The invention relates to plastic compositions and more particularly to synthetic plastic compositions having magnetic strength.

The combination of magnetic particles with a resinous binder enables the production of materials having both flexibility and magnetic strength. Such flexible magnets are of increasing interest for use in special applications such as door closure gaskets and, more particularly, because of their potential as a replacement for the more expensive and rigid metallic magnets used, for example, in electric motors. To improve efficiency and expand the application of the flexible magnets there is continued interest in providing plastic compositions containing more and more amounts of magnetic material and having correspondingly higher magnetic capacity. However, the provision of plastic magnets of high magnetic strength is not an easy matter as the product must have other properties which unfortunately are severely depressed by the presence of increased amounts of magnetic material. Notably among such properties is flexibilility which can become so poor that cracking will be found on a single bending of a thin strip of the product. Thus, when attempting to produce a strength flexible magnet containing about 90% magnetic material it has been found in the past that even thin strips of such compositions would crack on bending well before reaching an angle of 90°. Further increase in magnet content have been found to produce compositions which are not capable of sustaining even a 45° bend without cracking. Such low flexibility not only reduces the attractiveness of the product but also renders manufacture and handling difficult without high scrap loss due to cracking. Further, a major economic advantage of the plastic magnets rests basically in the ability to form or shape by molding or extrusion procedures, in contrast to the more expensive manufacturing operations required for the metallic magnets. Consequently, ability to process the high magnetic compositions by such conventional plastic forming techniques is also of major importance.

An object of the present invention is to provide new and improved filled plastic compositions combining high flexibility and high magnetic strength.

Another object is to provide new and improved flexible magnets of high magnetic strength sufficient for use in applications where metallic magnets have been employed.

Other objects and advantages will be evident from the following description of the invention.

In accordance with the invention it has been found that plastic composition of exceptionally high flexibility and magnetic strength is provided by combining fine magnetic particles with a highly specific chlorinated ethylene polymer which has been modified by addition of a normally liquid plasticizing material, the composition of the invention comprising: (A) 100 parts by weight of a chlorinated linear ethylene polymer having a chlorine content between about 33–55% by weight, less than 3% crystallinity as determined by differential thermal analysis, a glass transition temperature ranging from about minus 18° C. ± 10° C. for the 33% chlorine content chlorinated polyethylene up to about 63° C. ± 15° C. for the 55% chlorine content chlorinated polyethylene, and high molecular weight corresponding to an intrinsic viscosity between 3 to 6 in o-dichlorobenzene at 100° C.; (B) at least 30 up to about 130 parts by weight, preferably 40–70 parts, of a normally liquid plasticizer for said chlorinated polyethylene; and (C) at least 1400 parts by weight of fine magnetic particles. The compositions provided by this invention contain at least about 90% by weight of magnetic material and at such levels exhibit excellent flexibility as evidenced by bending through angles greater than 90°. It has been also discovered that further increasing the magnetic particle content above about 92–93% by weight results in compositions in which flexibility remains at a high level and is even improved over compositions containing less amounts of magnetic material. Hence, by the present invention it is possible to produce highly flexible magnetic compositions having magnetic particle content up to 95% by weight, or even more. In addition to high magnetic strength and flexibility the compositions of the present invention also combine good properties in general including good impact resistance, elongation, and tensile strength. The compositions may be readily processed in conventional apparatus.

