material returning immediately to its original size and shape.

The following sequence of illustrations demonstrates the molecular structure and its elastic behavior.

When at room temperature cross-linked polyethylene has a high degree of crystallinity as shown by the very expanded view shown below of two molecules. The crystals are responsible for the great strength at room temperature.

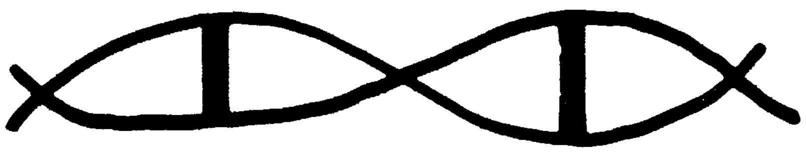


However, as the temperature is increased, the crystals melt and leave the cross-linked structure as shown below:

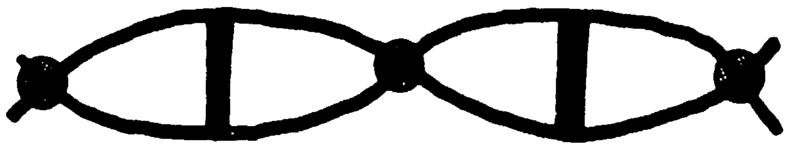


When a force is applied to this three dimensional system, the molecules distort in an elastic manner as shown here.

The greater the applied force, the stronger the material becomes just as an elastic band becomes when it is stretched. As long as the force is continuously applied, the molecules continue to resist with an equal and opposite force. When the force is released the molecules immediately return to their original position as indicated:



If the material is allowed to cool, the crystals reform as before.



If the material is cooled while a force is being applied, the crystals will form with the moleculc in its stretched condition as shown here.

Removal of the force after cooling will not allow the material to return to its original shape since the crystals have greater strength than the cross-links. Heating the material to remelt the crystals will permit the return of the original size and configuration.

PROPERTIES AT ELEVATED TEMPERATURES

Strength

For a hookup wire to be serviceable at elevated temperatures, it must be able to resist vibration, abrasion, cut through and other physical abuse and still maintain its electrical insulating qualities. Previous irradiated polyethylene systems have been weak gels which will maintain only form stability at temperatures above the crystalline melting range. The weak insulation does not have any measurable abrasion, cut through or deformation resistance above the crystalline melting temperature. The development of the irradiated modified polyolefin insulation has provided an insulation for thin wall hookup wire which has strengths approximately ten times that of the previously available irradiated polyethylene insulations.

Oxidation Resistance

The heat resistance of the irradiated polyolefin insulation is limited primarily by the degradation of the strength and flexibility properties with heat aging at elevated temperatures. In the absence of oxygen, polyolefins exhibit remarkable heat stability (weight loss of only approximately 0.2 per cent per minute at 385°C). Therefore, the stabilization of a polyolefin to oxidation becomes a major necessity if it is to permit high temperature service. A major improvement over previously known oxidation protection has been obtained by the novel use of a carefully designed anti-oxidant system. Evaluation of the oxidation resistance is made by use of the heat resistance test described in a later section.

Corrosion

Polyethylene which utilizes the conventional antimony trioxide-chlorinated hydrocarbon system as flame retardants releases hydrochloric acid after radiation when exposed to elevated temperatures. The release of hydrochloric acid and its corrosive effect is particularly noticeable upon examination of a shielded and jacketed hookup wire. Serious lifting occurs to both silver and tin coatings exposing bare copper which also shows evidence of severe corrosion. The release of the acid also leads to color instability which becomes immediately detectable at the time of radiation. The addition of acid acceptors provides only slight improvement.

The development of a new flame retardant system in the laboratories of Raychem Corporation has provided a means of obtaining a heat stable non-corrosive polyolefin insulation which does not change after massive doses of high energy electron radiation. The insulation is self-extinguishing as measured by a horizontal flammability test and has a maximum flame travel of three inches from the point of flame application.

Life Rating

Establishing a life rating at elevated temperatures for a hook-up wire is a controversial problem. Most wire insulations have a restrictive melting or softening temperature which simplifies the determination of a maximum temperature. The irradiated polyolefin maintains substantial strength at temperatures as high as 400°C. The limitation is the elapsed time within which a certain measure of property degradation occurs. Since degradation of properties is both temperature and time dependent, property degradation results have been studied on a time-temperature basis. The most severe limitation has been found to be the reduction in flexibility and strength during heat aging in an oxygen environment while under substantial stress. A conventional test has been modified to provide a means of establishing life ratings and to provide dependable and reproducible quality assurance inspection. This test provides for the heat aging of the sample while under a substantial deformation load. This is followed by a flexibility test and dielectric breakdown. The test is described in the following section.

