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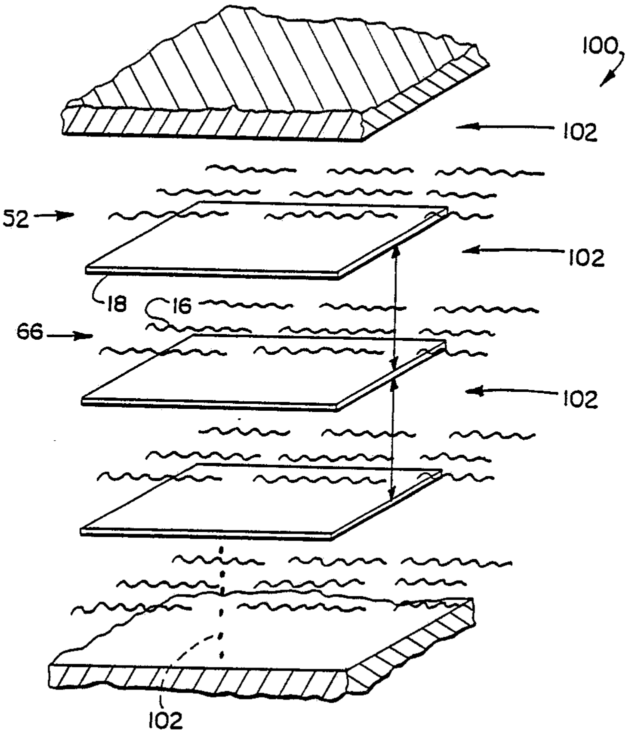
(54) Title: FILLED LAYERED PLASTIC AND METHOD

(57) Abstract

Improvements in filled polymers and methods and materials for making same are provided by using platelet-shape additive particles (18) of a size relation to the polymer (16) and of a loading in the polymer such that the additive aligns along three axes substantially throughout the polymer and interact with the polymer during extruding thereof to promote alignment and layering of polymer chains while permitting cross-linking of respective chains in and between layers to provide a product that has improved fatigue life over prior extruded polymers.



Filled Layered Plastic And Method

TECHNICAL FIELD

The present invention relates to improvements in filled plastics and, more particularly, to filled plastics with improved characteristics and method and apparatus for making the same.

BACKGROUND

The terms plastic and polymer are used interchangeably herein. The invention relates to such materials that usually are arranged molecularly in chains.

The use of additives for polymers is, of course, known. One purpose of such additives is to reduce the amount of polymer required for a given purpose. If the cost of the additive and the effort to add it to the polymer is less than the cost of the polymer itself, the cost of the overall part made therefrom may be reduced. Additives sometimes are referred to as fillers or extenders. Exemplary fillers are calcium carbonate, talc and carbon black. Exemplary filled material is polyethylene.

It is desirable to be able to maximize the amount of additive filler for a polymer in order to minimize cost, preferably without detrimentally affecting physical properties of the polymer. However, fillers often have been found to weaken the finished polymer product, for example reducing such characteristics as tensile strength, tensile impact and fatigue life, e.g. the latter manifest by stress cracking. Such weakening is believed due to the separation of polymer chains, the interference with the ordered alignment of the polymer chains by the filler, the cutting of polymer chains by the filler, e.g., during bending, and the creating of surface flaws by the filler. The lack of homogeneous alignment of the additive in the polymer also contributes to such weakening. Resulting weak spots or faults in the polymer product may be encountered; for example, too large particle size additive may tend to occupy space that should be occupied by a polymer chain thereby interfering with continuity of polymer chains through the polymer. If the additive particles are too small, the ability to achieve a preferred alignment of the particles is reduced appreciably, and it has been found that randomly aligned filler also may interfere with ordered positioning and linking of polymer chains. In the past, efforts have been made to try to achieve three axes alignment of additive particles to achieve homogeneity in the polymer and to avoid interfering with positioning and linking of polymer chains; however, such three axes alignment generally has been found only in areas of the product that are rather proximate the surface of the polymer product itself. The unordered or less ordered arrangement of additive particles deeper into the polymer product still would suffer the weakening mentioned above.

In polymer technology it is desirable to maintain substantially smooth flow of the polymer material through a die and into a mold. Turbulence in the flowing polymer tends to reduce strength in the finished product, e.g., by causing surface undulations at the extrusion die, which undulations freeze upon exiting the die and become sites for stress cracks. Lubricants have been added to improve laminar flow during molding. Nevertheless, some additive fillers tend to interfere with laminar flow, increasing turbulence so as to counteract the action of the lubricant. Accordingly, it would be desirable to improve laminar flow, thus reducing turbulence in the flowing polymer; and it correspondingly would be desirable to improve the strength and durability characteristics of the finished polymer product, the latter resulting from the improvement in laminar flow.

It has been found in the past that if the size of filler particles for polypropylene were adequately small, the filler would not tend to degrade the physical characteristics of the polypropylene for various connections of polymer chains, e.g., cross-linking of adjacent chains, generally would be unaffected. However, if the size were increased beyond a prescribed amount, the fillers would tend to create voids in the finished polymer product, for example, disrupting such cross-linking and/or other connections between polymer chains. Accordingly, good adhesion or bond strength between polymer and filler was needed, otherwise the voids would reduce the physical characteristics of the polypropylene.

According to the present invention, relatively small size filler particles are used in a way that effectively makes the voids substantially unrecognizable; and such filler particles also, as is described further below, cooperate with the polymer to effect alignment of polymer chains resulting in improved physical characteristics of the finished polymer product. Exemplary particles used according to the invention include talc, wood, flour, calcium carbonate, and carbon black.

In the past, fillers generally were added on a gross basis without grading for size or with little grading for size. This was true also for glass fibers used, for example, in fiberglass and resin type products. One convention followed in filling plastics was to try to increase the size of the filler particles in order to span more polymer chains, but, as was mentioned above, such increased size could result in voids detrimentally affecting the physical characteristics of the polymer. Further complicating the ability to grade filler particles on a size basis was the fact that generally in the past little effort had been made to define the size of filler particles currently available or to be used to fill a particular material. Ordinarily a user would just take the word of a supplier of the filler as to amount and size of filler to use to fill polymer or plastic material.

BRIEF SUMMARY OF THE INVENTION

Briefly, according to the invention, improvements in filled polymers are provided by using additive particles of a preferred size relation to the polymer and providing such additive particles in the polymer such that the particles are aligned along three axes substantially throughout the polymer and interact with the polymer to promote alignment of polymer chains with relatively minimal interruption of cross-linking or other connections between chains. Such improvements have been found to provide improved fatigue life, for example on the order of up to about seven times normal without decreasing other physical characteristics of the polymer.

Thus, as used herein, reference to three axes alignment means alignment or substantial alignment of particulate filler in a plastic material, for example, such that the three axes of respective particles are generally aligned in parallel or near parallel. Attendant alignment, bonding and layering of the molecular chains of the finished plastic product also is achieved as a result of such alignment of the filler.

According to one embodiment of the invention, the polymer is polyethylene used, for example, in rotating biological contacter devices and/or in other devices. Particle sizes on the order of from about 5 to about 7 microns in length were used, with widths and thickness characteristics being so related to width and to length of the polymer chains as to provide for substantial alignment along three axes, for control of roll, pitch and yaw of the filler, during molding and afterwards.

According to another aspect of the invention, the additive particles for a polymer may be used to cooperate with the polymer chains to achieve three axes alignment of the additive particles, as above, and improving the laminar flow characteristics of the combined polymer and additive during flow through a die.

According to another aspect of the invention, since the larger the size of the additive particles for a polymer, the greater the possibility of encountering a void, the invention relates to the determining of the smallest size filler particle that will accomplish the aforementioned characteristics and additionally will increase the number of bonds of adjacent polymer, thereby minimizing the number of unbonded voids that might otherwise occur if the particle size were too large.

Still another aspect of the invention is to improve the surface characteristics of a plastic material, for surface defects often result in reduced strength of the plastic material. Using an additive or filler according to the present invention to affect the flow characteristics of a polymer during molding, extruding, etc. to achieve laminar flow will improve the smooth surface characteristics of the finished product by minimizing disruption of continuity of smooth polymer chains in the product at and beneath the surface, thus overall improving physical internal strength of the plastic product.

According to still another object of the invention, a filler material of platelet shape particles having size characteristics mentioned above cooperate with the polymer to achieve three axes alignment of the particles, on the one hand, and improved ordered alignment of the polymer chains further to improve physical characteristics of the polymer.

Desirably the particle size of the additive for the polymer is adequately small to avoid decreasing polymer strength due to unbonded voids and is adequately large to achieve the alignment characteristics mentioned. Most desirably, the platelet shape particles of the invention achieve such cooperative alignment functions with minimum disruption of the plastic structure. Although spherical particles may work according to the invention, the preferred form is a platelet shape particle to maximize alignment functions.

Another aspect of the invention is that by maintaining alignment of the additive particles and the polymer chains both at the surface and well beneath the surface of extruded material, such as a plastic sheet, both surface defects and sub-surface defects are minimized. Consistent with this aspect, platelet shape particles will tend to dissipate stress to avoid cracking of the material. Such additive particles further provide a slip layer to minimize interrupting the interlocking of the polymer chains. Stress distribution is accomplished by blocking direct application of the stress from one layer to another or in any event distributing such stress over a relatively large area, namely the large surface area of the additive particles. Still further consistent with this aspect, the filler preferably causes a layered structure of the plastic so that respective layers buttress each other strengthwise and in reducing transmitting of cracks between layers.

The size of the particles used as the additive in the present invention may vary in order to optimize fatigue characteristics, flowability during molding, extruding, etc., and strength characteristics for different polymers or resins.

Another advantageous characteristic of the present invention is the ability to reduce the amount of shrink of molded or extruded plastic material. Platelet shape particles will tend to reduce the amount of shrink in at least one direction.

Even another aspect of the invention relates to grading of particles, particularly platelet shape particles, for use as an additive to a plastic. Such grading may be effected according to both length and aspect ratio and possibly also according to thickness of the particles. Aspect ratio is a function of a relationship of the effective length and effective width of the particles. Several materials useful as additives according to the invention include calcium carbonate, talc and mica, as well as others mentioned herein. A particular advantage of talc is that talc particles generally are platelet shape having an aspect ratio exceeding one thereby to assist in the desired alignment functions. Mica also is found in platelet shape particles; but the sides generally are more equal in length (i.e., the aspect ratio is closer to 1) than talc particles, which are relatively more oval in shape. Also mica is harder and sharper than talc and the edges may tend to cut the polymer chains during extruding and/or during flexing of an extruded product. Calcium carbonate is less desirable than talc or mica because particles thereof generally tend to be more spherical in shape, although such particles may be used according to the invention if the desired alignment and other characteristics can be accomplished.

According to the invention a layered structure of extruded polymer is created to improve fatigue life in the finished plastic material. Such aligned layers provide increased fatigue life relative to amorphous extruded plastic material by permitting the layers to slide over each other as the material bends without cutting respective polymer chains. The present invention provides such layered structure, while minimizing interference with cross-linking of respective layers to each other. Moreover, as will be appreciated from the following description, due to such alignment of polymer and reliance on the polymer itself for strength in the finished product, bonding or adhesion of the polymer and the filler is not necessary for strength in the finished product. Indeed, such bonding is undesirable during the extruding process, for the filler promotes the layering of polymer chains during the extruding process and to achieve that function needs to encounter some extent of relative movement or slip compared to the movement of the polymer chains as the mixture of polymer and filler passes through an extrusion die.

Although the preferred embodiment uses platelet shape particles as filler for the polymer, it will be appreciated that features of the invention may be achieved using more spherical shape particles. Such spherical shape particles could be used separately or in combination with the platelet shape particles. Although the spherical shape particles would not necessarily promote the desired three axes alignment of the filler particles themselves and, therefore, would not necessarily provide the alignment of the polymer, they could be used to spread forces during bending or stressing of the plastic product to reduce the possibility of concentrating the forces to an extent that would crack or otherwise damage the plastic. Preferably, though, the invention uses exclusively platelet shape particles of talc, as is described in greater detail below.

Even a further aspect of the invention relates to improving the process of extruding plastic through a die. The plastic tends to be compressed at the die resulting in viscosity changes and increased flow speed. The plastic then tends to slip past the filler, and such slippage or relative movement tends to promote alignment of the particles. Such slippage can be promoted further by using carbon black particles as a lubricant.

In the past strong plastics were made using filaments together with resin used as a binder; such materials are relatively expensive, and the same tend to mold or to extrude with reduced slippage at the die, for example. On the other hand, according to the present invention, relatively inexpensive fillers may be used to increase the fatigue life of the plastic while also reducing the amount of plastic required to make a part.

Another aspect of the invention relates to improvements in the extruding of plastic materials and in such extruded products by using a filler primarily to assist the extrusion die walls in effecting a preferred alignment of polymer chains in the extrusion due, whereby the chains align in the die generally in layers separated by filler particles and freeze in such layered arrangement to provide strength characteristics determined primarily by the polymer with minimal impact of filler on the finished product. Further consistent with this aspect, the filler is selected relative to size of polymer chain to be of minimum size that accomplishes the preferred alignment both of the polymer chains and of the filler particles themselves and also to be adequately small as to minimize interfering with cross-linking and the like bonding between relatively adjacent polymer chains and, thus, layers thereof. Due to such layered configuration and to minimizing disruptions of cross-linking, strength of the extruded product is based on the polymer itself and not on the filler.

According to the invention, then, filler is added to polymer intended for extruding for the purpose not for using the filler as a strengthening member, but rather to cause the polymer to align in a preferred manner to enhance the strength of the polymer chains and/or the products made therefrom. Therefore, the filler particles may be selected with attention to size and shape without major concern for adhesion thereof with respect to the polymer. Since adhesion between filler and polymer is not critical, special attention to preparation of filler to maximize such adhesion is unnecessary.

Still another aspect of the invention relates to the use of a filler to provide in an extrusion die multiple extrusion die-like areas (or in a sense sub-dies) at various times and places during and in the extrusion process, with the filler particles tending to move along with the polymer material being extruded in order to achieve preferred alignment of the polymer and of the filler particles. The filler particles travel through the extrusion die with the polymer, but at a slower velocity than the polymer; however, since the differential velocity is less than the differential velocity of the polymer and the fixed extrusion die surfaces, turbulence and differential flow are reduced thereby to minimize undulations in the flowing polymer and possible areas of stress cracking and the like. Differential velocity means the difference in velocity between constituents of the extruded material, namely the filler and the polymer. These characteristics of the invention are particularly advangageous when the extruded material is a non-Newtonian fluid, e.g. a thixotropic fluid.

