United States Patent Office 3,697,474
Patented Oct. 10, 1972

3,697,474
ORGANO-CLAY-POLYMER COMPOSITIONS

Horton H. Morris, James P. Oliver, and Paul I. Prescott, Macon, Ga., assignors to Freeport Sulphur Company, New York, N.Y.

No Drawing. Filed Oct. 30, 1969, Ser. No. 872,752
Int. Cl. C08f *45/06;* C08k *1/12*
U.S. Cl. 260—40 R 8 Claims

ABSTRACT OF THE DISCLOSURE

Polymeric materials which contain as a filler an inorganic material the surface of which has been reacted with an organo derivative of ortho titanic acid containing at least two hydrolyzable groups are described. The filled polymeric materials, which may contain other conventional ingredients, can be conventionally formed to provide products having improved properties.

BACKGROUND OF THE INVENTION

(a) Field of invention

This invention relates to filled polymeric compositions in which the fillers have been pretreated to enhance their compatibility with polymeric material and improve the properties of the polymeric materials. More particularly, the invention relates to organic polymer compositions containing one or more inorganic fillers the surfaces of which have been reacted with an organic derivative of ortho titanic acid containing at least two hydrolyzable groups. The compositions can be readily formed into fibers, films and other shapes by the conventional processes used in the plastics industry.

(b) Description of the prior art

Inorganic particulate materials such as clays, calcium carbonate, barium sulfate, zinc oxide, titanium dioxide, diatomaceous earth, etc. have long been used in polymeric compositions to provide opacity and to act as delustrants in the objects made therefrom. Fibers formed from such compositions are used in fabrics for garments, yard goods, curtains and draperies, upholstery, bedding, and table linens; in yarns and knit goods; in carpeting; in tapes; in synthetic paper; and in other woven and non-woven goods such as scrim, ropes, filters, rug backing, staple, synthetic hair, and as fillers for other polymer systems; films from such compositions have been used for packaging materials, including heat sealable flat stock and bags, as printed sheets and wrappers, as oriented films, as synthetic capacitor paper and in oil filled, synthetic paper, cable insulation and in other applications where flexible plastic sheet materials are required for moisture and air barriers. Films have also been used for covering, or containing objects, materials or surfaces. Additionally, such compositions have been molded, extruded or otherwise formed into various shapes for a wide variety of end uses.

Unfortunately, the amount of inorganic material that can be used is quite limited since large amounts thereof reduce the strength of the compositions markedly so that they are unacceptable for the intended use. For example, it has been found that fibers and thin films can tolerate no more than about 5 weight percent of inorganic filler without losing substantial strength properties.

Presumably, the loss of physical integrity when large amounts of inorganic filler is used is related to the surface energy of both the inorganic material and the polymer, which in turn relates to the adhesion of the polymer to the inorganic surface. The adhesion of the polymer to the filler is also dependent on the temperature of the system and on the degree of compatibility of the filler with the polymer. At constant temperature, the work of adhesion W_a, can be defined by the equation:

$$W_a = V_f + V_p - V_{fp}$$

where V_f represents the surface energy of the inorganic material, V_p represents the surface energy of the polymer system, and V_{fp} represents the surface energy of the interface or the degree of incompatibility of the inorganic material and polymer surfaces. When $W_a \geqq 2V_p$ the polymer should adhere strongly to the inorganic surface and the polymer can be said to wet the inorganic material. When $W_a < 2V_p$ the polymer should not wet the inorganic material and the inorganic material may be surrounded by a void. Filled compositions which have a high filler-polymer incompatibility and/or low filler surface energy will have a low filler tolerance level.

Cable insulation is another field in which inorganic fillers, primarily clays have been used with polymers in the form of extruded solid dielectric insulation. The fillers are added in the order of 2 to 150 weight percent based on the polymer and are used to impart a physical ruggedness to the insulation which manifests itself by an increase in the insulation tensile strength, hardness and deformation resistance. However, the addition of hydrophilic clays to power cable insulation results in the creation of paths through which moisture can readily penetrate. Moreover, the incorporation of clays with a low surface energy and/or a high degree of incompatibility between the clay and the polymer system (a high interfacial surface energy) results in the formation of voids in the extruded cross-linked insulation. Thus, hydrophilic clay in the insulation in the presence of moisture, results in an insulated cable with a high percent power factor (high dielectric losses). The high percent power factor in an energized cable results in excessive energy transmission losses and eventual cable failure through dielectric heating. Voids, 2 mils and larger, in a cable insulation will ionize (internal discharges across the void through gases trapped in the void) depending on the location of the void and the electrical stress across the cable insulation. The ionization in the void results in an increase in the size of the void and, since the intensity of the discharge across the void increases with the size of the void, the continued ionization results in cable failure by burnout. Therefore, as will be readily apparent to those skilled in the art of power cable insulation, it is highly desirable, in order to obtain the best cable insulation, that a hydrophobic filler with a surface energy equal to or greater than the surface