METHOD OF BUILDING CONSTRUCTION AND REPAIR USING CHLORINATED POLYOLEFIN FLASHING

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This invention relates to improvements in construction practices using a particular type of resilient sheet material as flashing.

It is standard construction practice to overcome leakage problems by using flashing in valleys between intersecting roof surfaces, over fascia boards, at joints such as those involving masonry, metal or wood (as where chimneys or vent pipes intersect a roof or where masonry parapet walls abut a roof) or between wooden and masonry members of sill structures at floors or windows, as well as in many other places where similar problems exist. The nature of the flashing employed generally varies according to the type and intended permanence of the structure. The more durable flashings heretofore employed have been sheet copper or sheet lead. Less permanent flashings can be made of galvanized iron, aluminum or a tar—impregnated "roofing paper." Recently, in quality installation, particular types of resilient plastic sheet materials have been used for the purpose.

Each of the conventional flashings has some serious recognized shortcomings. Thus, the sheet metal flashings are difficult to seal tightly, especially at joints involving wooden structural supports. Nails driven through such flashings to hold them in place establish potential leaks therein. These, of course, tend to become progressively worse if electrolysis occurs at the point of contact between the nail and the flashing.

There are atmospheric conditions, especially in factory districts or in coal-burning communities, which exert an accelerated corrosive effect on metal flashings. Joints in metal flashing must be made by welding or soldering. Such operations are slow and consequently expensive and, in addition, require considerable skill for proper results.

Flashings made of roofing paper are weak. As they age, they tend to develop leaks around nail holes. They also, particularly on aging, become brittle. They are, in addition, combustible.

In attempting to overcome some of the defects of prior flashing materials, some use has been made of natural rubber sheeting. While having a reasonable level of flexibility it is not long-lived, as it oxidizes and becomes brittle and weak in the course of a very few years. In addition, use has been made of sheeting prepared from synthetic rubber, e.g., butyl rubber sheeting. This type of sheeting, however, requires vulcanization for fabrication, is generally incapable of being joined into larger sheets in the absence of adhesives and is difficulty formulated to provide flame-resistant materials.

Particular types of plasticized, resilient, synthetic thermoplastic sheets formed from vinylidene chloride interpolymer have, despite their comparatively recent origin, been used as flashing with considerable satisfaction and success. Although these prior types of flashing made from synthetic resins give very good service when installed in fairly mild climates, a tendency to stiffen is frequently encountered when such materials are installed in areas where extremes in temperature and/or humidity exist. This loss of flexibility is due at least in part to a gradual volatilization or release of the plasticizing component from the flashing composition. Similar problems are also encountered when using flashing based on plasticized polyvinyl chloride resins.

Many of these same disadvantages of prior known flashing or sheeting are apparent when such materials are used as membranes to cover entire roofs, or to act as water and water vapor barriers under concrete slabs and/or when placed adjacent to sub-surface walls, etc.

Accordingly, it is the principal object of this invention to provide a long-lived, inherently resilient and non-combustible flashing or membrane for use in construction, which material additionally is: corrosion resistant, easily sealed to other sheets of like material by adhesives, solvent welding or dielectric, ultrasonic, or resistance welding techniques, capable of forming a tight seal around nails or other fastening devices driven through it, is not damaged or significantly deformed when subjected to temporary localized stress, and which is compatible with conventional roofing materials such as pitch and asphalt.

Another object is to provide such a flashing or membrane material which does not require the addition or presence of plasticizing ingredients and which retains substantially its original flexibility under a wide variation of climatic and environmental conditions over extended periods of time.

A related object is the provision of improved composite structures comprising the new flashing and membrane material.

Other and related objects and advantages will become evident from the following specification and claims.