The compositions of the invention are based on a specific chlorinated polymer of ethylene having about 33–55% by weight chemically combined chlorine and high molecular weight corresponding to an intrinsic viscosity of at least about 3 to 6 in o-dichlorobenzene at 100° C. The more preferred chlorinated polyethylenes have a chlorine content between about 35–50% and an intrinsic viscosity between about 3.5 to 5. The chlorinated polyethylenes employed in the invention are also characterized by having certain chlorine distribution on the basic polyethylene chain such that the chlorinated polymers have little or no crystallinity as determined by differential thermal analysis, the crystallinity of the polymers being less than about 3%, preferably 0% crystallinity. The chlorinated polyethylenes also have definite glass transition temperatures varying with chlorine content of the polymers. The glass transition temperatures of the chlorinated polyethylenes employed in the invention range from about −18° C. ± 10° C. for the 33% chlorine content chlorinated polyethylene up to about 63° C. ± 15° C. for the chlorinated polymers having 55% by weight chlorine. The more preferred chlorinated polyethylenes have glass transition temperature ranging from about −15° C. ± 10° C. for the 35% chlorine content chlorinated polyethylene up to about 35° C. ± 15° C. for the 50% chlorine content chlorinated polyethylene. The chlorinated polymers employed in the present invention are also those prepared by chlorination of a linear, high density polyethylene. The terms "linear, substantially linear," as used herein in the appended claims, shall mean a polyethylene characterized by high density and at most only nominal short chain branching in the form of methyl groups, usually less than about 10 methyl groups per 1,000 carbon atoms in the molecule, more commonly 0 to 5 methyl groups per 1,000 carbon atoms.
accept the large amounts of magnetic particles required to form the compositions of the invention. In order to obtain compositions of high magnetic strength it is necessary to blend the chlorinated polyethylene with a plasticizing material which is a liquid under normal conditions. It has also been found that certain liquid plasticizers which are also surfactants, i.e., have surface active properties, will produce a substantial improvement in both magnetic strength and the freedom of the plasticizing magnets having a given amount of magnetic particles.

The amount of plasticizer required to be effective is at least about 30 parts ranging up to about 120 parts per 100 parts of the chlorinated polyethylene. The more preferred compositions contain about 40 to 70 parts of plasticizing material. The plasticizer employed in the composition is normally liquid material and plasticizers of this type are well known. Such plasticizers include, by way of example, the chlorinated aliphatic and aromatic hydrocarbons, the liquid epoxy resins such as those prepared by reaction of epichlorohydrin and bisphenol A, the epoxidized drying oils such as epoxidized soybean oil and the monomeric and polyether plasticizers. The chlorinated hydrocarbons useful in the compositions of the invention have chlorine content generally between about 20% to 70% by weight and low molecular weight between about 200 to 4000. The more preferred hydrocarbon plasticizers are the normally liquid chlorinated aliphatic hydrocarbons having chlorine content between about 30% to 55% and molecular weight between about 200 to 2000. The monomeric ester plasticizers are generally preferred and include those formed from the acids such as phosphoric, phthalic, adipic, sebacic, etc. Suitable alcohols for forming the monomeric esters have generally 2 to 16 carbon atoms, more usually 4 to 12 carbons. Examples of such monomeric plasticizers include tricresyl phosphate, diethyl phthalate, dibutyl phthalate, 2-ethylhexyl phthalate, diocetyl phthalate, butyl cyanoacrylate, dihexyl phthalate, dibutylyl phthalate, diisobutyl phthalate, ocyl decyl phthalate, dimethyl phthalate, dicapryl phthalate, diethoxethyl phthalate, dibutoxyethyl phthalate, dioctyl isophthalate, diocetyl adipate, and dibutyl sebacate. Generally, the more preferred plasticizers are the monomeric esters of phthalic acid. Certain of the plasticizers are also surface active and have been found exceptionally beneficial in producing magnetic compositions combining both high magnetic strength and flexibility at a given loading of magnetic particles. Very suitable plasticizers of this type are the fatty acid esters of alcohols having 2 to 12 carbon atoms, preferably 3 to 8 carbon atoms. A specific example of such a fatty acid ester is butyl stearate. The surfactant plasticizers are employed in combination with the more conventional plasticizers and as little as about 2 parts per 100 parts of chlorinated polyethylene is effective in obtaining improved properties.

The surfactant plasticizers may be employed in amounts representing between about 2–85% by weight of the total plasticizing materials with best results obtained when the surface active materials represent between about 30–75% of the total plasticizer. The surface active plasticizers are especially effective at the higher magnetic loading contents above about 92–95% where the association between the chlorinated polyethylene binder and magnetic particles becomes a critical factor obtaining both high flexibility and magnetic strength.