Heat Resistance Test

One inch of the insulating compound shall be removed from each end of a 30 inch sample of the finished wire. The central portion of the specimen shall then be bent half-way around a cylindrical stainless steel mandrel, having a diameter as specified in Table I. Both ends of the conductor shall be tied together and then loaded with the weights specified in Table I in such a manner that the portion of the insulation between the conductor and mandrel is under compression, while the conductor is under the tension specified in Table I. (See Figure 1).

T A B L E   I

HEAT ENDURANCE TEST

Wire Size AWG	Mandrel Diameter Inches	Loading Pounds
30-24	1/8	0.5
22-20	1/4	0.75
18-14	1/4	1.0
12- 8	1/2	3.0

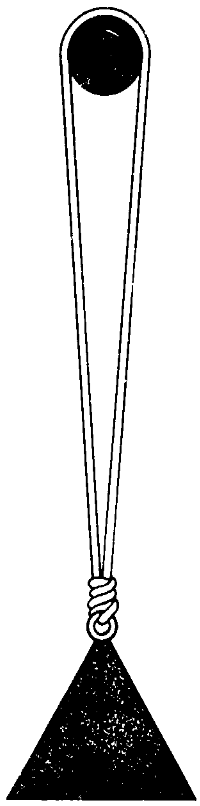


FIGURE 1

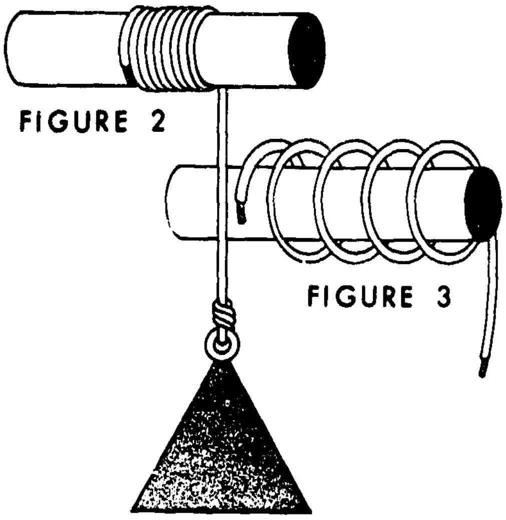
This condition shall be maintained for the period specified in Table II in an air gravity convection type oven maintained at the temperature specified in Table II.

The specimen shall not be subjected to direct radiation from the heating element. After completion of the air oven test, the specimen shall be cooled to between 20-25°C (68-77°F) within a period of one hour. When cooled, the wire shall be freed from tension, removed from the mandrel and straightened. One end of the specimen shall then be secured to the mandrel and the other end to the load weight specified in Table II. The mandrel shall be rotated at a rate not less than 12 RPM until the full length of the specimen is wrapped around the mandrel and is under the specified tension with adjoining coils in contact. The mandrel shall then be rotated in reverse direction until the full length of the wire which was outside during the first wrapping is now next to the mandrel. This procedure shall be repeated until two bends in each direction have been formed in the same section of the wire. (Figure 2). The specimen shall then be subjected to the dielectric breakdown test as follows:

The wire with six-inch leads protruding shall be immersed for one hour in water containing approximately 0.05% Aerosol OT wetting agent. The test procedure shall be that of ASTM D-149-55T using a 500 volts/second rate of rise and a one minute dwell at the test voltage of 2000 volts RMS. (Figure 3).