At the die the filler particles are less compressive than the polymer. Therefore, the polymer extrudes more rapidly and slippage occurs between the filler and polymer.

To be able to rely on polymer alignment for tensile strength, according to the invention, it is desirable that the filler particles be selected in a size range that is described in greater detail below. As a result of the filler particles being in such size range, a wind vane effect occurs such that the filler particles and the polymer chains undergo desired alignment; indeed, such alignment, particularly three axes alignment of the filler particles, is deep into the finished plastic product (preferably throughout) and, of course, is desirable to achieve polymer alignment throughout such product. Too small filler particles will be less likely to afford such alignment, strength, and like characteristics and operation; too large filler particles, such as long strand fillers, do tend to promote alignment thereof and of the polymer chains, but cause other problems, such as more extensive interruption of cross-linking of polymer chains, therefore requiring the use of binders to glue the polymer to the filler particle. Binders create difficulties in pushing/flowing through the extrusion die and, therefore, are undesirable.

Thus, an aspect of the invention is that binders need not be used.

Yet other aspects of the invention relate to techniques for determining the preferred size of filler particles for a polymer to accomplish the various results described herein.

Other aspects of the invention relate to determination of particle size for the additives, processes of molding or extruding the filled plastic material, and apparatus to effect the same.

By selecting the filler particles to be in a size range according to the description of the invention herein, the desired wind vane effect is achieved to obtain relative three axes alignment of filler particles, preferably throughout the finished plastic product, and to achieve the sub-die effect to influence the desired alignment of polymer chains with cross-linking between respective chains and/or layers of polymer thereby to obtain a strong finished product. Moreover, the foregoing preferably is achieved with a maximum of filler particles added to the polymer to minimize the amount of polymer required for the finished product.

Summarizing several important features, the invention improves, preferably maximizes, strength or other physical characteristics of a polymer. As a result, relatively inexpensive polymer can be made to perform like a more expensive engineered polymer.

Other objects, advantages, features and aspects of the invention will become more apparent as the following description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described in the specification and particularly pointed out in the claims, the following description and the annexed drawings setting forth in detail a certain illustrative embodiment of the invention, this being indicative, however, of but one of the various ways in which the principles of the invention may be employed.

It will be appreciated that although a preferred embodiment of the invention is disclosed in detail, it is intended that the scope of the invention be limited only by the scope of the claims directed to features of the invention and their equivalent.

BRIEF DESCRIPTION OF THE DRAWINGS

In the annexed drawings:

Fig. 1 is a schematic front section view of a filled plastic material according to the present invention;

Fig. 2 is a schematic side section view of the filled plastic material of Fig. 1;

Fig. 3 is a schematic block diagram of an apparatus for making the filled plastic material of Figs. 1 and 2;

Fig. 4 is a fragmentary schematic isometric view of an extruding die and platelet shape particles flowing therethrough according to the invention;

Fig. 5 is a fragmentary schematic front section view looking into the extruding die of Fig. 4;

Fig. 6 is a fragmentary schematic side section view looking into the extruding die of Fig. 4;

Fig. 7 is an isometric view of a platelet shape particle used in accordance with the present invention;

Fig. 8 is a top plan view of such platelet shape particle of Fig. 7;

Figs. 9 and 9a are fragmentary front views of a filler particle and polymer chains depicting the desired relationships thereof according to the preferred embodiment;

Fig. 10 is a view similar to Fig. 9 showing an alternate embodiment;

Fig. 11 is a fragmentary isometric view of a filler particle and polymer chains depicting the distribution of stress by the filler particle;

Fig. 12 is a fragmentary schematic view through an extruding die showing plastic produced having a fault in undulations formed in the surface;

Fig. 13 is a fragmentary schematic front section view through a circular extruding die for practicing the principles of the invention;

Figs. 14A, B and C are photographs taken with an electron microscope respectively of transverse, longitudinal and top cross sections of a sample of extruded filled plastic material generally not in accordance with the present invention, such photographs being provided for comparison with other examples hereof;

Figs. 15A, B and C are photographs similar to those in Figs. 14A, B and C, except that the particles actually are larger, but the same result of failure of three axes alignment occurred apparently primarily due to the non-platelet shape of the filler particles;

Figs. 16A, B and C are photographs taken with an electron microscope of transverse, longitudinal and top section views of cured or frozen output from an extrusion die of filled plastic material according to an embodiment of the present invention using a mixture of polyethylene and about 30 percent by weight talc as a particulate filler material having an average size on the order of about 5.5 microns in length;

Figs. 17A, B and C are photographs taken with an electron microscope of transverse, longitudinal and top section views of cured or frozen output from an extrusion die of filled plastic material according to an embodiment of the present invention using a mixture of polyethylene and about 10 percent by weight talc as a particulate filler material having an average size on the order of about 5.5 microns in length, the part made according to this example having exhibited on the order of about 7 times the fatigue life of a part made using the same polyethylene material unfilled;

Figs. 18A, B and C are photographs taken with an electron microscope of respective transverse, longitudinal and top section views of cured or frozen filled plastic material from an extrusion die generally according to the invention, the extruded material comprising a mixture of polyethylene, as used in the examples depicted in Figs. 16 and 17, 30 percent by weight talc as an additive filler having an average size on the order of about 5.5 microns in length, and a further lubricating type of polymer forming a general structure as in Fig. 10 above, this example depicting less alignment of the filler particles than in the photographs of Figs. 16 and 17; and

Fig. 19 is a schematic illustration of an extrusion die and extruded filled plastic according to an optimized model of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring, now, in detail to the drawings, wherein like reference numerals designate like parts in the several figures, and initially to Figs. 1 and 2, the preferred embodiment and best mode of the filled plastic material in accordance with the present invention is designated 10. The material 10 primarily is formed of a polymer 12 and one or more additives generally designated 14. According to the preferred embodiment and best mode of the invention, the polymer is polyethylene, which has a molecular chain type of structure, respective chains being designated 16, for example. It will be appreciated that other polymers may be used in accordance with the present invention; it is generally preferred, though, that the polymer used have a chain type of structure, and even more preferably such chain type of structure would have the capability of linear alignment such that respective chains generally can be aligned in parallel. Also, there should be some cross-linking between parallel chains of polymer, as is described further below, for inter-layer strength.

Exemplary polymers useful in the invention include polyethylene, polypropylene, nylon, compounds of one or more thereof, and other moldable, preferably extrudable, polymers.

Moreover, the additive 14 preferably is in the form of platelet shape particles meaning that they have generally much larger length and width dimensions relative to thickness; and most preferably such particles have an aspect ratio of length to width that exceeds 1, and is adequately large to achieve the three axes alignment described herein. Exemplary additives are mentioned herein; it will be understood that these and functionally equivalent materials may be used alone or in combination in accordance with the present invention. In Fig. 1 representative additive particles are designated 18. The additive 14 may be a filler, an extender, and/or other materials capable of functioning in accordance with the description hereof.

It has been found that by achieving alignment of filler particles, especially those of platelet shape, along three axes, the polymer chains of the filled plastic product also achieve alignment. Various strength and related characteristics of the filler plastic are achieved as a result, as is described in detail herein.

The filled plastic material according to the present invention may be used in rotating biological contacter devices that have relatively large sheet-like structures; and the filled plastic material may be used in other devices, as well. The ability to fill the plastic with additives according to the invention can reduce the effective cost of the filled plastic material relative to unfilled materials, for example, and, as is described herein, also may provide enhanced physical properties.

For convenience, identification of roll, pitch and yaw is provided. Looking at Fig. 1, the width dimension of particles 18 is shown. Assuming an axis coming straight out of the plane of the drawing of Fig. 1, roll would be about such axis; a particle undergoing some degree of roll is depicted in Fig. 5. Assuming a different axis in the plane of the drawing of Fig. 1, drawn vertically and, thus, parallel to the thickness dimension of the particles 18 shown in Fig. 1, yaw would be a rotation of a particle 18 about such axis. Pitch is a rotation of a particle 18 about a still further axis that is parallel to the plane of the drawing of Fig. 1 and through the width direction or dimension of a particle 18 causing the leading edge 20 (Fig. 2) of a particle 18 to be higher or lower than the trailing edge 22 of the same particle; an example of pitch is depicted in Fig. 6.

As seen in Figs. 1 and 2, each of the polymer chains 16 in the filled plastic material 10 is aligned in a generally linear fashion with respective chains oriented generally in parallel to each other. The filler particles 18 also are aligned along three axes, pitch, roll and yaw. The illustrations of Figs. 1 and 2 are optimized ones used to facilitate explaining the invention; it will be appreciated that perfect pitch, roll and yaw alignment may not be encountered in a particular product 10, although the probability of generally maximizing such alignment characteristics is the intention of the present invention in order to achieve material having the desired physical characteristics.

As is seen in the optimized model or illustration of Figs. 1 and 2, the width of the particles 18 (Fig. 1) extends directly between one molecular chain and the next one; see, for example, chains 16a, 16b and particle 18a. Also, as is seen in Figs. 1 and 2, the polymer chains 16 and the particles 18 are arranged in a layered configuration, and such arrangement intentionally is provided to try to assure that a polymer chain is located between each such particle and the next one and so that there are polymer chains at each surface of the particle 18, regardless of the dimension of such surface. Such layered arrangement, as is seen in Figs. 1 and 2, results in the particles 18 being generally parallel to each other and to the axes of the respective polymer chains without any (or with minimal) roll, pitch or yaw. Lack of roll is seen in Fig. 1; lack of pitch is seen in Fig. 2; and lack of yaw would be seen in a top view and in any event clearly is seen in Fig. 4 referred to in further detail below.

Turning to Figs. 3 and 4, apparatus and method for making the filled plastic 10 according to the present invention are depicted. The apparatus 30 includes a source 32 of polymer material 12 and a source 34 of filler material 14. Those sources may be conventional reservoirs, containers or the like with appropriate feed mechanisms to feed the respective materials to other parts of the apparatus 30. Control of such feed is effected by adjustable valves 36, 38 that are inserted in flow lines 40, 42 and are controlled by a conventional controller 44. The flow lines 40, 42 may be tubes or pipes. The valves 36, 38 may be electronically controlled or hydraulically controlled valves of conventional design. Such valves may be of the on/off type, although most preferred would be continuously or infinitely adjustable valves to provide complete control of the respective materials flowing through the flow lines 40, 42 to a mixer 46. The controller 44 may be a computer and associated drive circuitry to operate the valves 36, 38 according to the desired proportions of materials intended to be delivered to and mixed by the mixer 46, as is well known. The controller 44 alternatively may be a hydraulic type controller to control the valves 36, 38 in the case they are of the hydraulic type. The valves and the controller also may be of the pneumatic type or of any other type capable of providing the desired control function.

The mixer 46 may be a conventional mixer of the type typically used to mix materials prior to the supplying of such materials to an extruder. The mixer 46 is coupled by a further flow line 48 to a conventional extruder 50. Appropriate conventional means to force, to pump, or otherwise to supply the mixed material from the mixer 46 through the flow line 48 to an input of the extruder 50 may be employed.

The extruder 50 may be of the type that has a rotating screw or auger intended to force material through an extrusion die 52 in order to form a part 54 of the filled plastic material 10. The extruder 50 may include heating mechanism and/or other conventional mechanisms used in extruding plastic material. Heat may be generated, too, by the interaction of the rotating auger and relatively viscous material being extruded. An advantage of using an extruder 50 is that mixed material from the mixer 46 effectively further is mixed by the extruder and is forced under pressure through the die 52 to make the part 54. Alternatively, if desired, assuming the mixer 46 adequately mixes the material, a piston type or other type of device intended to receive a charge of mixed material and to force the same through the die 52 may be employed.

According to the preferred embodiment and best mode of the invention, the apparatus 30 includes an extrusion die 52 through which the mixture of polymer and filler is forced by the extruder 50 to form the part 54 of a particular shape, such as a sheet, a tube, etc. Conventional means may be provided periodically to cut the part 54 as it is output by the die 52 in order to limit the length of such parts. Alternatively, the mixed material provided from the mixer 46 may be forced by an extruder 50, other pump mechanism (not shown), or the like, into a mold, such as that used in a plastic injection molding machine to mold the part 54. In such case, there ordinarily is an entranceway into the mold, and such entranceway as well as the flow channels to it may provide the desired cooperative action with the mixture flowing therethrough to achieve desired alignment of polymer chains 16 and particles 18.

As is seen in Figs. 3 and 4, according to the preferred embodiment and best mode of the invention, the extruder forces a mixture of polymer 12 and additive 14 through the extrusion die 52. In Fig. 4 the extrusion die 52 partially is shown having two parallel plates 56, 58 having a relatively long width dimension 60, a smaller height or thickness dimension 62, and a length 64, which is adequate to achieve the desired alignment in the mixture 66 and the constituent parts of that mixture flowing through the die 52. Such die 52 may be used, for example, to extrude sheet material that is relatively wide (the width dimension 60) and is relatively thin (the thickness dimension 62). For clarity only the filler particles 18 of the mixture 66 are shown in Fig. 4; the polymer material also is present but is not illustrated in Fig. 4.

The present invention is useful for extruding various types of materials; however, a particular advantage inures to the invention when the material being extruded is a non-Newtonian fluid, such as a thixotropic fluid. Such non-Newtonian fluids, e.g., thixotropic fluids, as is known, change viscosity with respect to shear. In the past three axes alignment of particle fillers was achieved near the surface of extruded material near the surface of the material apparently due to the relatively high shear near the surface and, thus, greater slippage between the extruded material and the filler particles; this was not achieved deep down in the material, though. On the other hand, according to the present invention using filler particles of preferred size and shape, three axes alignment can be achieved relatively deeper into the extruded material. According to the present invention using the multiple dies or sub-dies, as are described herein, fluidization is more uniform or evened out because the effective shear is evened out throughout the extruded product.