The flashing or membrane comprising the present invention is a structure formed from an inherently resilient thermoplastic sheet of solid chlorinated olefin polymer, which polymer is prepared by the chlorination, in suspension in an inert diluent, of polyethylene or interpolymer containing at least about 90 mole percent of ethylene in the polymer molecule with any remainder being one or more ethylenically unsaturated comonomers, wherein such polymers are preferably of an essentially linear structure and have a molecular weight less than about 1,000,000, and preferably a molecular weight of from about 20,000 to 300,000. Such chlorinated olefin polymers may contain from about 15 to 45, and preferably between about 35 and 45, weight percent of chemically combined chlorine and are further characterized by having a relative crystallinity of between about 15 and 28 percent when containing about 25 weight percent chlorine and a relative crystallinity of less than about 10 percent when containing about 34 or more weight percent of chlorine, wherein said relative crystallinity is a measure of the ratio of the crystalline peak areas to the sum of the amorphous plus crystalline peak area as determined by conventional X-ray diffraction techniques; said sheet having a thickness of from about 0.005 to 0.25 of an inch, a tensile strength of at least about 1100 pounds per square inch, an elongation of between about 350 and
900 percent and a 100 percent modulus of about 130 and 1350 pounds per square inch. Polyoleins, including those contained in the flashing and membrane compositions of the present invention can be readily obtained by practice of a chlorination procedure which comprehends the suspension chlorination in an inert medium of polymers and interpolymer of ethylene, as hereinbefore fully defined, to a desired total of combined chlorine, wherein such polyolefin is first chlorinated at a temperature of up to about 95°C., and preferably at about 65°C. and 90°C. for a period sufficient to provide a chlorine content of not more than about 23 weight percent chlorine, based on the total weight of the polymer; followed by the sequential suspension chlorination of such polymer, in a particular form, at a temperature above that employed for the herein described first chlorination and not more than about 150°C. and preferably below the crystalizing melting point of the polymer.

Exemplary of preferred polyolefinic materials to be chlorinated are those distice structure and species and varieties of essentially linear and unbranched highly porous, finely divided polymers containing at least about 90 mole percent ethylene in the polymer molecule with the remainder being one or more ethylenically unsaturated comonomers such as the non-aromatic hydrocarbon olefins having 3 or more ring atoms, including propylene, butene, and butene-2, and 1,7-octadiene and the like; cycloaliphatic olefins such as 1,5-cyclopentene and cyclooctadiene and the like; substituted olefins such as acrylic acid and its esters; conjugated diolefins such as butadiene and the like; and the alkenyl aromatic compounds such as styrene and its derivatives, among many other polymericizable materials known to the art.

Advantageously, the polymers and interpolymer, described herein, are prepared under the influence of catalyst systems comprising admixtures of strong reducing agents such as triethyl aluminum and compounds of groups IV-B, V-B and VI-B metals of the Periodic System, such as titanium tetrachloride, and the like, and are characterized by having molecular weights ranging generally less than about 1,000,000 and preferably between about 20,000 and 300,000.

The liquid which is employed to suspend the finely divided polymer may be any liquid which is inert to the polymer and is not affected to an appreciable extent by chlorine, or which, while wetting the polymer will not have an appreciable solvent effect on it. While water may be employed with especial advantage, as a suspending liquid for the polyolefin to be chlorinated, the polymers may also be suspended in other inert liquids.

A variety of wetting agents, including organic sulfonates, sulfates, polyphosphates and other types of ionic and anionic sulfonate materials may be suitably employed, if desired, to assist the inert suspending liquid (particularly when such liquid is water) to wet the polymer. Such materials as sodium lauryl sulfate, alkyaryl polyether alcohols and pentasodium pentacarpyl pyrophosphate are illustrative of specific wetting agents that may be utilized. The employment of a wetting agent facilitates the mechanical handling of the suspended polymer during the suspension chlorination. In some cases, however, it may not be necessary to employ wetting agents, especially when a freshly prepared polymer is employed that is undried after its preparation or when efficient agitation is available for producing and maintaining the polymer slurry.