The chlorinated polyethylene employed in practice of this invention is not readily satisfactorily plasticized by conventional procedures at or about room temperatures. In preparation of the compositions this problem may be overcome by incorporation of the plasticizer for the chlorinated polyethylene at an elevated temperature about about 200°F. but not in excess of about 430°F. At such temperatures the chlorinated polyethylene readily accept the plasticizing material and form there-with a composition of especially good homogeneity and also high flexibility and magnetic filler and loading content. The chlorinated polyethylene is subject to decomposing and thermosteric shrinkage at the higher temperatures and therefore it is desirable to first admix the chlorinated polyethylene with a heat stabilizer to protect the polymer against degradation as it is subsequently heated to the plasticizing temperatures. The heat stabilizers employed may be those well-known materials commonly used with the halogen-containing magnetic particles and include such stabilizers as the inorganic salts and organic complexes of salts and metals such as barium, cadmium, tin, zinc, lead, sodium, etc. Also suitable are the liquid epoxy resins such as those prepared by reaction of epichlorohydrin and bisphenol A. The stabilizing materials also serve to protect the polymer during subsequent extrusion, molding or other forming operations conducted at elevated temperatures. The amount of heat stabilizer added is usually between about 1 to 15 parts to 100 parts of the chlorinated polyethylene, more usually between about 2 to 10 parts. Admixing of the plasticizing material at elevated temperatures is satisfactorily accomplished in conventional compounding apparatus, for example, a Banbury mixer or rubber roll mill. Heating of the chlorinated polyethylene during mixing may be accomplished by supplying heat through the mixing apparatus and/or the frictional heat of the mixing operation. The plasticizers may be initially admixed with the chlorinated polyethylene at room temperature or at elevated temperatures on the mixing apparatus either before or after the chlorinated polyethylene is heated to the desired elevated temperature. It is generally preferred in obtaining best results and efficient operation to rapidly heat the plasticizer and chlorinated polyethylene to the plasticizing temperature within a short period of about 5 minutes, preferably less than 3 minutes. This may be suitably accomplished by pre-heating of the mixing apparatus and/or chlorinated polymer above about 150°F. According to a preferred procedure the plasticizer is premixed with the chlorinated polymer and the mixture is then admixed with the chlorinated polyethylene to the plasticizing temperature and a homogeneous mass is formed in a matter of minutes, usually between 1 to 10 minutes after charging to the mixing apparatus. The magnetic particles are then admixed with the resulting plasticized chlorinated polyethylene composition, preferably after the formation mass is to a reduced temperature about between 150–220°F. It has been found desirable when selecting the highly filled magnetic compositions to add the magnetic particles in stages. For example, a preferred procedure involves the addition of a major portion but not all of the magnetic particles. After thorough mixing of the first charged particles the balance of the magnetic material may be added and mixing continued to form a homogeneous product. Such procedure aids in distribution of the magnetic particles in the binder and is also a factor in obtaining the combination high flexibility and magnetic strength. Another preferred method involves addition of the magnetic particles prior to heating of the polymer to the plasticizing temperature to take advantage of the frictional heat generated by mixing of the solid filler material. The heat-stabilized chlorinated polyethylene with or without the plasticizer is charged to a two roll mill or other mixing apparatus preheated to a temperature above about 150°F. usually between 180–230°F. After about 1–2 minutes mixing of the chlorinated polyethylene with the plasticizing material the magnetic particles are added, preferably in stages. Heat generated by mixing of the magnetic particles facilitates the rise in temperature of the mass and the plasticizing temperature is reached within a short time and plastification and formation of the filled composition readily
obtained. In this procedure cooling of the mixing apparatus is recommended as by the use of ordinary water to control the temperatures below about 470 F. The composition of the mixing apparatus is described in the preceding section of this article. In the compositions the magnetic mixer will have particle size ranging from about 0.5 to 15 microns with average particle size preferably between about 1 to 3 microns. The more preferred magnetic mixers are those complex metal oxides well known as "ferrites" of which, as used herein, designates an inorganic material of the formula MoO₂, wherein M is a divalent metal and m and n are whole numbers. The more preferred metal ferrites are the barium ferrites, for example, the barium ferrites represented by the formula BaFe₃O₄.