Mort specifically, non-Newtonean fluids become less viscous near the surface, i.e. near the die, because there is greater shear there. When that occurs there is the probability of greater velocity difference between the flowing plastic and the filler particles. The plastic flow relatively fast near the die surface to provide such alignment of the filler particles near the surface of the extruded material. Typically, though, the viscosity of the non-Newtonian fluid is greater near the center of the flowing extruded stream in the extrusion die, and such viscous material would tend to carry along the filler particles. In the present invention, though, due to the size, shape, loading and/or distribution of the filler particles in the material being extruded, the flow through the extrusion die is evened out across the entire cross-section of such extruded material in the die. Due to the evening of flow, turbulence is reduced. Due to the reduced turbulence and due to the size, shape, loading and/or distribution of the filler particles, a relatively small difference in the velocity of the filler particles and the fluid is needed to achieve the desired three axes alignment of the filler particles.

In operation of the apparatus 30, including the extrusion die 52, a mixture 66 of polymer and filler is forced through the extrusion die 52, as is seen in Fig. 4, for example. Due to size considerations vis-a-vis the particles 18 and the polymer chains 16, only several of which are represented in Fig. 4, for example, such mixture flows through the die 52 while accomplishing certain alignment functions. Specifically, the particles flowing in the center of the stream through the die 52 tend to align (sometimes referred to herein as to flatten) with respect to the stream flow through the die in the manner illustrated; such alignment being with regard to all three axes (roll, pitch, and yaw). Such aligned center particles tend to help further flatten and to align particles nearer the outside of the die. The flow speed nearer the outer part of the flow, i.e. that more proximate the walls of the die (hereinafter referred to as the outside of the die) is slower than at the center, as is well known in fluid dynamics, particularly for Newtonian fluids. Therefore, nearer the outside of the die there is less difference between the flow speed of the polymer through the die and the drag applied to the particles. Accordingly, interaction of the aligned particles closer to the center of the flow with the particles closer to the outside of the die will tend to help align the latter in the absence of adequate flow/drag difference there. Such drag considerations are described further below. At this point, though, it is noted that drag is the force applied to the particles tending to oppose or to resist the flow forces that would tend to carry the particles in the direction of flow. Thus, it will be appreciated that the present invention is useful in connection with both Newtonian and non-Newtonian fluids.

Interaction of the polymer chains and particles, the flow/drag considerations, and interaction of the mixture 66 with respect to the walls of the extrusion die 52 all cooperate to achieve the three axes alignment illustrated in the drawings and described herein.

Schematic representations of the extrusion die 52 and what occurs therein also are seen in Figs. 5 and 6. In Fig. 5 a particle 18b is shown having undergone a slight roll motion, and in Fig. 6 a particle 18c is shown having undergone a slight pitch motion. It will be appreciated that the illustrations of Figs. 4, 5 and 6 only show a single layer of particles 18 flowing through the die and several polymer chains 16 flowing through the die, for example in the direction of the arrows 68. However, it is to be understood that the illustrations in Figs. 4, 5 and 6 are schematically representative of the concept of the invention only, and in actual operation of the apparatus 30, including the extrusion die 52, there would be multiple layers of particles 18 and multiple layers of polymer, particularly polymer chains 16; and the possibility of multiple layers is depicted specifically in Figs. 1 and 2, for example, and also by the dots 70 in Fig. 1 representing expansion of overall thickness of the filled plastic 10.

Particle Size Considerations

Referring to Fig. 7, a particle 18 is shown in isometric view having length L, width W and thickness T dimensions. The particle 18 is generally platelet shape, e.g. having a small flattened body, according to the preferred embodiment and best mode of the invention. It is anticipated that the actual shape of particles used in accordance with the invention would have a degree of curvature where corners are shown in the particle 18 of Fig. 7 so that such particles would tend to be more oval in shape than rectangular. Nevertheless, the rectangular shape has been found to represent a reasonably appropriate model of such platelet particles.

In Fig. 8 is a plan view of the particle 18. Several dimensions "a" and "b" are depicted in Fig. 8. The force of flow F and the force of drag D are represented in Fig. 8, as well. Flow F represents the force of the moving polymer chains that tend to carry the particle 18 through the extrusion die 52, for example. Drag D is the resistance of the particle 18 to undergo such flow. The flow F and drag D forces are functions of the exposed surface areas of the particle 18 that are perpendicular to and, thus, directly exposed to such forces, and the actual extends of such areas are directly proportional to the dimensions "a" and "b". Moreover, such dimensions "a" and "b" are a function of the orientational alignment of the particle 18 relative to the direction of the flow F and drag D forces.

The aspect ratio of a particle 18 will be defined herein as the length dimension L divided by the width dimension W. The effective aspect ratio will be the dimension "a" divided by the dimension "b", as is depicted in Fig. 8. It will be appreciated that the force tending to orient the particle 18 such that the length dimension is generally parallel to the parallel polymer chains 16 is a function of the aspect ratio and, accordingly, the influence of the flow force F, drag force D and difference thereof acting on the effective surfaces exposed directly thereto.

It has been found that to effect alignment of particle length with the direction of parallel polymer chains, substantially full alignment occurs with on the order of about plus or minus 2° misalignment when the aspect ratio is on the order of from about (25-30) to 1, in one example, on the order of 28.64:1. Such alignment with about plus or minus 5° misalignment has been achieved using an aspect ratio on the order of from about (7-14) to 1, in one example 11.43:1. In a still further example, such alignment would occur with misalignment on the order of plus or minus 10° when the aspect ratio is on the order of from about (4-7) to 1, in a specific example 5.76:1.

A practical misalignment range is on the order of plus or minus 5°. Such misalignment can be reduced by increasing aspect ratio.

The same types of forces that tend to effect alignment of the length of a particle 18 with respect to parallel polymer chains also will act on various edge surfaces and top and bottom surfaces of the particles 18 to achieve alignment along other axes thereby accomplishing overall the three axes alignment characteristic of the invention.

To achieve the desired alignment of the particles 18, it is important to the invention to have slip at the extrusion die 52. Such slip results in a difference between the flow force F and drag force D, and that force difference tends to promote the desired alignment of the particles. Moreover, aligned filler particles in turn promote alignment of the polymer itself. For example, the flowing plastic is an amorphous structure. Therefore, hydrodynamic considerations will cause the flowing stream of polymer through the die to be generally aligned with the longitudinal axis of the stream in the direction 68, e.g. as is shown in Fig. 4; and this together with the action of the aligned platelets on the polymer chains themselves help to assure overall preferantial linear alignment of the polymer chains and of the particles.

Desirably the platelet shape particles 18 are rather thin compared to length; and such relationship assures good pitch control as the particles are carried by, bond to, and align with linear polymer chains.

Control of roll is a function of the relationship of particle thickness to particle width. Slight roll is shown in particle 18b in Fig. 5. Pitch and roll alignment functions of the filler particles are achieved by interaction of the polymer chains directly on the respective surfaces of the particles. Indeed, slippage of the particles relative to the polymer chains, as the mixture 66 flows through the extrusion die 52, helps assure such alignment. Such slippage is promoted by a certain degree of compressibility of the polymer material and/or the velocity change encountered at the extrusion die.

Exemplary computations to determine desired size of filler particles are presented with respect to the description of Examples 1-3 below.

It is desirable to minimize particle size while still promoting the desired three axes alignment functions. Minimal size minimizes voids, as was mentioned above, and maximizes bonding for strength of the material, e.g., by allowing relatively maximum opportunity for polymer chains in the same or different layers to cross-link or otherwise to bond to each other. Too small a size, though, may not achieve the desired three axes alignment.

As to thickness, the particles 18 should be as thin as possible to minimize the number of polymer layers disrupted by the particles. In the illustrated example and model of the invention, the particles should be on the order of one diameter or less of the effective working diameter of a polymer chain 16 in order to achieve the direct interaction of the polymer chains on the particles for alignment. The working diameter of the polymer is the effective thickness, i.e. outside diameter, of one polymer chain or, less desirably, but perhaps more practically, the diameter of a flow stream of plural polymer chains. If the polymer chain is in the form of a helix, the working diameter would be the outside diameter of the total loop of the helix.

Such polymer chain diameter characteristic assumes that the polymer chains pass through the extrusion die 52 in respective flow streams which flow generally linearly through the die; this is an idealized condition that may not be a totally accurate representation but is adequate on the average for modeling the invention and achieving the objective thereof. The polymer chain may tend to stretch out during extrusion and thus have a thinner diameter in the extruding die. Thus, more preferably the working diameter of the polymer chain with which the present invention is concerned is that encountered during normal extruding operation, particularly that diameter encountered in the extruding die.

The thickness of the particles should be adequate so that the particles have substance and strength. However, the thickness of the particles is not particularly crucial to the invention other than the thickness and width should be adequate to achieve optimum pitch and roll control. Generally, though, length and width considerations have much greater impact on operation of the particles 18 than does thickness.

If a platelet 18 were too thin, there would not be assurance it would encounter a direct confrontation with a polymer chain at the edge of the particle, and ideal alignment would probably not occur. Therefore, particle thickness should be about that of one polymer chain diameter, as was mentioned above. Further, as is seen in several of the figures, utilizing particles having the prescribed thickness characteristics, a convenient ordered alignment of particles and polymer chains with on the average at least one polymer chain between each pair of adjacent particles in a particular layer of chain and particles will occur; see, for example, Fig. 1, layer 72. The locating of at least one polymer chain between each pair of otherwise relatively adjacent particles 18 helps to assure cross-linking among polymer chains for distances between adjacent chains are minimized and helps achieve some bonding of polymer and filler particles. This also helps achieve alignment in the yaw direction.

Concerning width of the particles 18, desirably each particle should have a width that is at least three diameters of the working polymer 16 when the respective polymer chains are aligned in generally parallel planar relation plus the distance between two, pairs of adjacent polymer chains, as is depicted, for example, in Figs. 1, 5, and 9. The width dimension of the particles 18 may be larger than the just-mentioned minimum; the minimum, though, helps to assure that at least two polymer chains will be located in direct confrontation with the major surface area 74 (Fig. 7) to prevent roll. The width dimension should be large enough so the particles do not fall in "cracks" or space between adjacent polymer chains.

For relatively low molecular weight polymer, which may consist of large diameter and small diameter polymer chains 16, 76, as is seen in Fig. 10, it is necessary to rely on the relatively larger diameter polymer chains 16 for determining the width of platelets 18 plus the space taken by the smaller diameter polymer chains 76. Thus, as is illustrated in Fig. 10, the width dimension of a platelet particle 18 is equal to the working diameter of three large diameter polymer chains 16 plus the approximate diameter of two small diameter polymer chains.

Fundamentally, though, the intent is that the particle width be at least large enough to span three large diameter polymer chains, regardless of what other polymer chains might be intermixed therewith in order to achieve maximum alignment interaction between the polymer chains and the particles to prevent roll.

Looking in the direction of flow of polymer material through an extruder die, for example, the minimum width of the filler should be a width that provides the desired interaction between the filler and polymer. The width dimension provides the drive for the particulate in the polymer moving it along through the extrusion die.

The just-described width characteristics relative to polymer chain diameter also achieve desired bonding and some degree of pitch control.

The length of the platelets 18 should be at least twice the effective length of a polymer chain to assure overlap of the platelet with at least part of two, possibly three or even more, polymer chains lengthwise. The effective length of a polymer chain is the maximum length that occurs during the extruding process as the polymer is extruded through the extrusion die 52, even though the polymer may be somewhat helical or other shape so that if stretched fully it would be longer than its effective length. The reason for relying on the polymer chain length in the extrusion die is that it is in the extrusion die where alignment characteristics are most notably achieved and have greatest impact on the polymer and ultimate finished part.

Moreover, the length of the filler particles should be longer than the width of the particles so that the particles will align with respect to the flow of material, particularly the polymer, through an extruding die. Reference is made to Fig. 8 of the drawings where the width dimension of the particle 18 clearly is shorter than the length dimension so that the drag force D and flow force F act on the particle 18 tending to align it in the extruding die in parallel with the polymer chains flowing through the extruding die. Such alignment occurs because the dimension a, which is the projected area of drag, is less than the dimension b. In general, though, the length of the particle 18 should be longer than the length of a polymer chain and preferably should be the length of at least two polymer chains so that the particle will not fall between polymer chains and will tend to interact with the polymer chains to achieve the desired alignment of the particles and of the chains.

In practice it may not be possible to obtain platelet shape additive particles having ideal dimensional characteristics, as was described above. However, it will be appreciated that other sizes may be used, but such sizes should be designed generally along the principles described herein. Moreover, since it is not possible precisely to place a particular particle relative to particular polymer chains, the mixture percentages based on size or weight with appropriate length, width, thickness and diameter grading will provide a statistical average assuring near optimum distribution of particles in the polymer, for example in the manner illustrated in the several figures.

One structural advantage that inures to the invention, when a filled plastic 10 has particles 18 and polymer chains 16 related as above, is the distribution of stress over several polymer chains, as is seen in Fig. 11. By distributing stress, as is illustrated, the strength of the filled plastic product is enhanced over products not made according to the invention; stress failures are reduced in the filled plastic of the invention.

According to the invention, improved characteristics are achieved in the filled plastics described. Such improved characteristics are accomplished by using filler that tends to align the plastic molecular chains and also particles that themselves align in three axes. The filler is selected as to be so small that minimum displacement of the polymer chains occurs, thus decreasing the realized appearance of voids, which accordingly decreases the need for separate binders or other mechanisms to bond the polymer and filler particles.

Another important aspect of the invention achieved using the aligned particles is the alignment effected by the particles on the polymer chains. Referring to Fig. 12, for example, schematically illustrated are a number of polymer chains being extruded through an extrusion die 80 in the direction of arrows 82 without benefit of the particle filler of the invention. Such polymer chains tend to have undulations, and those undulations especially tend to appear at the surface. Such surface irregularities tend to be areas where stress can be concentrated and breakage in a finished product too easily can occur.

However, the platelets 18 of the invention tend to smooth out such wave function or undulations. The forces between the platelets and the polymer chains as a function of the slippage occurring in the die, generally regardless of the shape of the die since the cross-sectional dimensions of the platelets are extremely small relative to even an incremental surface area of the die, helps to maintain smooth laminar-like alignment and flow of the polymer through the die.

Moreover, an internal lubricant, such as carbon black, may be used further to aid in the reducing of undulations in the polymer chains and finished product produced by the extrusion die 52. Such internal lubricant would tend to promote slippage between the polymer chains and platelets, thus increasing the planar parallel three axes alignment characteristics described.