Further, if it is desired to accelerate the chlorination rate of the reaction, the reaction may be assisted by the employment of small quantities of catalysts, such as the free-radical types and/or ultra-violet light. When a free-radical catalyst is employed, the rate of reaction which is accomplished through the assistance of the catalyst will depend on such factors as the catalyst concentration, the temperature of the suspending medium in which the catalyst is dissolved, the pH of the solution and the chlorine pressure. Various azo type compounds and peroxides selected from the group of free-radical catalysts consists of azo-3,3-dinitrophenol; acetaldehyde; hydrogen peroxide; tert-butyl peroxide; tert-butyl hydroperoxide; potassium persulfate; diazidodisobutynitrile; methylethyl ketone peroxide and the like, may advantageously be employed. Preferably, when catalysts are employed, such catalyst should be one which has an efficient rate of decomposition in the suspending medium in which it is dissolved, in the required temperature range. In this regard it may be advantageous to employ a mixture of such catalysts, one of which has a temperature of efficient decomposition at or near the optimum initial chlorination temperature, and the other having an efficient decomposition rate at or near the optimum sequential chlorination temperature. Such catalysts may be added in a single step or continuously depending upon the reaction conditions and catalyst used.

The suspension chlorination procedure described herein as a preferred chlorination technique may be carried out at atmospheric pressure, however, better results are generally obtained wherein superatmospheric pressures are employed. Such chlorination pressure is not critical except as necessary to obtain an efficient rate of reaction. In this regard, it is pointed out that for a given catalyst or admixture thereof, at a given concentration in the suspending medium, the reaction rate is conveniently controlled by the rate of feed of chlorine and/or its partial pressure in the reaction vessel.

After the polyolefinic material has been suspension chlorinated to a desired degree, it may be easily separated from the inert suspending liquid by conventional means and washed and dried to prepare it for subsequent use. The entire chlorination procedure or any desired part of it may be carried out batchwise or by continuous processing arrangements. For batch operations it is ordinarily suitable to employ conventional autoclaves and kettles or the like for conducting the reaction. However, it may also be conveniently conducted in a continuous process by any one of several suitable techniques. For example, it may be conducted by counter-current movement of the reactants through either horizontally or vertically disposed reactors which may be in the form of tubes and towers, or by using a cascading principle with a series of interconnected reaction chambers.

Substantially quantitative yields, based on the weight of the polymer to be chlorinated, may be frequently obtained by the chlorinating technique described herein. The attainment of such yields, as has been indicated, may often be facilitated by the practice of recycling techniques for unreacted portions of the chlorine and by conducting the involved reactions at more moderate or near the optimum sequential chlorination temperature. It is furthermore possible and has proved of special advantage to carry out the chlorination in the presence of essentially chemical inert substances of inorganic or organic chemical nature which are such that they can be retained in the final product. Exemplary of such materials are: carbon black, titanium dioxide, barium sulfate, and the like as well as organic plastic materials such as polyvinyl chloride and the like. Such materials may be employed for the desired purpose without significantly detracting from the highly desirable elastomeric properties of the chlorinated polymer. The addition of such fillers serves to inhibit excessive particle growth during chlorination, which agglomeration is undesirable in later manufacturing and fabrication steps. It is to be noted however, that such materials may also be post-blended with the chlorinated product as one method of obtaining the most desirable values of the various physical properties.

It is to be understood, that the herein described chlorination procedures may be varied depending upon the particular polyolefins being halogenated, upon the types and amounts of wetting agents being employed, and with other factors. In any case, it is imperative that the flashing or membrane material of the present invention is charac-

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terized by the highly desirable, and heretofore unobtainable, combination of properties as previously specifically described.

Other suitable materials which may be blended with the chlorinated olefin polymer include both the pigment fillers and fibrous fillers. Examples of pigment fillers are the clays, calcium sulfate, and mica, among others including coarse fillers such as pulverized marble or limestone, if desired. Suitable fibrous fillers include asbestos, cork, wood, flour, etc.