The chlorinated polyethylene is desirable prepared for use in the invention by chlorination of high molecular weight linear polyethylene in a heterogeneous medium in stages defined by introduction of chlorine at a temperature first below and then above the crystalline melting point of the polyethylene. Several different apparatuses have been used especially an apparatus similar to the apparatus of Pisanchyn et al., U.S. Pat. No. 3463093, filed Feb. 1, 1961, now abandoned. Preparation of the chlorinated polyethylene is most desirably accomplished by double-stage suspension chlorination of the linear, high molecular weight polyethylene with first-stage chlorination being carried out at a temperature below the crystalline melting point of the polyethylene, preferably about 50 C. to 130 C., more preferably at 90 C. to 120 C., until at least about 5 percent, preferably about 10 percent, of chlorine has been introduced into the polymer. In the second stage the chlorination is continued in the apparatus at a temperature above the crystalline melting point of the polymer but below the softening point of the chlorinated outer coating thereof until the desired chlorine is added. The second-stage chlorination temperatures are generally of the order of about 135 C. and preferably of the order of about 135 C. to 150 C. If desired, in the second stage of chlorination the temperature may be carried out at a temperature above the crystalline melting point of the polymer for time sufficient to add at least about 5 percent of chlorine to the polymer, preferably at least about 25 percent of chlorine to the polymer, and the chlorination then continued at a lower temperature, e.g., about 110 C. to 120 C., until the desired total chlorine is added.

The suitable chlorinated polyethylene are derived from a linear polymer of ethylene having a molecular weight of at least about 700,000 ranging up to about 3,000,000, preferably between about 1,000,000 to 3,000,000. Chlorination of the linear polyethylene of 1.5 molecular weight by the subject stage-stage process will produce the particularly preferred chlorinated polyethylene having 33-55% by weight chlorine and high molecular weight corresponding to an intrinsic viscosity within the range of about 3.5 in o-dichlorobenzene at 100 C. These preferred chlorinated polyethylene are also chemically inert and insoluble at 20-25 C. in organic solvents such as esters, acids and alcohols. They have tensile strength values according to ASTM Method D 638-58T (at drawing rate of 2 inches per minute) of at least about 2,500 p.s.i. and about 4,500 p.s.i. The chlorinated polyethylene also have true ultimate tensile strength values according to ASTM Method D 638-58T of at least about 11,000 p.s.i., with the preferred materials of 35-50% chlorine content having true ultimate tensile strength values between about 11,000 to 20,000. The chlorinated polyethylene have less than about 3% crystallinity by differential thermal analysis, preferably 0% crystallinity, and also are characterized by low glass transition temperatures ranging from about minus 18 C. to 18 C.

For preparation of the chlorinated polyethylene a particularly suitable high molecular weight polyethylene which may also be characterized by containing long chain polyethylene branches is produced, as described in British Patent 858,674 of June 11, 1961 to Allied Chemical Corporation, by gas phase polymerization of anhydrous, oxygen-free ethylene over a porous, frangible catalyst of an inorganic compound of chromium and oxygen and an active metal alkyl on a support of a group consisting of silica and silica-alumina. The polyethylene produced thereby contain residue of the chromium-silica catalyst systems dispersed throughout the polyethylene an amount of not less than 0.39 and not more than 0.95 and a crystallinity of not less than 75%, and customarily in the range of 80% to 85%, as determined, for example, by differential thermal analysis. The preferred polyethylene produced by British Patent 858,674 have weight average molecular weight between 1.0 million and about 5.0 million, preferably between 1.0 to 3.5 million, as calculated according to the method of P. S. Francis et al. from the viscosity of about 0.35 to 0.1 gram per 100 cc. solution in decalin at 135 C. using the equation:

\[ n = 6.77 \times 10^{-4} M^{0.87} \]

where

\[ n = \text{intrinsic viscosity} \]

\[ M = \text{weight average molecular weight} \] (J. Polymer Science, vol. 31, pp. 453-466, September 1958)

The following examples in which parts and percentages are by weight demonstrate the practice and advantages of the present invention.