An aspect of the invention is the promoting of layering such that the platelets are in respective layers, and those layers are separated by respective layers of polymer chains, for example without platelets therein. Such layering further increases yield strength of the finished product. Layering is promoted since the extrusion die 52 is a flow through device without a dead end, and the polymer chains 16 and particles 18 will tend to align statistically in layers generally in the manner illustrated in the drawings, for example Figs. 1 and 2. Further, with the particles 18 selected to be of a size large enough to meet the above criteria of length, width and thickness, such particles will tend to produce a reactionary force with the plastic strata to generate layers.

One method for determining a relatively optimum size for particles 18 for use with a particular polymer would be to mix an array of fillers of sizes that are believed to be useful for achieving the alignment function with the polymer in question. Thereafter, the mixture would be extruded or molded. An electron microscope or like device would be used to observe which size particles achieved alignment along three axes and which did not; those particles sizes that did align would be selected for use with the particular polymer. Alternatively, the electron microscope could be used for photographing longitudinal, transverse and planar sections of the extruded product, and thereafter the number of aligned particles and the sizes thereof could be counted to obtain an indication of those which achieved the best alignment characteristics. Moreover, such method could be refined further by selecting the smallest size particles that would undergo the three axes alignment and selecting such particles for use with the particular polymer.

Another aspect of the invention relates to the facilitating of re-forming the extruded filled plastic material. In particular, in the past a filler would tend to stiffen a part and that part would not be particularly conducive to subsequent forming. In the present invention, though, stiffness is achieved when the material is frozen; however, when the material is warmed, the slip planes and layers in the material may be used to promote forming, e.g. to form an intricate part by vacuum forming processes. Upon re-freezing of the part, excellent stiffness would occur.

Accordingly, an aspect of the invention is a product formed by making a layered structure of polymer chains and platelet shape particles that provide increased fatigue life and increased thermoformability over prior filled plastic materials. Such improvements being due, on the one hand, to the layered configuration and stress distribution represented, for example, in Fig. 11, and due to the slip planes created when the material is warmed, as was described above.

Three axes alignment of particulate filler 18 has been found as deep as 50 mils into the filled plastic material extruded through a die according to the invention. The size of the particulate filler should be so selected in relation to the polymer according to the description herein that the polymer chains tend to align and the filler tends to align on three axes. In effect, a unidirectional mat tends to be achieved. Such alignment of polymer chains tends to increase the tensile strength of the plastic material at least in the direction of the aligned polymer chains. Also, weak spots in the filled plastic product are minimized because faults are eliminated and because of the stress distribution mentioned earlier.

Further to maximize the uniform layering and desired alignment characteristics of the filled plastic material of the invention, it is desirable for the extrusion die 52 to be rather open to avoid presenting turbulence creating points.

The present invention facilitates using regrind polymer material because of the improved characteristics created by the platelet filler. Thus, regrind material can be substituted for previously required virgin material which in turn reduces the overall cost for the finished product.

Although in the past filler was added to plastic materials as a function of weight percent or volume percent, in the present invention filler is added according to size, shape and alignment characteristics, and then a blend of filler and polymer is made that statistically would result in the desired relation of filler particles 18 to polymer chains 16. More specifically, referring to Figs. 1 and 2, the statistical number should be determined so that the number of particles and the number of chains in the optimum case would result in alternating layers of all polymer chains, on the one hand, and of a mixture of polymer chains and filler particles. Moreover, in those layers which have a mixture of polymer chains and filler particles, at least one polymer chain would separate each otherwise relatively adjacent pair of filler particles. This arrangement is shown in Fig. 1. Furthermore, in the length direction of the filler particles and of the filled plastic product as viewed in Fig. 2, for example, in each layer of a mixture of polymer chains and filler particles there should be at least one polymer chain 16 between each pair of otherwise relatively adjacent filler particles. Taking such criteria into account together with the size criteria described above, one can determine the effective statistical mixture based on weight, volume, etc., of course having known in advance density and/or other characteristics of the materials being mixed. The inventor has discovered that three axes alignment has been achieved in materials made according to the description herein with such alignment occurring 50 mils deep into the material, a dimension that is rather large compared to the previously encountered surface alignment in the prior art.

As is seen in Fig. 13, principles of the invention apply to circular cross-section extrusions as well as polygonal ones. In the circular die 90 the filled plastic material 10 of circular cross-section flows with three axes alignment of the particles 18 about the central axis of the die, in a sense according to a polar coordinate system. The polymer chains 16 flow longitudinally through the die 90. The relationship of particle size to polymer chain size and ratio of number of particles to number of chains is according to other description herein.

Briefly referring to Figs. 3 and 4 again, the extruding process according to the invention is depicted. The particles 18 and the polymer chains 16 tend to flow through the die 52. The particles flowing in the center of the stream tend to flatten and to align with respect to the stream flowing on all three axes. Such aligned center particles tend to help further flatten and to align particles nearer the outside of the die. The flow speed nearer the outside of the die is slower than at the center, as is well known in fluid dynamics; therefore, nearer the outside there is less difference between the flow speed and the drag. Accordingly, the interaction between the aligned particles closer to the center and the outside particles, which are flowing more slowly, helps to align outside particles in the absence of the flow/drag difference there. Thus, three axes alignment is achieved over a wide cross-sectional area of the flowing material schematically depicted in Fig. 4 even though there is a difference in flow rate at the center and outside portions of the die.

Considering speed of the material flowing through the extruder die, it is most desirable to have the particles move at the same speed as the polymer sheet through the die. Uniform speed minimizes fault areas.

It is desirable, therefore, for the particles to have a minimum width of the diameter of at least three polymer chains so that they do not fall through cracks between polymer chains and yet remain aligned on three axes as aforesaid. Also, to achieve the desired alignment characteristics and to assure that the particles do not fall between longitudinally aligned polymer chains, the length of the particles should be at least about seven times the width of the particles, and the length should be such that the particles span at least two polymer chains in length.

If the particles were too large, the differential drag during extrusion may not be adequate to achieve the desired alignment along three axes and voids could occur in the plastic. If the particles were too small, influences to promote the three axes alignment would not occur as much in the inner layers of the extruded filled plastic material as did occur in the outer layers near the die face. In thixotropic fluids ordinarily there would appear to be more shear at the die face than internally of the fluid flowing through the die. By employing the filler of the invention with thixotropic fluids, though, the layering created by the platelets makes the shear more uniform throughout the extruded plastic in the die to avoid turbulence in the die, to even out viscosity of the material throughout the die and otherwise to provide a finished product that has improved characteristics, e.g. strength, compared to the same extruded plastic without the filler hereof.

Talc particles tend to be relatively longer and thinner than they are wide. Talc particles can be graded on maximum size bases insofar as length and aspect ratio are concerned. Accordingly, talc is an example of a preferred particle used in accordance with the invention.

Examples 1, 2 and 3

Talc particles with polyester polymer chains, according to the dimensional relationships described above, were extruded through an extrusion die. In Example 1 plus or minus 10° of particle misalignment occurred when the aspect ratio (width to length) of the particles averaged about 5.76:1. In Example 2 plus and minus 5° misalignment occurred with an aspect ratio of 11.43:1; and in Example 3 plus or minus 2° misalignment occurred when the aspect ratio was on the order of 28.64:1.

Although three axes alignment may have occurred in the past, the prior art does not disclose achieving three axes alignment using minimum particle size according to the present invention, nor does the prior art disclose three axes alignment deep into the finished plastic product. In the past, if strength of a material was the result of the polymer per se, then adding an additive to the polymer tended to reduce the strength; on the contrary, in the present invention, though, adding an additive to the polymer tends to enhance strength by achieving three axes alignment and consequently improving fatigue life of the material while reducing the amount of the polymer material required. The invention appears to provide true layering and, therefore, does not just rely on bonding of materials for strength, particularly insofar as tensile strength and stress resisting strength are concerned.

Previous discussion concerning size of the filler particles was related to the size of the polymer in which the particles are to be used so as to assure the described impact on the filler particles. The following description concerns a mathematical technique to compute the estimated size parameters of filler particles that may be used according to the invention; and such technique is demonstrated by the experimental results described in Examples 1-3. The technique is generally theoretical and ignores frictional considerations.

The invention seeks to determine the minimum size (L, length; W, width; and T, thickness) for particles that will display hydrodynamic stability within the extruded streams at the extrusion die to displace the fewest number of polymer molecules while facilitating the greatest possible alignment of the polymer molecules. Desirably the invention minimizes (or at least reduces) the amount of polymer required to achieve certain function while preferably maximizing (or at least increasing) strength and/or other characteristics of the finished polymer. Also, the invention preferably maximizes (or at least increases) the strength characteristics of a particular polymer above those characteristics that inure to such a polymer that is made in a pure or unfilled condition. Further, the invention provides in a filled relatively inexpensive polymer the ability to achieve characteristics of a more expensive specially engineered polymer or resin material. As is mentioned elsewhere herein, such features are achieved by selecting a filler that has a preferred size relation to the polymer as to react in the manner described, e.g., as is demonstrated by achieving alignment of the filler particles along three axes in the finished filled polymer product substantially throughout the polymer or at least at and substantially deep beneath the surface thereof.

Referring to Fig. 8, there is shown the drag force D due to slippage as the particle 18 tends generally to flow with the polymer while slipping relative to the faster flowing polymer. The drag force D is the force which tends to align the particle such that the axis M thereof would tend to align in the direction of flow F to minimize yaw.

For the purpose of this description, it is assumed that the particle 18 is rectangular with right angle corners. (Although this is an approximation, it is a good model to determine the theoretical particle size for use in the invention.) Therefore, relative to the axis N along which the flow direction F and drag force D occur, an angle alpha ( ) can be defined in the manner illustrated in Fig. 8. The projected area "a" is a function of that angle and the length L of the particle 18; specifically "a" equals L times the Sine of angle ( ) alpha. Likewise the projected area "b" equals the width dimension W times the Cosine of angle ( ) alpha. Note equations (1) and (2) below:

(1) a = L x Sin ( )

(2) b = W x Cos ( )

For hydrodynamic balance of the particle, the projected areas "a" and "b" must be equal. Therefore, setting "a" equal to "b", one derives the equation (3) relationship of length to width, as follows:

(3) L/W = Cos ( )/Sin ( ).

Equation (3) can be solved to determine the ratio of length L to width W, i.e., the aspect ratio, of particles 18 that would achieve axial alignment within the tolerance of angle ( ) alpha. For example, for alignment within plus or minus two degrees, i.e., angle ( ) alpha is two degrees, the ratio L/W should be about 28.64. Other relationships are presented in the following:

TABLE 1

L/W	Angle ( ) Alpha
28.64	2 degrees
11.43	5 degrees
5.67	10 degrees
3.73	15 degrees
2.747	20 degrees

Relying on the above values and the above relationships between the particle size and the polymer size, e.g., particle width W should at least equal three polymer working diameters (plus packing space) and particle length L should equal at least two polymer effective lengths in the extruding die, one can determine the desired size parameters for particles to be used as a filler for a particular polymer. Then, with such determination having been made, one can determine what size filler particles are commercially or otherwise available to be obtained and used as a filler for the particular polymer.

Similar computations can be carried out to determine the preferred ratio of particle width W to particle thickness T, as is shown in Fig. 9a. Roll of particles about the particle axis M should be minimized to a tolerable amount. Forces contributing to roll are due to incompressibility of the extrusion die face and the action thereof via the polymer chains to apply force directly to the face 18f of respective particles. Since such forces act on the projected areas of the surface 18f along the width dimension W thereof and along the thickness dimension T thereof, a set of equations similar to equations 1-3 above can be drawn with respect to roll. Specifically, the angle of roll will generally be limited to the following relationship:

(4) T/W = Cos ( )/Sin ( ),

wherein T is thickness and W is width of the particle as shown in Figs. 7-9, and angle ( ) theta is the angle of roll of the particle about the axis M, for example from an orientation that generally places the surface 18f in parallel to the surface of the extrusion die face.

Applicant has found that as a practical matter axial alignment (both yaw and roll, as well as pitch, which can be detrmined according to the mathematical modeling techniques just described for yaw and roll, for example) of the particles within plus or minus about 5 degrees to 10 degrees satisfactorily accomplishes the objectives of the invention. In some instances a greater degree of alignment may be preferred. Nevertheless, the noted range of 5-10 degrees permits use of commercially available filler particles, particularly talc, that have an aspect ratio on the order of from about 5 to 1 to about 10 to 1 with size values that would satisfy dimensional requirements for use with polyethylene, as is described herein.

The strength characteristics of the present invention appear to be achieved at least in part due to the layering that occurs in the filled plastic material. By aligning the filler particles according to the techniques described herein, it is possible to control turbulence in the polymer during extrusion thereof. For example, in a circumstance where there is substantial misalignment of the filler particles, there are relatively low pressure void areas in the shadow of the flowing filler, e.g. in the area 18v depicted in Fig. 8. Such voids tend to create vortices which allow the flowing polymer to enter the void and at least partly to fill the same. In this way the polymer from one layer can cross mix with the polymer of another layer. Accordingly, it will be appreciated that by controlling the degree of misalignment, particularly in the yaw direction, the degree of cross mixing in the polymer can be determined and controlled thereby to determine particular structural, strength, etc., characteristics of the finished plastic product made using the invention.

Quantities of Materials Used

The present invention uses the polymer material as the strength member of the filled plastic. The particulates are used to enhance strength and certain forming characteristics while minimizing the amount of polymer required. Figs. 1 and 2 depict an exemplary optimized model of the invention to achieve a substantially maximum amount of filler material in the filled plastic 10. Desirably, the filler particles are not so great in number or size that two particles would tend to be directly adjacent each other without being separated by at least one polymer chain.

According to the invention, then, a particulate is selected that yields three axes alignment while minimizing particle size and maintaining or increasing strength characteristics of the filled plastic product and also minimizing the amount of polymer and maximizing the number of particles in the product. As a corrollary, the invention relates to maximization of the filler amount with minimal effect on the product characteristics, and preferably the foregoing is accomplished without relying on internal bonding of the polymer to the particles. The invention provides for internal streamlining in the extruder die while decreasing turbulence and achieving all the other characteristics described herein.

In the past, low viscosity fluids were used with flowing polymers to control flow characteristics from the outside, one exemplary flow characteristic would be turbulence. In contrast to using materials to alter viscosity to control flow in an extruder die, the present invention controls flow characteristics from within a high viscosity fluid, namely the polymer. By evening out viscosity the characteristics of the flow also are evened out across the cross section thereof.

