United States Patent Office

3,260,694

Patented July 12, 1966

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3,260,694
CROSS-LINKED CHLORINATED POLYETHYLENE

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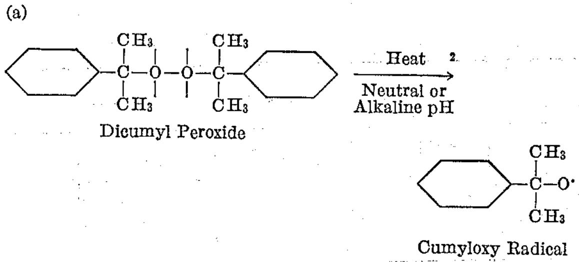
No Drawing. Filed Jan. 9, 1962, Ser. No. 165,224
14 Claims. (Cl. 260—41)

This invention relates to novel thermosetting halogenated polyethylenes and a process for preparing same. Chlorinated polyethylene polymers possess excellent electrical insulation properties, however, in the past these polymers have failed to attain appreciable acceptance as electrical insulation material due to inferior mechanical properties. For example, high molecular weight chlorinated polyethylene polymer is stiff and brittle, while the low molecular weight form has poor tensile strength and deforms readily at room temperature.

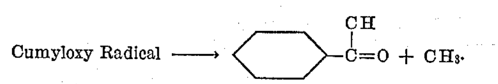
By this invention halogenated polyethylene may be cross-linked to yield in the case where a high and low molecular weight variant of the halogenated polyethylene is cross-linked, a polymeric material having excellent electrical and mechanical properties. The relative amounts of the high and low molecular weight components may be altered over a wide range to provide a final polymer having a varying degree of flexibility. The invention is likewise useful in preparing polymers of cross-linked low molecular weight components, per se and similarly cross-linked polymers of high molecular weight halogenated polyethylenes.

The process of this invention broadly comprises reacting a halogenated polyethylene in the presence of a cross-linking agent. Of special interest from the standpoint of preparing a useful electrical insulation material is the cross-linking of a high and low molecular weight variant of a halogenated polyethylene. The reaction is believed to proceed according to the following sequence of reaction steps using dicumyl peroxide as illustrative of the cross-linking agents.

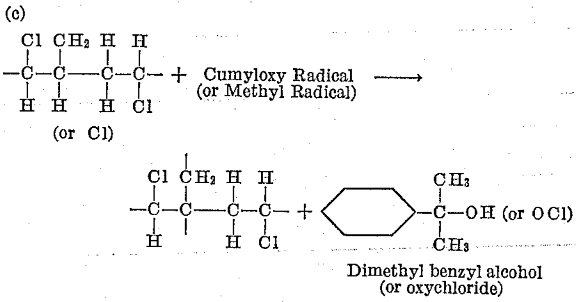
(a)



(b)



(c)



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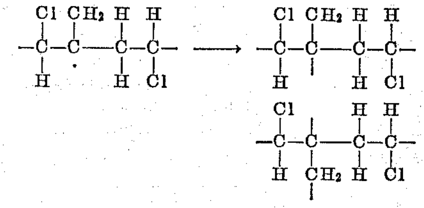
(d) Crosslinking



For purposes of this disclosure, the term "high molecular weight" is meant to include halogenated polyethylenes having a molecular weight greater than 35,000 and "low molecular weight" to include halogenated polyethylenes having a molecular weight below 20,000.

To achieve compositions useful as electrical insulation material, it has been found that the high molecular weight variant may be present in an amount from 30 to 90% by weight of total halopolyethylene and the low molecular variant from 10 to 70% of the total halopolyethylene added. Preferred range is 15–45% of low molecular weight variant.

The invention is exemplified by reference to chlorinated polyethylene. However, it is to be understood that fluorinated, brominated and iodated polyethylenes may likewise be cross-linked. Fluorinated polyethylenes under conditions similar to those in the case of chlorinated polyethylene, whereas brominated and iodated polyethylenes require higher reaction temperatures.

I have not found there to be a limitation on the halogen content of the polyethylene and have found, in the case of chlorine, that a chlorine content of 20–50% by weight of the variant is preferred.

Additionally, fillers such as alkaline or neutral carbon blacks, clays, and whitings may be added. The filler material is believed to impart additional strength characteristics to the polymer due to the formation of chemical bonds between the polymer and filler. The filler may be present in an amount of 15–100 parts per 100 parts of halogenated polyethylene. Preferred amounts are from 30–80 parts. Calcined clays such as Whitetex or Harwick #12 have given best results but fillers such as zinc oxide, whitings, magnesium hydroxides and silicas are satisfactory.

Organic peroxides may be used as the agents to cross-link the high and low molecular weight halopolyethylenes. Typical of the peroxides are dicumyl peroxide, dietertiary butyl peroxide, perbenzoates, perphthalates, 2,5-dimethyl-2,5-di (t-butyl peroxy hexane). Generally, organic peroxides that are sufficiently stable to withstand blending temperatures of the reaction components are satisfactory. The amount of organic peroxide may be varied from 1.5 to 6% by weight of the total composition.

The addition of amine or aminetype accelerators has been found to promote the cross-linking reaction; this is particularly the case where acidic types of fillers, such as, silica and acidic clays are used. The number of cross-links per unit of polyethylene chain length is a factor of the amount of peroxide and the time and temperature of the reaction. Generally, each of these factors independently operates to increase the number of crosslinks per unit molecule as the factor is increased and likewise when operating in concert produces a greater cross-linking.

Typical of the amine or aminetype accelerators are guanidine, di and tri aliphatic and aromatic amines, urea, thioureas, and derivatives of said compounds. The accelerators are generally added in the blending step in an amount of 0.2–2% by weight of the total composition.

The cross-linking reaction may be conducted at temperatures between about 260–450° F. For molded articles, a temperature of 300–360° F. is preferred and a platen pressure of 500 p.s.i. or above. For continuous