Stabilizers are included in the compositions to protect the chlorinated olefin polymer against decomposition by the heat of processing or by subsequent exposure of the fabricated sheet material to climatic and environmental conditions. Suitable stabilizers include those materials conventionally employed in the preparation of vinyl polymer and copolymer sheet compositions, e.g., organic complexes and/or salts of lead, tin, barium, cadmium, zinc, sodium, lithium, and particularly the barium-cadmium soaps as well as dibutyl tin laurate and dibutyl tin maleate, among others. Stabilizers are preferably used in amounts between about 1 and 5 parts by weight per 100 parts of the chlorinated olefin polymer constituent. Other conventional additives, such as epoxidized and non-epoxidized oils may be used. Low molecular weight polymers and waxes may also be employed, if desired, in amounts of up to about 15 parts per 100 parts of chlorinated olefin polymer.

Although the chlorinated olefin polymers employed for the purposes of the present invention are inherently resistant to burning, it may in some instances be advantageous to incorporate minor amounts, i.e., from about 1 to 10 parts per hundred parts of chlorinated olefin polymer, of one or more flame-retarding agents, e.g., oxides of antimony and/or various halogenated materials such as tetrabromophthalic anhydride, perchloroethylene, cyclohexane, tris (2,3-dibromopropyl) phosphate, tetrabromomethane, among many others.

It is generally unnecessary to add conventionally employed plasticizers to the compositions from which the sheet-like materials of the present invention are formed, however, those materials as conventionally employed for vinyl polymers may be used in concentration less than about 10 percent as processing aids if desired.

The flashing and membrane materials of the present invention may be prepared by conventional techniques wherein the chlorinated olefin polymer is prepared as described herein and blended with the desired fillers and stabilizers, etc., substantially in the manner conventionally employed in preparing vinyl chloride polymer and copolymer sheeting compositions. Thus, for example, the necessary ingredients may be initially dry blended in a mixer such as a ribbon blender and subsequently milled as on a two-roll compounding mill at roll temperatures between about 240°F and 400°F, until the mixture becomes homogeneous. The blend may then be extruded into sheet form or calendered to give the desired sheet thickness. In general, sheet-like structures have a thickness of between about 0.005 and 0.25 of an inch preferably between about 0.020 and 0.1 of an inch are utilized as flashing and/or membranes in construction assemblies.

It is to be noted that the present invention contemplates utilization of such sheet-like structures in both a substantially unvulcanized or vulcanized form.

It is further to be understood that the present invention contemplates utilization of the sheet-like structure as defined herein, in lamination with one or more self-supporting reinforcing materials such as woven or non-woven fabrics prepared from naturally occurring materials including glass fibers, wool, cotton, hemp, jute, and the like, and synthetic materials such as polyamide, polyesters, and acrylics, and among other materials. It is still further to be understood that the present invention contemplates utilization of the sheet-like structures of this invention as flashings and as roof membranes in any manner peculiar to the industry and includes the coating or other contacting of such materials with various adhesives and paints which include natural and synthetic polymer solutions, including solutions of the chlorinated olefin polymers as defined herein.

The following example wherein all parts and percentages are to be taken by weight, illustrates the present invention but is not to be construed as limiting its scope.

Example 1

To 4000 grams of deionized water was added, with stirring, 200 grams of a polyethylene having an essentially linear and unbranched structure (containing less than about 1 percent of monomer unit). Having a melt index of about 1 and a molecular weight of about 67,000. Such polyethylene had been previously prepared by a process using a catalyst composed of trisobutyl aluminum and titanium tetrachloride. The resulting admixture was then charged to a 1½ gallon autoclave with 8 grams of calcium chloride; about 0.5 cc. of a 70 percent solution of di tert-buty1 peroxide in butanol; and about 10 drops of a commercially available wetting agent.

The charge was then chlorinated, in a first chlorination step, under about 30 p.s.i. (gauge) of chlorine pressure at a temperature of about 90°C until a chlorine content of about 20 percent was obtained. The charge was then chlorinated in a second suspension chlorination step, at a temperature of about 126°C until a total chlorine content of about 42 percent was obtained. The chlorination product was then isolated from the dispersion by filtration, washed free of residual hydrochloric acid and dried.