**Examples 1-6**

Chlorinated polyethylene of 45% chlorine was prepared by staged aqueous chlorination of linear polyethylene having a weight average molecular weight of about 1.5 million and density of 0.94. The polyethylene employed was prepared in accordance with British Patent 858,674 (Example 6) by gas phase polymerization of anhydrous oxygen-free ethylene over a catalyst made of magnesium dichromate in a porous support with aluminum triisobutyl. The support was composed of 90% silica and 10% aluminum. Chlorination of the polyethylene in a first stage was carried out at a temperature of about 100 C. until 17% chlorine was added to the ethylene polymer followed by second stage chlorination at a tempera-
ture of 140° C. until a total of about 35% chlorine was added. Chlorination was then continued at a temperature of 110–120° C. until a total of 45% by weight chlorine was added. The chlorinated polyethylene recovered from the slurry was washed and dried overnight at a temperature of 60° C. The chlorinated polyethylene had a glass transition temperature of about 5° C. (ASTM D1053–63) and 0% crystallinity as measured by differential thermal analysis. The chlorinated polyethylene also had high molecular weight corresponding to an intrinsic viscosity of 4.0 in o-dichlorobenzene at 100° C.

A series of magnetic compositions was prepared by the following procedure from the above prepared chlorinated polyethylene. 100 parts of the chlorinated polymer was admixed with 3 parts of a barium-cadmium organic heat stabilizer and 0.5 parts of dioctyl phthalate as plasticizer to form a homogeneous mass which was sheeted out from the mill to form sheets of 0.14 inch thickness. Specimens of each of the compositions were then evaluated and the results are tabulated below in Table II.

Table I 5

<table>
<thead>
<tr>
<th>Example No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td>Barium Ferrite, parts by weight</td>
<td>1,469</td>
<td>1,628</td>
<td>1,740</td>
<td>1,880</td>
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<td>2,340</td>
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<tr>
<td>Barium Ferrite, percent by weight</td>
<td>91</td>
<td>91.5</td>
<td>92</td>
<td>92.5</td>
<td>97.3</td>
<td>98.1</td>
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<tr>
<td>Specific Gravity</td>
<td>2.40</td>
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<td>2.58</td>
<td>2.67</td>
<td>2.77</td>
<td>2.87</td>
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<tr>
<td>Spacing distance</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Magnetomechanical strength, 1 inch mandrel</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Magnetic strength, 0.005 inch gap</td>
<td>0.221</td>
<td>0.228</td>
<td>0.236</td>
<td>0.246</td>
<td>0.259</td>
<td>0.298</td>
</tr>
</tbody>
</table>

1 Determined with 2 inch specimen on Tinius Olsen Stiffness Tester at 50 load dial reading employing a 0.995 pound collaring weight. Maximum angle obtainable in stiffness tester is 90°.
2 Lbs. lb/inch length.

Table I shows the compositions of the invention to have high magnetic strength and flexibility. The compositions of Examples 1–4 inclusive containing up to 92% by weight barium ferrite all sustain a full 180° bend around a 1 inch mandrel. The compositions of Examples 5 and 6 containing substantially greater amounts of barium ferrite resist cracking after bending under load through the angle of at least 50° in the Olsen Stiffness Tester. The composition of Example 1 was further evaluated and found to have a tensile strength of 700 p.s.i. and unusually good elongation of 85%.

Examples 7–10

A series of four additional compositions were prepared employing components and procedure similar to Example 1 except that the plasticizing material was a combination of 23 parts dioctyl phthalate and 30 parts butyl stearate. These compositions were then evaluated as in Examples 1–6 and the results are tabulated below in Table II.