Example 4

According to an example of the invention, a filled plastic product was made. The polymer selected was polyethylene. The particles were talc and had a length of 5-1/2 microns. Relative quantities and size relationships were as described above. A mixture was made as is described herein and the mixture was extruded. Upon examination of the particles in the extruded product through an electron microscope, substantially all of the particles appeared to be aligned on three axes according to the invention.

Example 5

An example that did not work in accordance with the invention was the combination of polyethylene and filler particles having a size (length) on the order of 2 microns with relatively large aspect ratio and other size relationships as above. The three axes alignment did not occur in such material. Apparently the particles were too small.

The present invention provides one or more of the following advantages:

1. Vortex generation and turbulence in a fluid during flow through a die or other confined path is reduced and can be controlled.

2. Particulate filler having a preference for three axes alignment in the fluid promotes unidirectional flow of the fluid increasing strength of the finished product and facilitating flow and flow control during extruding, for example.

3. Particulate filler for the flowing polymer of the invention promotes an increase in fatigue life, distributes forces through the finished product, and does not detrimentally affect the finished plastic product; indeed, the filler reduces defects in the plastic product.

An important aspect of the invention is the use of filler to do work internally of material that is being extruded during the extruding process by achieving alignment characteristics of the polymer and of the filler itself.

Particle spacing should be such that there is at least one polymer chain between each pair of relatively adjacent particles in all directions. Moreover, if the particles are in layers, then there should be a complete layer of polymer chains with which bonding may occur with respect to other polymer chains and/or to the particles themselves and/or with respect to the polymer chains located between adjacent particles in a particular layer that contains such particles. Spacing should be such that two particles do not overlap each other without being separated by a polymer chain.

The length of the particles should be such that they span at least two polymer chain lengths while on the other hand minimizing particle size and providing a length to width ratio of at least 7:1. Spacing of particles lengthwise should be such that there is a polymer chain between each pair of relatively adjacent particles.

According to the foregoing, then, maximum loading by volume according to the invention is on the order of about 25 percent filler particles to polymer. Experimental results have demonstrated increased fatigue life of filled plastic relative to unfilled plastic when the filler particles were on the order of from about 10 percent to about 20 percent by volume of the finished product. However, it also was experienced that beyond a point of anywhere of 25 percent to 30 percent by volume of filler particles, the fatigue life tended to decrease again.

Example 6

An example of the invention includes use of a polyethylene polymer and a talc filler. The talc filler was platelet shape. The polymer chain had an effective length on the order of about 0.8 micron. The chain was generally helical in shape and if stretched out the actual length would have been longer than the effective length mentioned. The talc particles were about ten times the length of the particle chains, i.e. from about 5 to 10 microns in length. The width of the talc particles was about 2 to 3 microns. Loading was about 20 percent by weight of filler to polymer. An effective filled plastic polymer having an increased fatigue life over unfilled polymer was achieved.

Turning, now, to Figs. 14-18, photomicrographs of several samples made in accordance with the invention are shown. Comments on the respective photographs follow.

Example 7 (Fig. 14)

Referring to Figs. 14A, B and C, a mixture of polyethylene (Phillips Resin HXM50100) was mixed with a 30% by weight particulate filler material of calcium carbonate. The size of the filler particles was relatively small and not in accordance with the size constraints described above according to the invention. The calcium carbonate filler particles were spherical. The mixture of polyethylene and filler particles was extruded through an extrusion die of rectangular cross section. Figs. 14A, B and C are, respectively, photographs taken with an electron microscope of transverse, longitudinal and top section views of the cured or frozen output from such extrusion die in the form of a filled plastic material according to this example. Such Figures show a random distribution of the particles in the plastic without any apparent alignment or regular aligned orientation of the particles.

Example 8 (Fig. 15)

The same materials and steps as in the Example of Figs. 14 were employed except the size of the particles was larger but still spherical. The result was the same as can be seen in Figs. 15A, B, C, which are transverse, longitudinal and top views of the filled plastic material

The failure of alignment detection in Examples of Figs. 14 and 15 above appears to be due primarily to the non-platelet, i.e. spherical, shape of the filler particles.

Example 9 (Fig. 16)

A mixture of polyethylene (Phillips Resin HXM50100) was mixed with a 30% by weight particulate filler material of talc having an average size of about 5.5 microns in length and generally meeting the other size restrictions described above according to the invention. The mixture was extruded through a rectangular extrusion die, as above. Figs. 16A, B and C are photographs taken with an electron microscope of respective transverse, longitudinal and top section views of the solidified filled plastic material output from the extrusion die, according to this example. In Figs. 16A and B the axial alignment of the filler particles is quite evident. Moreover, looking at Fig. 16C, there is a general alignment of the particles. Based on an inspection of the photographs of Figs. 16, it is clear that there is a greater homogeneous distribution and alignment of filler particles near the center of the material and a somewhat more turbulent condition nearer the exterior or surface. This clearly demonstrates that according to the invention the alignment function tends to work from the inside toward the outside (exterior surface) of plastic material.

Example 10 (Fig. 17)

A mixture of polyethylene (Phillips Resin HXM50100) was mixed with a 10% by weight particulate filler material of talc having an average size of about 5.5 microns in length and generally meeting the other size restrictions described above according to the invention. The equipment, procedures, and results of the above Example 9 referred to regarding Fig. 16 were the same in this example. However, upon testing it was found that the fatigue life of a part made of the filled plastic material according to this example was about 7 times the fatigue life of a part made using unfilled plastic material derived following the same steps and equipment as this example but using only polyethylene (Phillips Resin HXM50100) without any filler particles.

In Figs. 17A and B, the axial alignment of the filler particles is quite evident. Moreover, looking at Fig. 17C, there is a general alignment of the particles. Based on an inspection of the photographs of Figs. 17, it is clear that there is a greater homogeneous distribution and alignment of filler particles near the center of the material and a somewhat more turbulent condition nearer the exterior or surface. This also clearly demonstrates that according to the invention the alignment function tends to work from the inside toward the outside (exterior surface) of plastic material.

Example 11 (Fig. 18)

In the example depicted by photographs of Figs. 18, a mixture of polyethylene (Phillips Resin HXM50100) and a further lubricating type polymer forming a general structure as in Fig. 10 was mixed with a 30% by weight particulate filler material of talc having an average size of about 5.5 microns in length and generally meeting the other size restrictions described above according to the invention. The materials, equipment and process were otherwise substantially the same as in Example 9 depicted by Figs. 16 above. The results showed some alignment in the transverse and longitudinal photographs, but such alignment was much less than in the examples of Figs. 16 and 17; and in the top photograph Fig. 18C the alignment also was less than was encountered in examples of Figs. 16 and 17, although there was greater apparent alignment in all three photographs of this example relative to Examples 7 and 8 depicted by Figs. 14 and 15 above.

Turning to Fig. 19, a theoretical model 100 depicting operation of the invention is illustrated. In the model 100 a mixture 66 of polymer 16 and particulate filler 18 according to the invention is flowing through an extrusion die 52. The polymer may be polyethylene having a molecular chain structure, several representative chains being designated 16. Such polymer chains are generally elongate overall and are aligned generally in parallel as they flow through the extrusion die 52. Such parallel alignment is due in part to the tendency to align in the flow direction through the die. Such alignment also is due to the interaction of the surfaces of the die and of the particulate filler 18 on the polymer chains. The size and loading of the filler particles 18 are according to the description above.

As is known in fluid dynamics, the flow profile of a fluid flowing through an orifice usually is such that the velocity near the orifice walls (boundary layer, etc.) is noticeably slower than the velocity away from the walls. Also, as is known, due to velocity differences in plastic flowing through an extrusion die defects, undulations, etc. may too easily occur in the finished plastic product. Such defects often tend to occur at or close to the surface of the product where flow through the extrusion die is much slower than at the center. Surface defects or near surface defects are often the area where cracks and other failure conditions of the finished plastic part occur.

The present invention tends to reduce the difference in the velocity of flow near the center of the die and the velocity of the flow near the die face. The effort to reduce such difference in velocity in effect provides the work effort that contributes to the aligning of the filler particles along the three axes as is described herein. This is achieved by the interaction of the filler particles 18 on the polymer chains 16, on each other, and with respect to the surfaces of the extrusion die 52 in effect to create a plurality of discrete sub-dies, orifices or venturi-like areas between which the polymer effectively flows. Such areas are designated 102 in Fig. 19. The existence of such sub-die areas 102 and their interaction with the polymer, as is described below, helps to promote further the three axes alignment of filler particles 18 deep into the plastic rather than just at the surface.

The existence of the areas 102 is possible due to the alignment of the filler particles 18 on three axes, as was described above. Such alignment at least in part is due to the characteristics of flow through the extrusion die 52. As the polymer 16 and filler particles 18 flow through the extrusion die 52, there tends to be created (due to three axes alignment of the platelets) the effect of a plurality of polymer streams being extruded through respective extrusion dies or sub-dies 102, which are defined by the incompressible platelet (flat) filler particles. Such sub-dies are at and near the surface of the extruded material as it flows through the extrusion die 52 and are deep into the material in a sense creating a deep alignment effect within the flowing material. This is believed to contribute significantly to the ability of the invention to achieve three axes alignment deep into the finished product as opposed to only surface alignment achieved in the prior art.

The invention relies on some differential velocity between the filler particles 18 and the polymer 16 to achieve the three axes alignment of the filler particles. Such velocity differential and the desired size and shape of the filler particles 18, as are described herein, promote a wind vane effect between the incompressible filler particles and the extrudible plastic to obtain the three axes alignment of the filler particles. The invention tends to even out the flow profile through the material being extruded through the extrusion die and, therefore, tends to decrease the velocity differential between respective sub-die areas 102; and the invention also tends to increase the velocity differential between the flowing plastic and the filler particles in order to achieve a wind vane effect to provide three axes alignment of the particles deep into the extruded plastic material. Various advantages and improvements to the finished plastic product are believed to inure to the invention, such as reduced failures, cracking, etc., increased fatigue life, uniformity of material, and so on.

It is known that in plastics the strength of the material often is manifest primarily in the surface strength or characteristics of the plastic. The invention improves fatigue life by reducing surface faults, as was described just above and elsewhere herein. Moreover, the invention promotes forming the plastic product in a layered type of structure in which respective layers of polymer chains are separated in part by a layer of filler particles, while still providing for some cross-linking or other bonding between layers, as is illustrated in the several drawings. By providing such layered structure, in the event a defect occurs in one layer, the probability of that defect permeating to another layer is reduced; and, therefore, the overall strength, particularly fatigue life, of the plastic is improved over prior extruded plastic materials.

Another advantage to the layered structure of the invention is the ability of the layers of polymer in the finished plastic product to slide over each other to some extent, preferably without breaking the cross-linking between layers. Therefore, as the plastic is flexed, such sliding is possible so that cracking will not occur in response to such flexing. Moreover, since the strength of the finished plastic product is due to the layered structure, aligned polymer chains and inter-layer and intra-layer cross-linking between and among polymer chains, the fact that the polymer may not bond to the filler particles is substantially immaterial to the strength, fatigue life and the like characteristics of the plastic material. Rather, the contribution of the filler particles is to the achieving of layered structure and permissible polymer cross-linking in the plastic product, especially in an extruded product.

Further, by selecting the filler particles to be of a size and loading relative to the polymer, as is described in greater detail above, the number of disruptions of normal polymer interconnections, cross-linking, and the like is minimized. Also, the possibility that a filler particle might cut through a polymer chain or through a layer in the solidified plastic part is reduced, as was mentioned above. These further help to provide added overall strength and fatigue life characteristics to the finished plastic product.

Talc is a particularly good filler according to the invention. Another good filler would be milled Teflon or similar material. Mica may be used, but a disadvantage to mica is the rigidity of the mica and the sharp edges of mica, both of which may contribute to the mica cutting polymer chains when the plastic is flexed; and, therefore, mica is a less desirable filler than talc or Teflon type filler.

INDUSTRIAL APPLICATION

It will be appreciated that the present invention provides for the filling of plastic material to reduce the amount of polymer required in the finished plastic product and preferably while also improving strength and/or fatigue life characteristics of the product.

CLAIMS

1. A method of making a product comprising:

a. mixing polymer and non-fluid particulates,

b. said particulates having a size characteristic to tend to cause three axes alignment thereof when mixed with and flowing with such polymer, and

c. with such polymer in fluid form directing such fluid with said particulates along a flow path during which flow such axial alignment occurs.

2. The method of claim 1, wherein such particulates have a size relation to the polymer such that the width of the particulates is at least three working diameters of the chains forming the polymer.

3. The method of claim 1, wherein such particulates have a size relation to the polymer such that the length of the particulates is at least twice the working diameter of the chains forming the polymer.

4. The method of claim 1, wherein such particulates function during extruding of the polymer and particulates through a die such that the particulates nearer the center of the die apply alignment forces to particulates nearer the die walls.

5. A method for producing improved streamlining in a flowing fluid, comprising

mixing with the fluid non-fluid particulates having size characteristics that would promote alignment along three axes to form a mixture, and

directing the mixture along a generally non-turbulent flow path.

6. The method of claim 5, said directing comprising extruding the mixture through an extruder die.

7. The method of claim 5, said particulates effecting longitudinal alignment of chains forming the polymer.

8. A product comprising

a. a polymer

b. a particulates filler in said polymer,

c. said polymer comprising plural polymer chains that are unidirectional with minimal stress riser causing defects, and

d. said particulates being aligned in three axes.

9. The product of claim 8, said polymer comprising polyethylene.

10. The product of claim 9, said particulates comprising talc.

11. The product of claim 9, said particulates being platelet shape.

12. The product of claim 8, said particulates comprising talc.

13. The product of claim 8, said particulates being platelet shape.

14. A composition of matter, comprising

a. a polymer, and

b. a filler for said polymer, said filler being selected to maximize distribution of stress from layer to layer in the polymer and to minimize the amount of polymer displaced by the filler.

15. The composition of claim 14, said polymer comprising polyethylene.

16. The product of claim 15, said particulates comprising talc.

17. The product of claim 15, said particulates being platelet shape.

18. The product of claim 14, said particulates comprising talc.

19. The product of claim 14, said particulates being platelet shape.

20. A method for improving fatigue life of a product formed of a polymer, comprising

a. mixing with such polymer a non-fluidic particulate capable of generally three axis alignment when flowing with a fluid state of such polymer, and

b. causing the flowing of such fluidic polymer and particulates to effect such three axis alignment while forming such product.