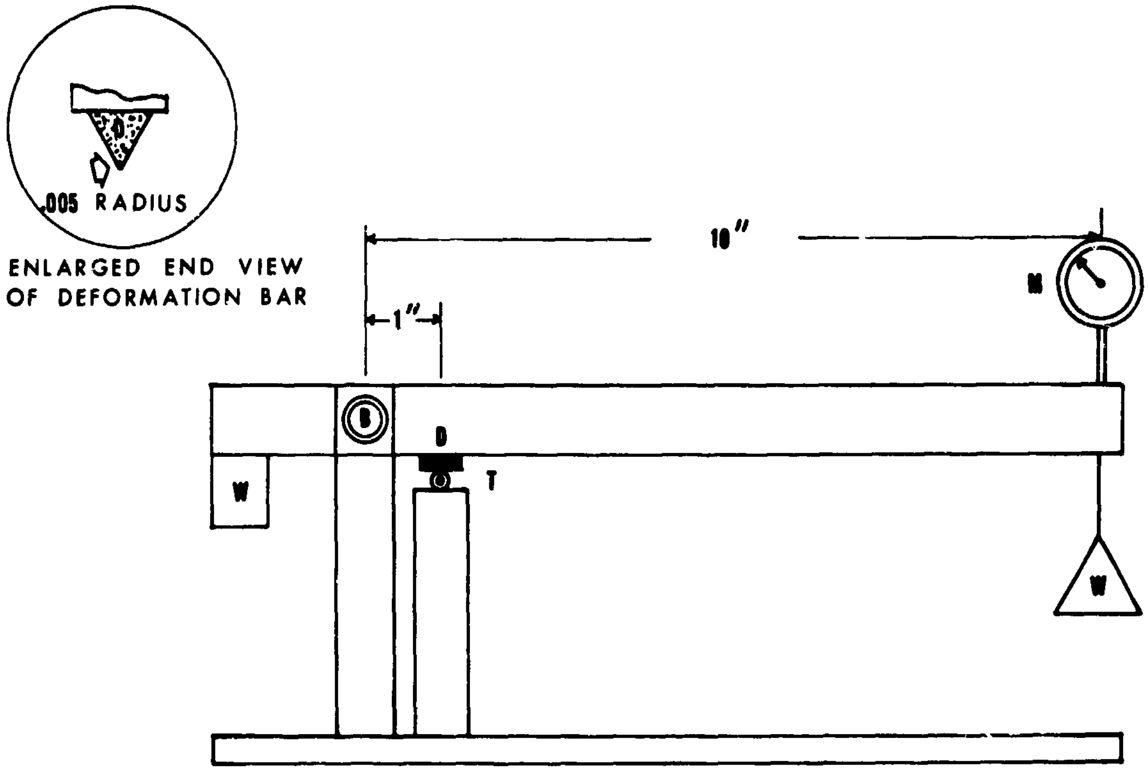
TABLE II

Ambient Temperature	Period
150°C	2200 Hours
175°C	336 Hours
200°C	48 Hours
250°C	4 Hours
300°C	1 Hour



DEFORMATION UNDER LOAD

In an effort to evaluate actual end use conditions, a new deformation under load test has been devised which was designed to test hookup wire under the most severe conditions of sharp edge penetration such as would result from improper electronic assembly techniques or poor adjustment of automatic stripping and marking machines. Figure 4 is a schematic diagram of the deformation load tester. A 90^{o} deformation bar was used with a 0.005" radius adopted because it represented the sharpest cutting edge commonly found in electronic assembly equipment. A near frictionless lever arm with a ten times multiplier ratio was used to apply the stress. A dial micrometer served to measure the deformation. The point at which the insulation cuts through was indicated by the ringing of a bell. A comparison was made of a conventional irradiated polyethylene hookup wire, the new Raychem irradiated polyolefin wire and Teflon hookup wire (Type E, MIL-W-16878). The results are presented in Table III.



T Test Sample
D Deformation Bar
B Frictionless Bearing
M Dial Micrometer
W Weights

LOAD DEFORMATION TESTER

FIGURE 4

TABLE III

LOAD DEFORMATION TEST

Wire Type		Irradiated Conventional Polyethylene	Irradiated Modified Polyolefin	Teflon Type E MIL-W-16878
Wire Diameter		.060"	.061"	.060"
Load	**Time**	**Deformation**	**Deformation**	**Deformation**
.13 lbs.	0 min.	.003"	.002"	.002"
.38	0 min.	.010"	.008"	.007"
	5 min.	.011"	.009"	.009"
	10 min.	.011"	.010"	.009"
.63 lbs.	0 min.	cut through immediately	.011"	.011"
	5 min.		.013"	.013"
	10 min.		.014"	.014"
.88 lbs.	0 min.		.015"	all cut through at 1 to 1.75 min.
	5 min.		.017"	
	10 min.		.018"	
1.13 lbs.	0 min.		all cut through at .1 to .3 min.	
	5 min.			
	10 min.			

All results based on average of three determinations each.

All wires 20 AWG stranded (19/32) with 10 mil wall insulation.

All measurements were made ± 0.0001" and reported as an average to the nearest one thousandth of an inch.

CONCLUSION

A new electronic hookup wire ~~has been~~ developed for service over a wide temperature range based upon a heat stabilized flame retarded cross-linked polyolefin insulation. Cross-linking is accomplished by exposure of the wire to massive doses of high energy electron radiation. Previous limitations of low softening temperature, poor corrosion characteristics with conventional flame retardants, poor oxidation resistance, and lack of toughness and abrasion resistance that retarded the use of polyethylene as thin wall hookup wire insulation have been eliminated. A strong elastomeric three dimensional network gives substantial strength at elevated temperatures along with a remarkable oxidation resistance giving extended high temperature service even while under severe stress. A new flame retarded system has eliminated any corrosion problems. The deformation of the insulation by a small radius under high unit stress is remarkably good and indicative of the ability to withstand rugged handling and assembly practices.

Additional advantages of this new hookup wire include outstanding radiation resistance, chemical resistance and abrasive resistance. The wire is a light weight, relatively low cost product for service in difficult environmental situations.