The dried material was then used to prepare the following formulation by dry-blending of the designated materials in a ribbon blender:

Material: Parts by weight
Chlorinated polyethylene 100
Liquid barium-cadmium heat stabilizer 4
Phosphate stabilizer 0.5
Epoxidized oil 3.0
Antimony oxide 1.0
Chlorinated wax 2.0
Talc 10
Carbon black 2.5
Stearic acid 2

The above dry blend was then conveyed into the feed hopper of a two-stage vacuum vented single screw extruder. The first stage was operated at about 375–400°F and the second stage at 325–400°F. The vacuum was about 26 inches of mercury. The melt was then extruded through a sheet die to form a sheet having a thickness of about 0.06 of an inch. This material is hereinafter identified as Sample Number 1.

For purposes of comparison, a sheet having a thickness of about 0.06 of an inch and having the following composition was prepared as described herein:

Materials: Parts by weight
82% vinylidene chloride/18% acrylonitrile copolymer 100
Carbon black (average particle size of about 450 micrometers) 55
Dicarbodiethyl phthalate (plasticizer) 30
Tetrasodium pyrophosphate (heat stabilizer) 1
Stearic acid 2

This sample is hereinafter designated as Comparative Example No. 1.

In another comparison, a commercially available flashing material having a thickness of about 0.06 of an inch and based on polyvinyl chloride containing carbon black and from about 25 to 30 percent weight percent of a C₂-C₅ dialkyl phthalate plasticizer and minor amounts of an aliphatic ester, was used.
This sample is hereinafter designated as Comparative Example No. 2.

The following Table I summarizes the physical properties determined for the above-described sheet materials.

<table>
<thead>
<tr>
<th>ASTM Test Method</th>
<th>The Invention, Sample 1</th>
<th>For Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, p.s.i. at 100° F.</td>
<td>3,399,091</td>
<td>Sample 1</td>
</tr>
<tr>
<td>Elongation, percent</td>
<td>40%</td>
<td>40%</td>
</tr>
<tr>
<td>100% modulus (tensile stress at 100% elongation)</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Brittleness temperature, °F</td>
<td>-70°F</td>
<td>Not-burning</td>
</tr>
<tr>
<td>Flammability</td>
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<td>-50°F</td>
</tr>
</tbody>
</table>

It is apparent from the data presented above that the flashing material of the present invention has greatly enhanced low temperature flexibility and significantly improved modulus and elongation as compared to the conventionally employed materials based on plasticized vinyl chloride polymer and polyvinyl chloride respectively. The composite materials of the present invention are further characterized by being inherently flexible under widely differing climatic and environmental conditions, are resistant to burning, and are susceptible to adhesion with conventionally employed adhesives. Further, by way of comparison, it has been found that utilization of chlorinated olefin polymers having molecular weights exceeding 1 million are generally incapable of being fabricated into sheet-like structures without the addition of significant amounts of plasticizers or other processing aids. By way of illustration, it has been found that the non-plasticized chlorinated polyolefins as described in Example I above can be extruded through a standard Instron rheometer orifice, using a 190° C. barrel temperature, at a 150-1 sec. shear rate with a resultant shear stress of from 25-35 p.s.i., whereas, under the same conditions chlorinated polyolefins having a molecular weight of from 1 million to 5 million are characterized by a shear stress of greater than about 85 p.s.i. and often cannot be made to pass through the orifice of the rheometer.

Still further, it has been found that utilization of chlorinated polyolefins as herein described, but having a chlorine content of greater than about 50 weight percent provides sheet material having reduced resistance to heat. Also, chlorinated polyolefins, as herein described, but having a chlorine content of less than about 25 weight percent are characterized by reduced solvent weldability properties and are less resistant to burning.

It is further to be noted that the present invention contemplates the utilization of a chlorinated polyolefin where in the chlorination is accomplished in suspension in an inert liquid. Such chlorination technique eliminates the difficulties inherent in the solution chlorination of polyolefins. In addition, such chlorination technique provides a chlorinated product characterized by the major portion of the polymer chain being chlorinated in a random manner characteristic of that obtained by solution chlorination techniques, and only minor portions of the polymer chain being chlorinated in a block fashion. Thus, the chlorina-