21. The method of claim 20, such polymer comprising polyethylene.

22. The method of claim 20, such particulate comprising platelet shape particles.

23. The method of claim 20, such particulate comprising talc.

24. The method of claim 20, said causing comprising extruding a mixture of such polymer and particulate.

25. The method of claim 24, wherein such particulates near the center of an extruder die effecting the extruding flow faster than the particulates near the walls of the die and cooperate with such particulates near the walls of the die to provide three axes alignment thereof.

26. A method for reducing defects in a plastic material, comprising

a. mixing with such polymer a non-fluidic particulate capable of generally three axis alignment when flowing with a fluid state of such polymer, and

b. causing the flowing of such fluidic polymer and particulates to effect such three axis alignment while forming such product.

27. A method for determining the size of non-fluid particulates for addition to a fluid polymer to achieve three axis alignment of such particulates, comprising:

a. mixing together plural particulates of plural respective size characteristics,

b. mixing such mixed particulates with a fluid polymer,

c. passing such mixture of particulates and polymer along a flow path,

d. freezing the mixture after such flowing,

e. inspecting the frozen product to determine the smallest size particulate that aligns.

28. The method of claim 27, said passing comprising extruding, and such inspecting including cutting and inspecting along three orthogonal axes.

29. A method of producing a deep sub-venturi-like effect in an extruded material, comprising mixing a particulate filler with the material intended to be extruded, selecting the filler particles to be of a size relative

to the extruded material and a loading relative to the extruded material such that the filler particles cooperate with each other and with the extruded material to form plural sub-venturi-like areas in an extrusion die during the extruding of the mixture.

30. The method of claim 29, further comprising extruding the mixture through an extrusion die.

31. The method of claim 30, further comprising selecting the extruded material as chain polymer type material, and selecting the filler particles to be of a size relative to the polymer to undergo generally parallel alignment along three axes during the extruding.

32. The method of claim 31, further comprising selecting the filler particles to be of a size such that the length thereof is at least as long as the effective length of two polymer chains, the width thereof is at least as wide as the effective diameter of at least three polymer chains, and the thickness thereof is on the order of about the effective diameter of one polymer chain.

33. A method of controlling the relative velocity of an extruded material through an extrusion die to average out venturi effects, comprising producing a sub-die in the extruded material as it flows through an extrusion die, said producing comprising mixing a particulate filler with the material intended to be extruded, selecting the filler particles to be of a size relative to the extruded material and a loading relative to the extruded material such that the filler particles cooperate with each other and with the extruded material to form plural sub-die areas in the extrusion die during the extruding of the mixture to interact with the extruded material to determine the respective velocity differentials between the extruded material and respective filler particles as the same pass through the extrusion die.

34. The method of claim 33, further comprising selecting the extruded material as chain polymer type material, and selecting the filler particles to be of a size relative to the polymer to undergo generally parallel alignment along three axes during the extruding.

35. The method of claim 34, further comprising selecting the filler particles to be of a size such that the length thereof is at least as long as the effective length of two polymer chains, the width thereof is at least as wide as the effective diameter of at least three polymer chains, and the thickness thereof is on the order of about the effective diameter of one polymer chain.

