

PATENT SPECIFICATION

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(54) METHOD OF THERMALLY CURING POLYMERIC MATERIALS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, 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:—

The present invention relates to methods of curing polymeric materials.

The growth and magnitude of the rubber and plastics industry and the expansion of the number and kinds of products and articles formed from the many curable polymeric materials developed has prompted extensive efforts directed to accelerating the rate and improving the efficiency of effecting high temperature induced cures such as the common vulcanization and cross-linking of elastomers and polymers.

Steam, the traditional heating medium in most commercial vulcanization and other heat induced polymeric curing processes, as is well known, inherently involves progressively disproportionately greater increases in pressure for increases in its temperature, which in turn requires expensive and massive confining measures for its generation, transmission and application in order to hasten curing procedures by increasing steam temperatures. Also, the high pressure conditions incurred with high temperatures steam drives the ambient water vapor of the steam atmosphere into the polymeric material which often necessitates a post curing drying operation to thereafter expel this moisture from the products formed therefrom.

Moreover, the rate of carrying out heat induced curing processes is especially significant when the manufacturing procedure is of a continuous nature with respect to both the production facility and product formation,

such as with the continuous extrusion or forming of articles or products of interminable length exemplified by hose or tubing and covered wire or cable. When such a product of extended length is continuously formed, the forming and curing operations are best continuously carried out in an uninterrupted tandem sequence, because the time requirements for increasing the temperature throughout a mass of polymeric material up to its curing temperature conditions for most cure systems are normally considerably longer than the time needed to complete the forming process.

The limitations of steam and of other prior art techniques, and the incentive of substantial savings through increased production rates, has for some years fostered the development of a variety of new curing means and systems by the industry. Notwithstanding such efforts, the development of curing techniques and systems has not kept abreast of the advances in plastic forming procedures and technology in increasing production rates and in lower costs whereby the decidedly slower curing rates have retarded currently attainable product formation speeds in continuous systems with the result of substantial losses in production.

The present invention provides a method of inducing a cure in heat curable polymer compositions comprising contacting a body of heat curable polymer composition with a stream of hot gas heated to a temperature of at least 500°F and moving at a velocity of at least 3000 feet per minute while said gas is under a pressure of at least 45 lbs. per square inch.

The invention is based upon the discovery that curing rates can be markedly accelerated and thus overall production increased and costs reduced by applying a heated gas, in direct contact flowing over the surfaces of the body or mass of a curable polymeric composition, or the product formed thereof, at ultra high velocities and moderately increased pres-

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5 sures whereby the gas stream in effect pene-
trates through and/or drives away the therm-
allyinsulating static boundary layer or stagnant
film of air or other gas molecules residing on
10 or about the surface of the body or mass
of polymeric composition, or which may be
retained entrapped thereon by turbulent flow
patterns such as Eddy currents due to an over
passing gas stream of moderate velocities.
15 In other words, heat is transmitted by gas
convection at such temperatures, pressures
and very high velocities, to the surfaces of
the article to be cured so as to effectively
sweep away substantially all intermediate air
or gas molecules residing between the moving
hot fluid stream and the article surface which
otherwise would in effect function as an inter-
mediate insulating blanket or heat barrier of
static air or gas enveloping the surface of the
20 polymeric composition to be cured and thereby
obstructing efficient heat transfer through the
mechanism of gas convection.

25 The drawing comprises a graph illustrating
relative exemplary cure times for varying
conditions of gas temperatures and velocities.

The velocity of the heated gas is preferably
within the range of 5,000 to 10,000 feet per
minute.

30 The temperatures of the heated gas for
accelerating typical heat incited cross-linking
or vulcanizing curing systems of polymeric
materials should comprise at least 500°F, and
preferably 600 up to about 1000°F, for
optimum effectiveness with most common
35 polymeric compositions. However, the tem-
peratures and/or dwell period of exposure
to such temperatures should be adjusted, if
need be, to complement the characteristics
of particular polymeric compositions under-
going curing so that the required tempera-
40 ture level for the cure is quickly attained
throughout the polymer mass and the heat
cure is thereby rapidly achieved without over-
heating and deterioration which is a common
hazard with some compositions such as halogen
45 containing polymers.

50 The pressure requirements of the heated
gas of the high velocity curing system of this
invention are generally moderate and need
only be about three atmospheres in most
applications, and generally pressures within the
range of 45 to 200 lbs. per square inch will
produce substantially non-porous and uniform
cured products with most common polymeric
55 compositions. The efficiency and high rate
of heat transfer attained with this invention
and the very high curing capacities achieved
thereby, are especially advantageous when
applied in production systems with uninter-
rupted tandem production line facilities com-
prising a continuous extrusion forming opera-
60 tion combined in operating sequence with a
continuous curing operation for the manufac-
ture of articles of extended or indeterminable
65 lengths whereby the curing phase can be in-

creased and adjusted in rate to accept and
handle the very high production forming rates
obtainable with contemporary extrusion
apparatus.