Table II

<table>
<thead>
<tr>
<th>Example No.</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Ferrite, parts by weight</td>
<td>1,358</td>
<td>1,400</td>
<td>1,401</td>
<td>2,379</td>
</tr>
<tr>
<td>Barium Ferrite, percent by weight</td>
<td>93</td>
<td>93.5</td>
<td>94</td>
<td>93.8</td>
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<tr>
<td>Specific Gravity</td>
<td>3.83</td>
<td>3.93</td>
<td>4.03</td>
<td>4.01</td>
</tr>
<tr>
<td>Spacing distance</td>
<td>&gt;900 &gt;700 &gt;600 &gt;500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetomechanical strength, 0.003 inch gap</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>Mandrel Bond, 4 inch mandrel</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Magnetic strength, 0.002 inch gap</td>
<td>0.220</td>
<td>0.225</td>
<td>0.247</td>
<td>0.280</td>
</tr>
</tbody>
</table>

1 Determined with 2 inch specimen on Tinius Olsen Stiffness Tester at 50 load dial reading employing a 0.995 pound collaring weight. Maximum angle obtainable in stiffness tester is 90°.
2 Lbs. lb/inch length.

The Table II compositions all have excellent flexibility and high magnetic strength which increases approximately proportionately with the amount of magnetic particles. Table II also clearly demonstrates the ability of the compositions of the invention to exhibit improved flexibility along with high magnetic strength upon increase of the amount of magnetic particles above about 92%. Hence, the composition of Example 9 containing 92% magnetic particles has a crack angle of 50° and mandrel bond of about 135° while the composition of Example 10 containing some 300 parts more of the particles has substantially improved flexibility with a crack angle greater than 90° and flexibility around the 1 inch mandrel of 180°. The Table II also clearly demonstrates the effectiveness of the butyl stearate in improving magnetic strength, particularly at the higher contents of magnetic particles. Hence, the composition of Example 10 containing 93% magnetic material has superior magnetic strength and also flexibility over the composition of Example 6 containing 93.5% magnetic particles.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

I claim:

1. A highly flexible highly magnetic plastic composition comprising a binder of a chlorinated linear polymer of ethylene and at least 30 parts up to about 130 parts of a normally liquid plasticizer per 100 parts of the chlorinated polyethylene and at least 90% by weight of fine magnetic particles having size less than about 10 microns, said chlorinated polyethylene having a chemically combined chlorine content between 33–55% by weight, less than 3% crystallinity as determined by differential thermal analysis, and a transition temperature ranging from about minus 15° C.—20° C. for 33% chlorine content chlorinated polyethylene up to about 63° C.±15° C. for the 55% chlorine content chlorinated polyethylene, and molecular weight corresponding to an intrinsic viscosity between about 3 to 6 in o-dichlorobenzene at 100° C.

2. The composition of claim 1 in which the chlorinated polyethylene has a chlorine content between about 35–50% by weight and 0% crystallinity as measured by differential thermal analysis.

3. The composition of claim 1 in which the amount of plasticizer is between about 40–70 parts.

4. A highly flexible highly magnetic plastic composition comprising a binder of a chlorinated linear polymer of ethylene and between about 30 to 130 parts per 100 parts of the chlorinated polyethylene of a normally liquid plasticizer of which between 2–85% by weight is a plasticizer which is also a surfactant and at least about 90% by weight of fine magnetic particles having size less than about 10 microns, said chlorinated polyethylene having a chemically combined chlorine content between 35–50% by weight, 0% crystallinity as determined by differential thermal analysis, glass transition temperature ranging from about minus 15° C.±10° C. for 35% chlorine content chlorinated polyethylene up to about
3,379,643

35° C. ± 15° C. for the 50% chlorine content chlorinated polyethylene, and molecular weight corresponding to an intrinsic viscosity between about 3 to 6 o-dichlorobenzene at 100° C.

5. The composition of claim 4 in which the amount of liquid plasticizer is between about 40–70 parts of which between about 30–75% by weight is a fatty acid ester of an alcohol of 2–12 carbon atoms.

6. The composition of claim 4 in which the liquid plasticizer is a mixture of a phthalate plasticizer and between about 30–75% parts by total plasticizer weight of butyl stearate.

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TOBIAS E. LEVOW, Primary Examiner.
ROBERT D. EDMONDS, Examiner.