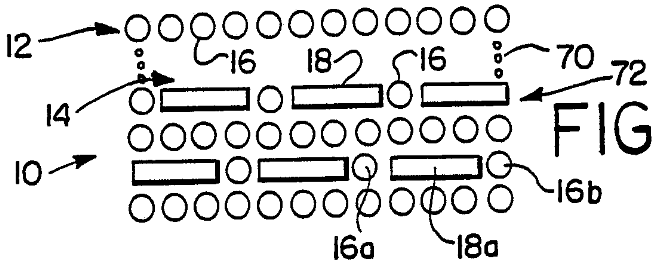


FIG.1

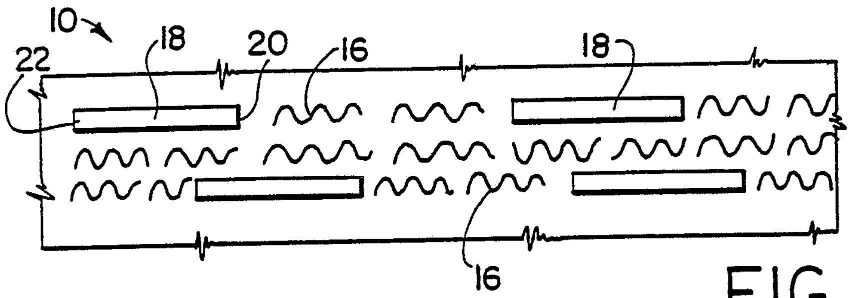


FIG.2

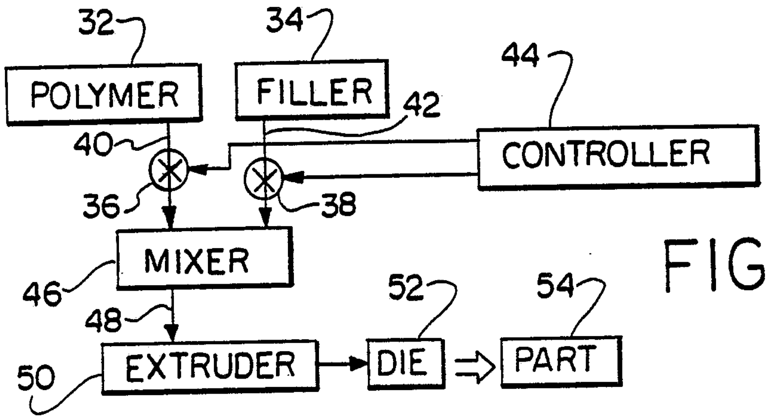


FIG.3

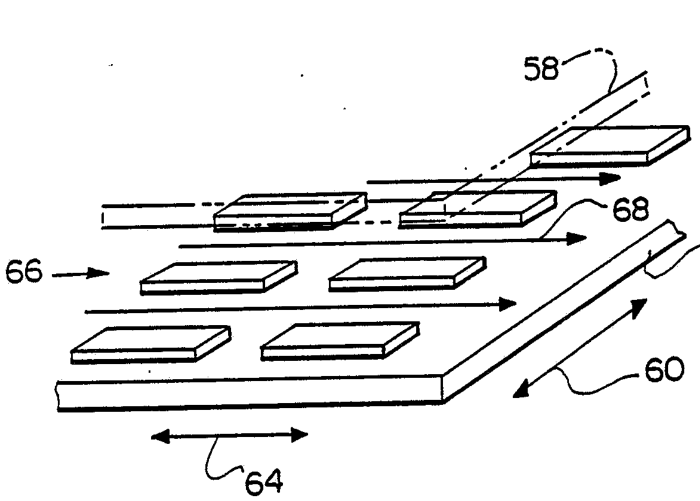


FIG.4

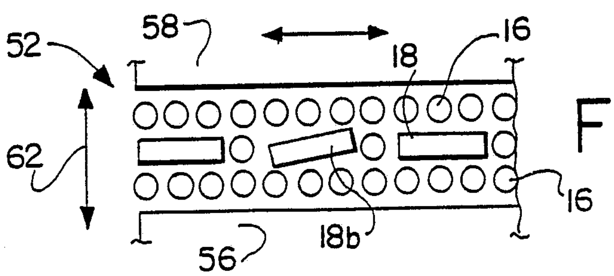


FIG.5

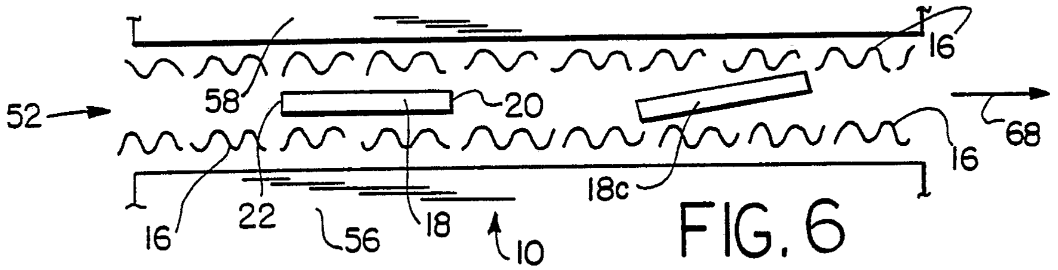


FIG. 6

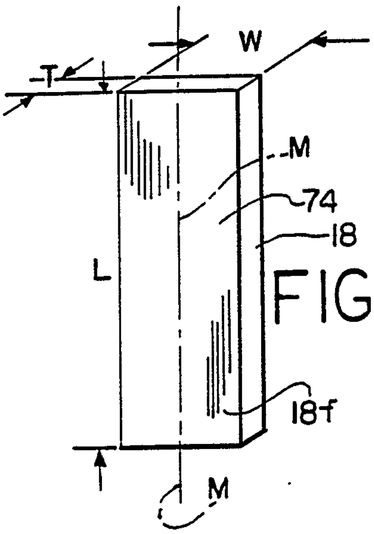


FIG. 7

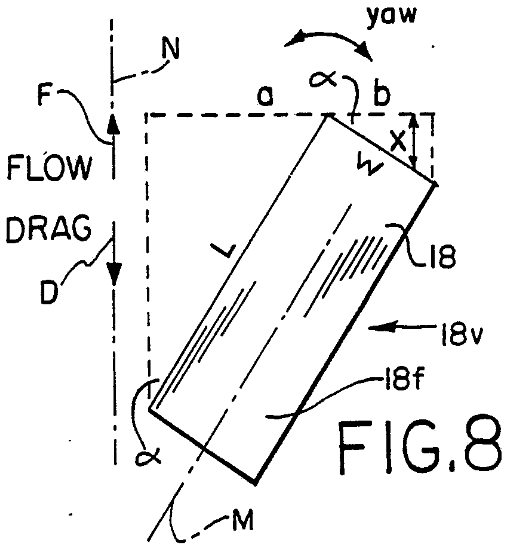


FIG. 8

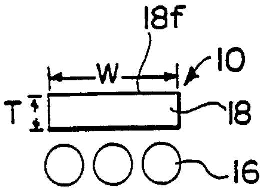


FIG. 9

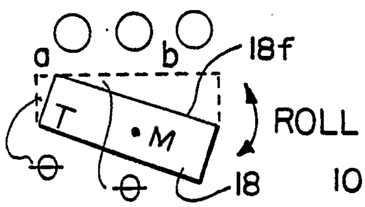


FIG. 9A

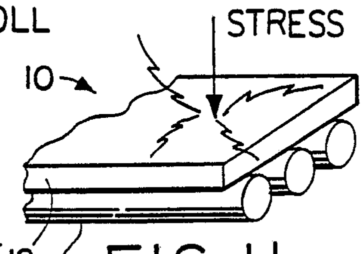


FIG. 11

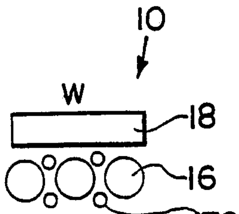


FIG. 10

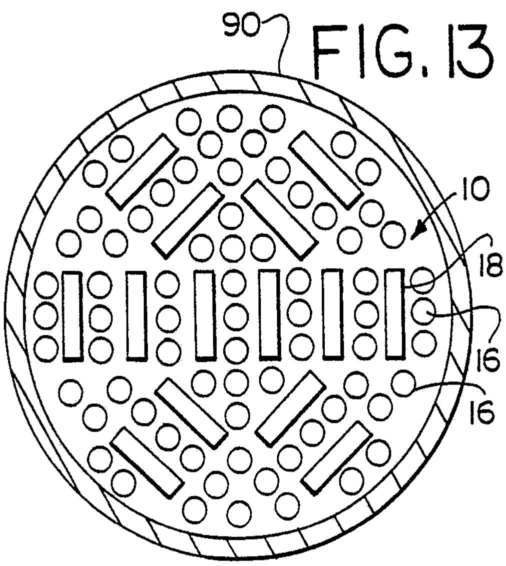


FIG. 13

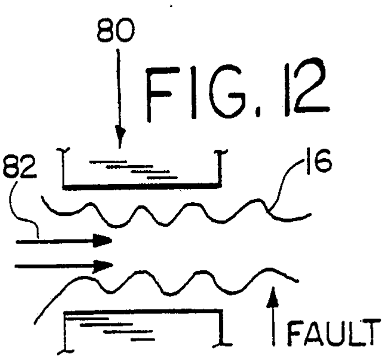


FIG. 12

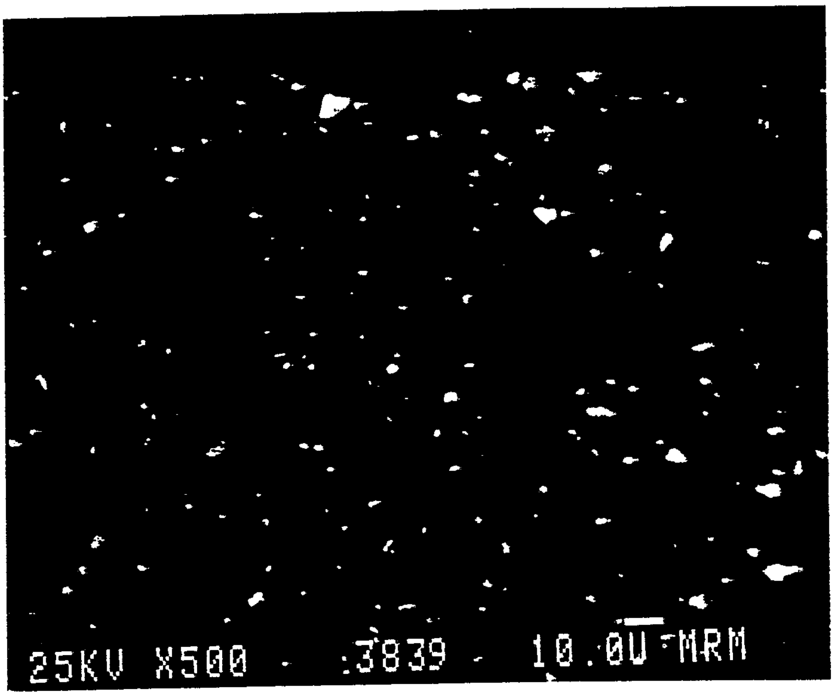


FIG. 14A

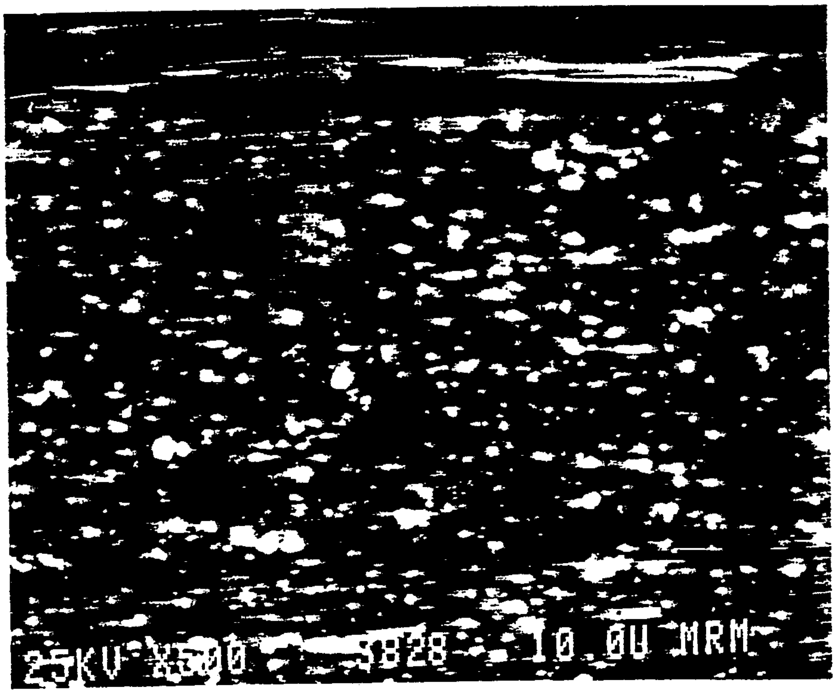


FIG. 14B

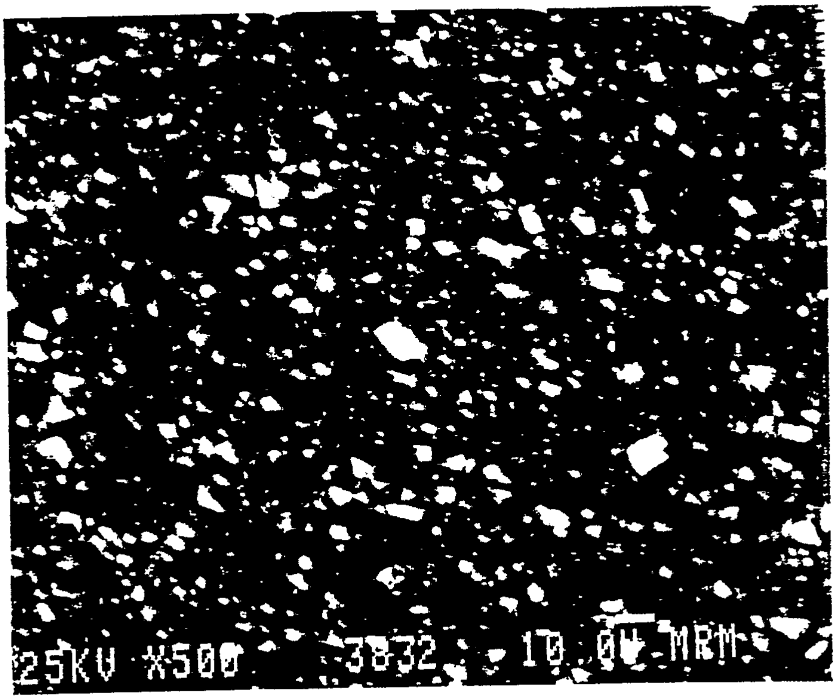


FIG. 14C

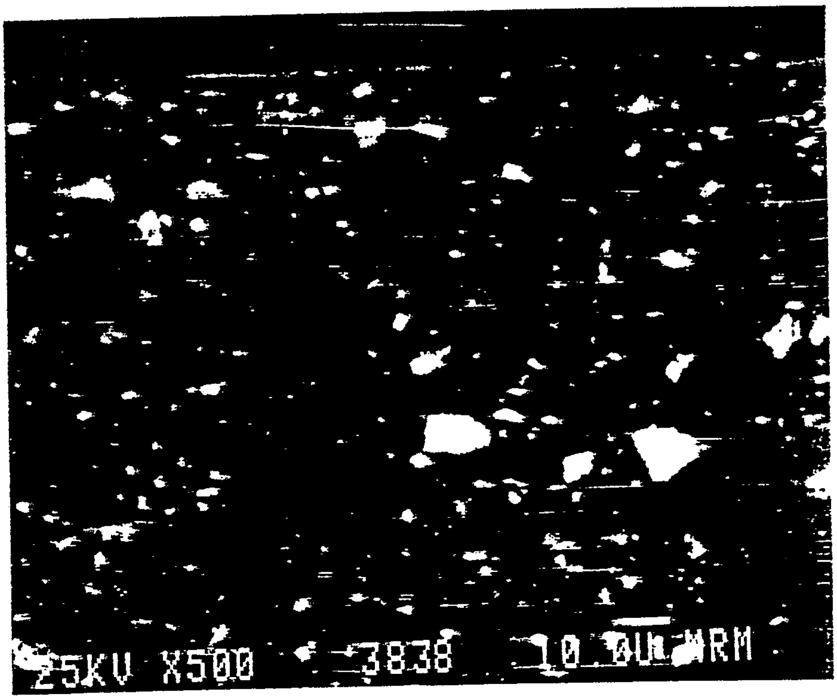


FIG. 15A

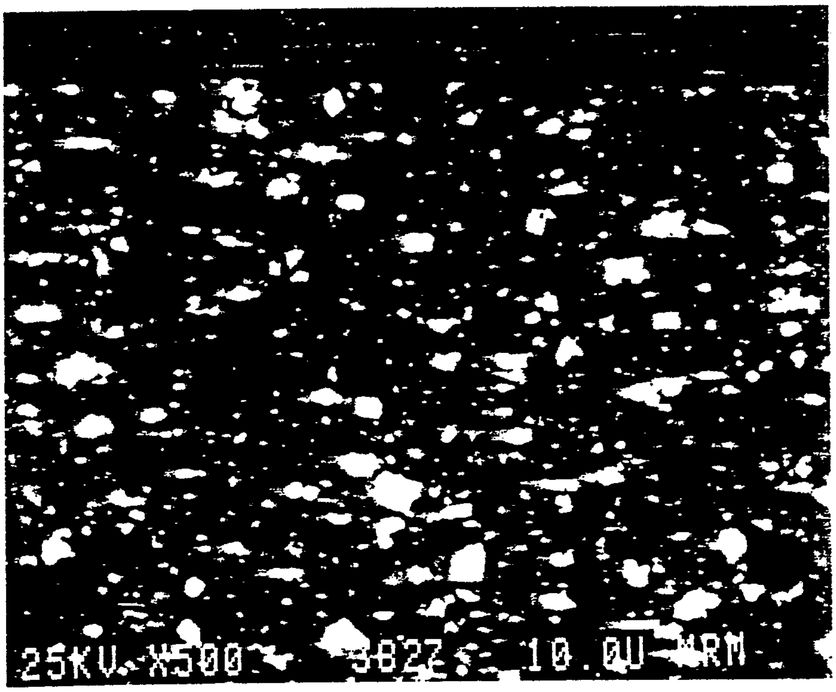


FIG. 15B

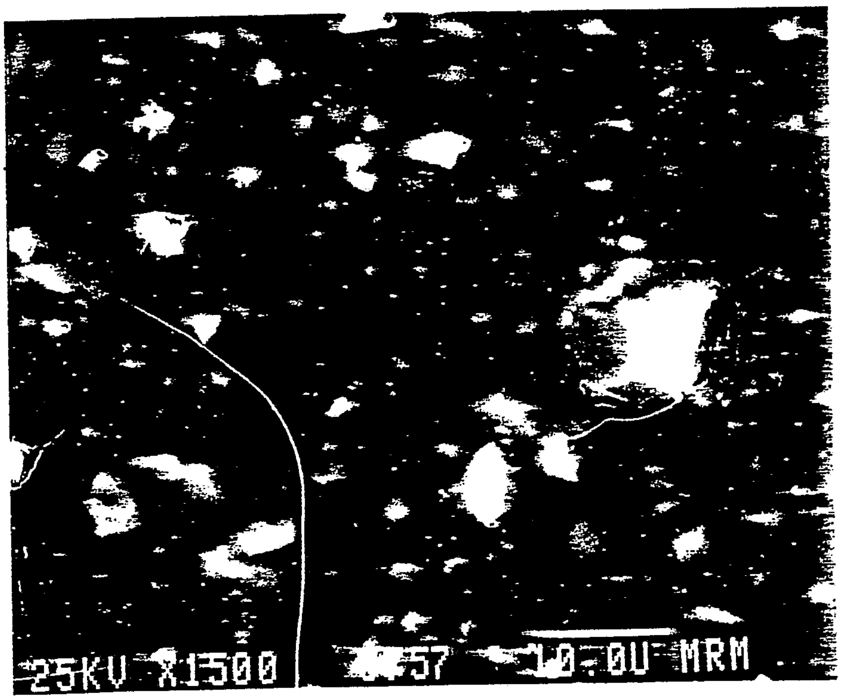


FIG. 15C

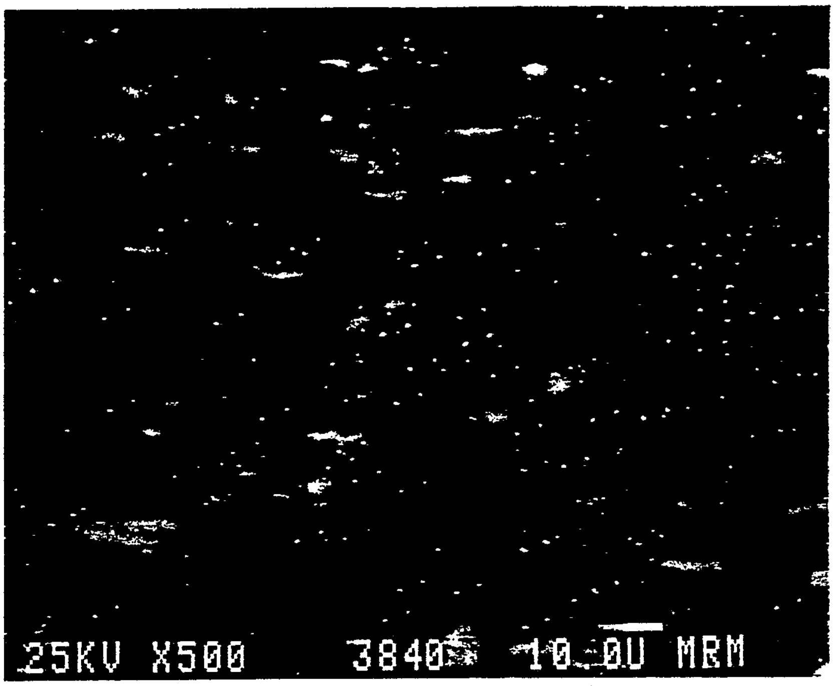


FIG. 16A

FIG. 16B

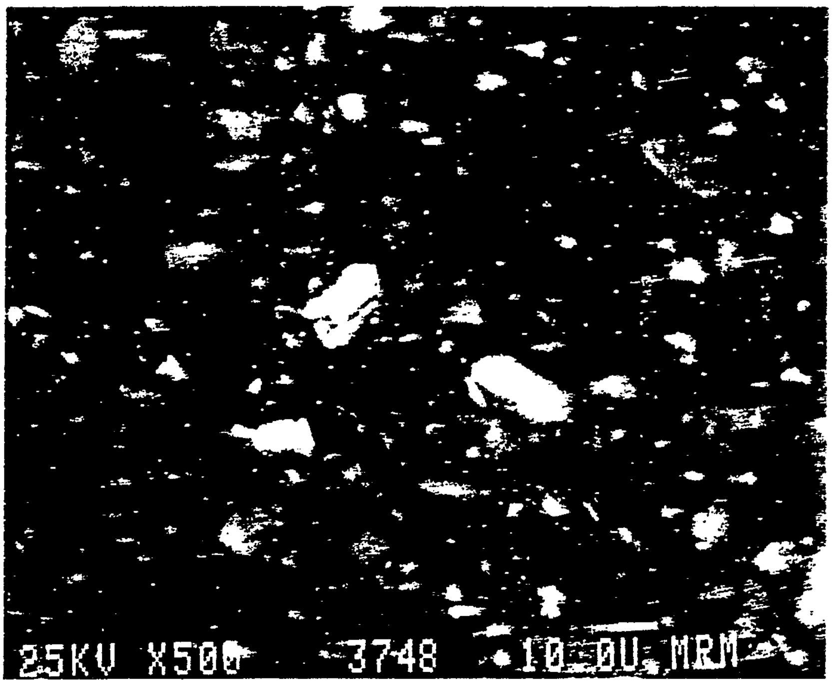


FIG. 16C

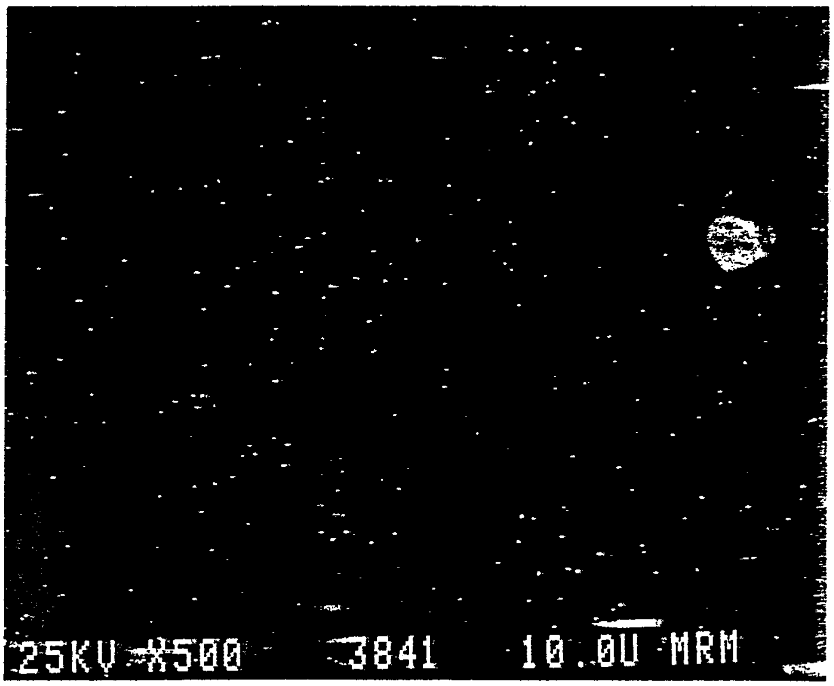


FIG. 17A

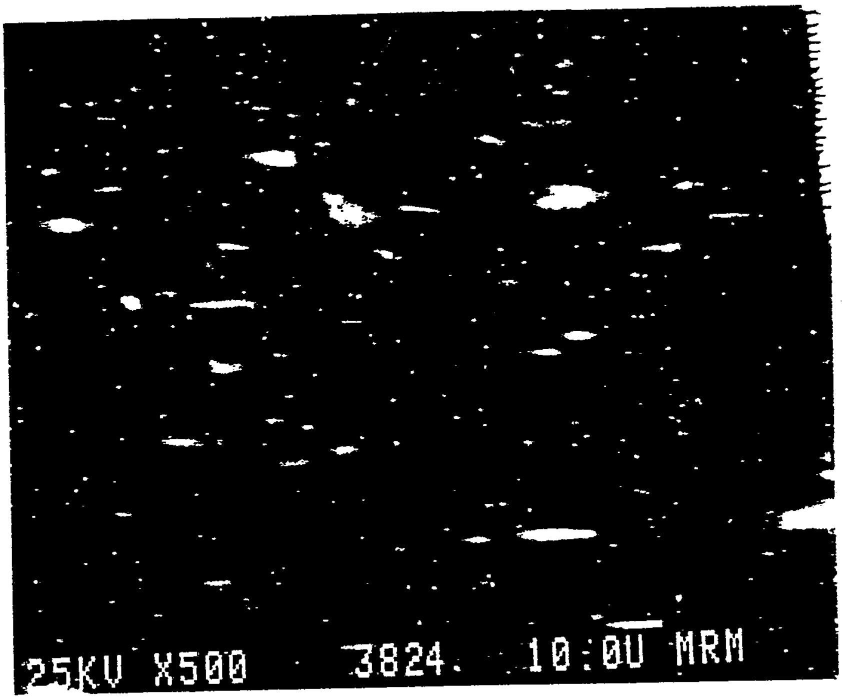


FIG. 17B

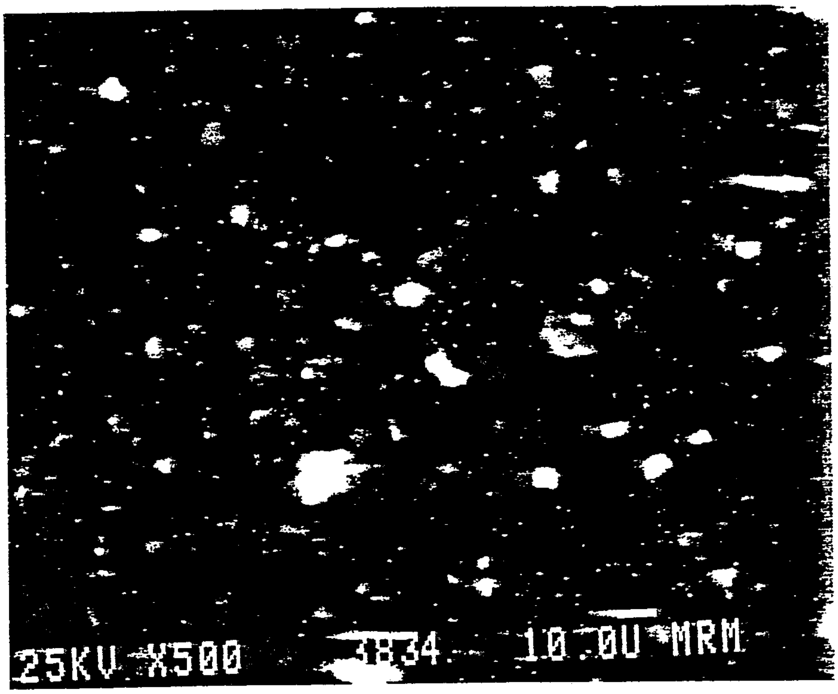


FIG. 17C

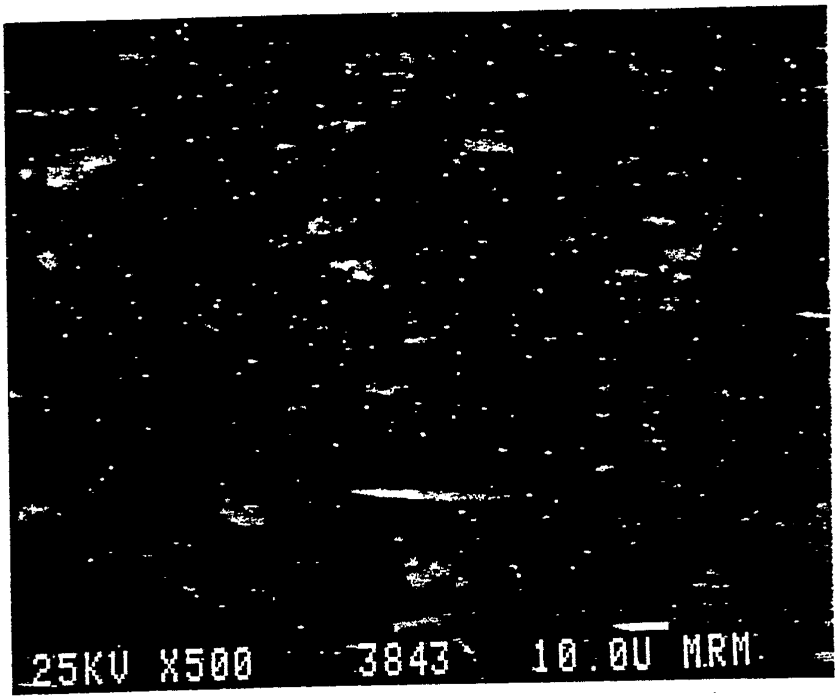


FIG. 18A