70 Apparatus suitable for carrying out this in-
vention may include many different embodi-
ments, however the invention is most con-
veniently and effectively performed within
the confines of an elongated curing chamber
or housing such as may be provided by a sec-
75 tion of pipe of appropriate diameter to accom-
modate the article or body undergoing curing
and the enveloping pressurized high velocity
gas stream, and of a length to provide the
needed residence or dwell time to achieve
80 the required degree of heat transfer to raise
the temperature to the designed level through-
out the mass of material to effect a sub-
stantial cure therethrough. Typically, although
not always necessarily, the confined curing
85 area will be connected with or simply extended
to provide a cooling unit or area which most
expediently comprises a similar elongated
chamber or housing containing cooling means
such as a cooling fluid, the most practical of
90 which comprises water. Cooling is normally
desirable to prevent internal gasing and/or
expansion of the mass of the material upon
exposure to atmospheric temperatures and
pressures. Thus the overall curing apparatus
95 may include a long section of pipe, comprising
a heat curing area wherein a stream of hot
gases is passed under pressure at velocities
of at least 3000 feet per minute which extends
directly into a water leg or area containing a
100 cooling liquid. The heating area of the pipe
or continuous chamber is appropriately con-
nected with a suitable source of gas, heating
means for the gas, and high velocity fans or
blowers, and the cooling area thereof is pro-
105 vided with the necessary cooling fluid trans-
mitting conduits. Also it is desirable is means
are provided for the recirculation of the heated
gas for reasons of economy, especially when
the heat carrying gas is other than air. 110

115 The following comprises specific illustrations
of the application of this invention to the
manufacture of peroxide cross-link cured poly-
ethylene compositions for electrical insulation
coverings extruded about a metallic conductor.

120 The cross-link curable polyethylene insulat-
ing compound employed in the following
illustrations comprised, in parts by weight:
100-polyethylene; 50-calcined clay filler;
5-carbon black; 3.5-di- α -cumyl peroxide
(Hercules Di-Cup*); and 1.75-polytri-
methylidihydroquinoline antioxidant (Mon-
santo Flectro* H). This compound was con-
tinuously extruded onto a moving core of a
solid copper conductor, No. 14 AWG, in two
125 different product thicknesses of 0.030 inch
and 0.047 inch. The insulated wire product
with the 0.030 inch thick of uncured poly-

*Registered Trade Mark.

ethylene composition was moved from the extruder directly into and through a high velocity gas curing system at a rate of about 70 feet per minute, and the product with the 0.047 inch thick of uncured polyethylene composition was moved from the extruder directly into and through the same cure system at a rate of about 154 feet per minute. The cure system or apparatus consisted of a 1 inch internal diameter pipe in three 10 foot sections connected together to provide first a high velocity gas curing section of 10 foot length, an intermediate pressure gas lock section, and a cooling water leg of 10 foot length.

The heating gas, nitrogen, in each run was heated to a temperature of 600 to 700°F by means of Calrod* electrical resistance heating elements and circulated by means of fans through the first 10 foot curing section at a

pressure of about 125 lbs. per square inch gauge and a velocity of about 10,000 feet per minute in direct contact over the surface of the peroxide containing polyethylene compound formed about the wire core as it passed therethrough. Circulation of the heated gas at moderate pressures and ultra high velocity was along the 10 foot curing section in the same direction of travel as the insulated wire undergoing rapid cure, and the cycle is completed by a return conduit passing through a fan blower and heater to maintain the curing conditions. However the direction of contact of the heated gas and curable material, whether concurrent or countercurrent, is not critical.

The cure times for each thickness of the insulation and other data, together with the cure times for the same polyethylene insulated wire product obtained with steam as a standard, were as follows:

	Polyethylene Insulation Wall Thickness	Approx. Gas Cure Time	Steam (400°F) Cure Time
45	0.047 in.	8 sec.	48 sec.
	0.030 in.	4-5 sec.	28 sec.

These examples demonstrate a cure rate of 5 to 7 times faster than steam.

Typical approximate cure times for such filled polyethylene compositions as given above, when formed by extrusion as an insulation of about 0.158 inch average thickness about copper wire conductor of 0.064 inch diameter, while passing through a cure chamber of 1 inch diameter are illustrated in the graph in the drawing. The data shown in the graph represents curing gas velocities of both 3000 and 6000 feet per minute at gas temperature levels of each 600, 700 and 800°F, all at an absolute pressure of 5 atmospheres.

Although nitrogen comprises perhaps the best all around gas composition for the heat transfer medium in the practice of this invention because of its relatively low cost and generally inert properties with respect to most elastomer and polymer compositions, as well as being normally non-toxic or corrosive, other gases can be utilized, including for example, air, carbon dioxide, argon, and the like. However, the gas should be chemically inert or non-reactive with respect to the particular polymeric composition being cured so as not to degrade it since the mechanism of this invention requires direct exposure of the material to the gas to obtain the primary advantage of substantially accelerated curing rates through more rapid and effective heat transfer.

The hot, pressurized and high velocity gas stream curing conditions and accelerated rates of curing through the improved heat

transfer attributable thereto of this invention, are generally applicable to effect heat induced cures for polymeric type material generally, and including hydrocarbon polymers or elastomers of a relatively high degree of unsaturation such as natural and common synthetic rubbers through the medium of conventional sulfur-accelerated curing system, and also those of relatively low degrees of unsaturation such as polyethylene and similar polyolefins requiring peroxide type curing systems which form free radicals upon thermal decomposition to effect a cross-linking between polymer chains. This latter system of peroxide free radical effected cure is more fully described in U.S. patents 2,888,424 and 3,079,370 and others, and this invention is particularly applicable thereto. Specifically included are homopolymers of ethylene, copolymers of ethylene and other polymerizable materials such as vinyl acetate and propylene, and blends of polyethylene and other polymers, either filled or unfilled.

WHAT WE CLAIM IS:—

1. A method of inducing a cure in heat curable polymer compositions comprising contacting a body of heat curable polymer composition with a stream of hot gas heated to a temperature of at least 500°F and moving at a velocity of at least 3000 feet per minute while said gas is under a pressure of at least 45 lbs. per square inch.
2. A method according to claim 1, wherein the moving gas is heated to a temperature within the range of 600 to 1000°F.

ethylene composition was moved from the extruder directly into and through a high velocity gas curing system at a rate of about 70 feet per minute, and the product with the 0.047 inch thick of uncured polyethylene composition was moved from the extruder directly into and through the same cure system at a rate of about 154 feet per minute. The cure system or apparatus consisted of a 1 inch internal diameter pipe in three 10 foot sections connected together to provide first a high velocity gas curing section of 10 foot length, an intermediate pressure gas lock section, and a cooling water leg of 10 foot length.

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WHAT WE CLAIM IS:—

1. A method of inducing a cure in heat curable polymer compositions comprising contacting a body of heat curable polymer composition with a stream of hot gas heated to a temperature of at least 500°F and moving at a velocity of at least 3000 feet per minute while said gas is under a pressure of at least 45 lbs. per square inch.

2. A method according to claim 1, wherein the moving gas is heated to a temperature within the range of 600 to 1000°F.



3. A method according to claim 1 or claim 2, wherein the heated gas is moving at a velocity within the range of 3,000 to 10,000 feet per minute.
5. 4. A method according to any one of claims 1 to 3, wherein the heated gas is under a pressure within the range 45 to 200 lbs. per square inch.
10. 5. A method according to any one of the preceding claims, wherein the heated gas comprises nitrogen.
15. 6. A method according to any one of the preceding claims, wherein the curable polymeric composition comprises at least one cross-linkable ethylene polymeric material selected from the group consisting of homopolymers of ethylene, copolymers of ethylene and other polymerizable materials, and blends of polyethylene and other polymers.
20. 7. A method according to claim 6, wherein the polymeric composition is cross-link cured with a peroxide.
25. 8. A method according to any one of the preceding claims, wherein the polymeric composition comprises an electrical insulation formed about an elongated conductor.
30. 9. A method according to claim 8, wherein the polymeric composition comprises a covering on a wire.
35. 10. A method according to any one of the preceding claims for continuously effecting a heat induced cure in polymeric compositions, comprising moving the polymeric composition to be cured through an elongated enclosure while passing over the surface of the polymeric composition a gas heated to a temperature of at least 500°F moving at a relative velocity of at least 3000 feet per minute and under a pressure of at least 45 lbs. per square inch.
40. 11. A method according to claim 10 for continuously effecting a heat induced cure in polymeric compositions covering elongated conductors, comprising moving an elongated conductor covered with a heat curable polymeric composition through an elongated curing chamber, passing gas heated to a temperature of at least 500°F through said elongated curing chamber and over the surface of said heat curable polymeric composition at a relative velocity of at least 3000 feet per minute and at a pressure of at least 45 lbs. per square inch.
50. 12. A method according to claim 11, wherein the heated gas is at a temperature within the range 600 to 1000°F and passed over the surface of the heat curable polymeric composition at a velocity of 3000 to 10,000 feet per minute and at a pressure within the range 45 to 200 lbs. per square inch.
55. 13. A method of continuously producing and curing a heat curable polymeric covering on an elongated conductor, comprising the steps of continuously forming a curable polymeric composition about an elongated conductor with the heat curable polymeric composition through an elongated chamber, passing gas heated to a temperature of 600 to 1000°F through said elongated chamber and over the surface of said heat curable polymeric composition at a relative velocity of 3000 to 10,000 feet per minute and at a pressure of at least 45 lbs. per square inch.
60. 14. A method according to claim 13, wherein the heat curable polymeric composition comprises at least one cross-linkable ethylene polymeric material selected from the group consisting of homopolymers of ethylene, copolymers of ethylene and other polymerizable materials, and blends of polyethylene and other polymers.
65. 15. A method according to claim 1 of inducing a cure in heat curable polymer compositions, substantially as hereinbefore described.
70. 16. A polymeric composition heat cured by the method according to any one of the preceding claims.
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