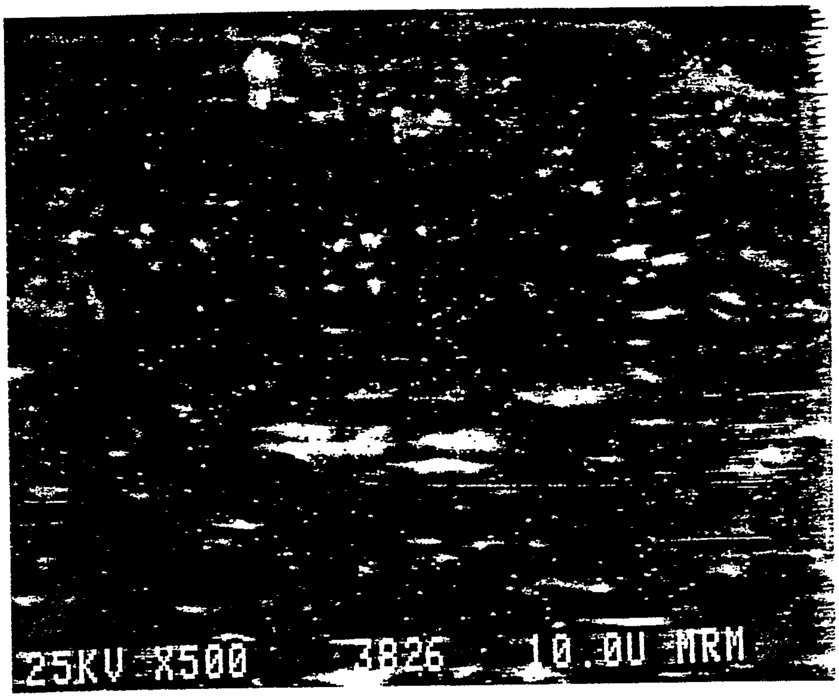


FIG. 18B

SUBSTITUTE SHEET

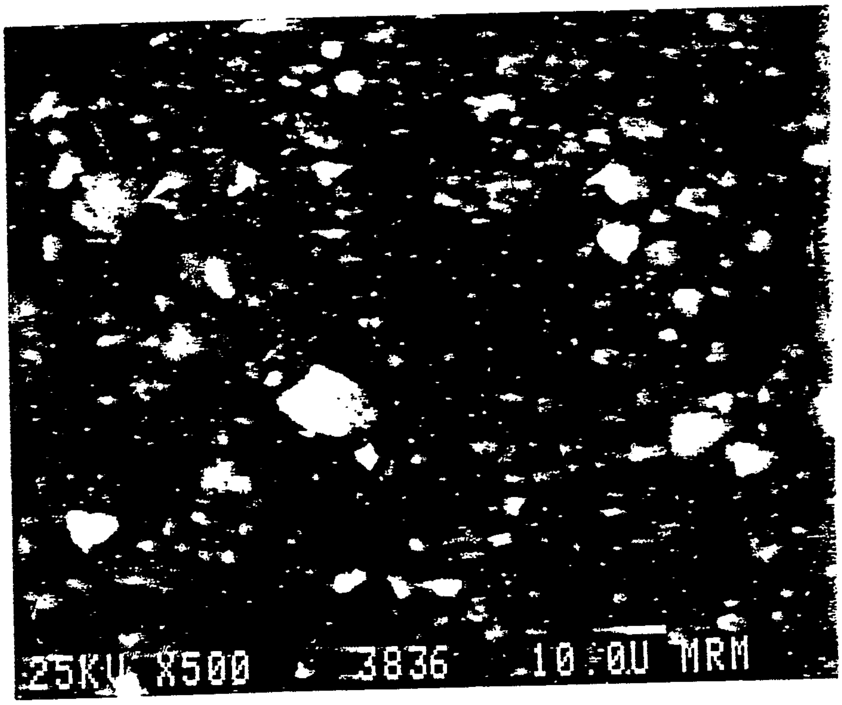


FIG. 18C

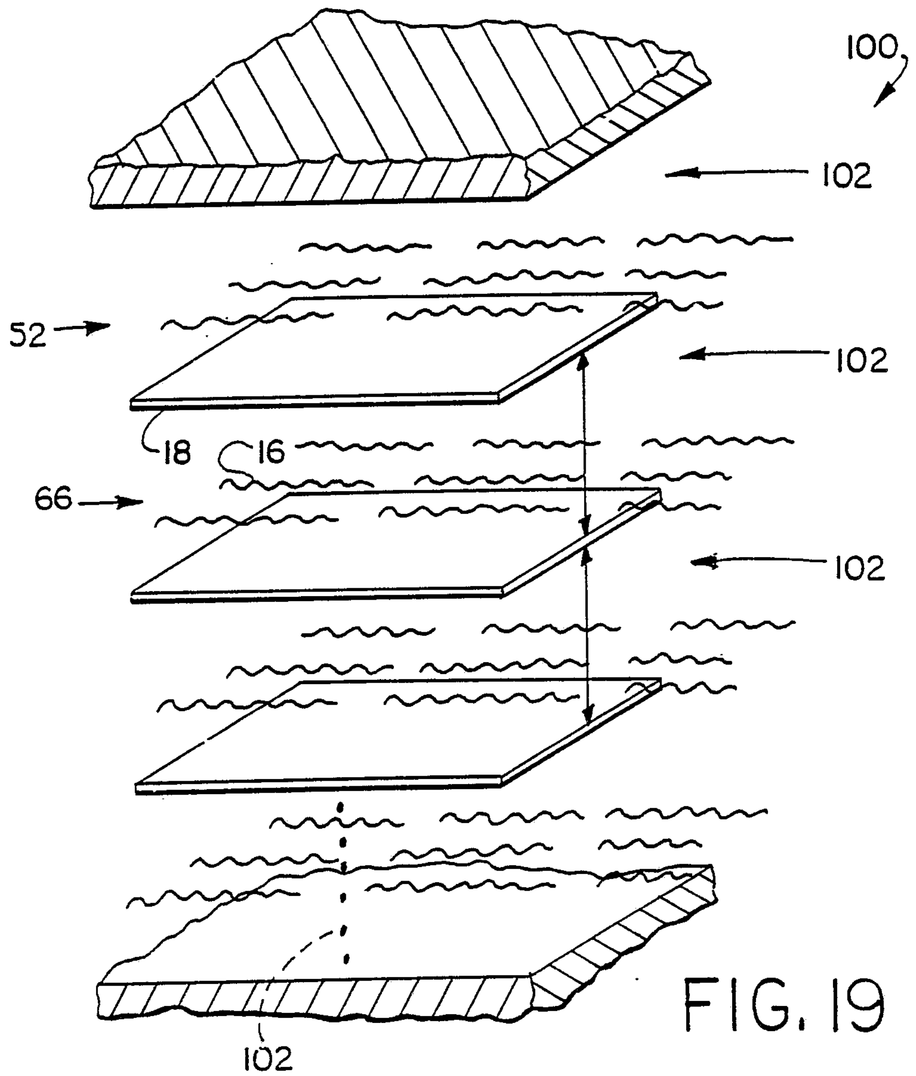


FIG. 19

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/03680

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): B29B 15/08; C08K 3/36; C08K 7/00

U.S.CL.: 264/40.1, 108; 524/451

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	264/40.1, 108, 176.1 524/449, 451, 586

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 2,704,105 (ROBINSON) 15 MARCH 1955 SEE COLUMN 1 LINES 70-81, COLUMN 2 LINES 1-9, AND THE FIGURE.	8-19
X	GB, A, 2,115,739 (KOSTECKI) 14 SEPTEMBER 1983, SEE PAGE 2 LINES 3-23.	1-3, 5, 7, 20-23, 26
X	US, A, 3,060,552 (SCHEYER) 30 OCTOBER 1962, SEE COLUMN 1 LINES 54-72, COLUMN 2, LINES 1-25 AND 34-47, COLUMN 4, LINES 45-49 AND COLUMN 5 LINES 5-7.	1-7, 20-26, 29-35
Y,P	US, A, 4,728,478 (SACKS) 01 MARCH 1988 SEE COLUMN 1 LINES 42-46 AND 61-65 AND COLUMN 2 LINES 20-59	1-26, 29-35

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
06 February 1989	21 MAR 1989
International Searching Authority	Signature of Authorized Officer
ISA/US	Jill Heitbrink Jill Heitbrink

Form PCT/ISA/210 (second sheet) (Rev.11-87)

International Application No. PCT/US88/03680

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers , because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

3.☐ Claim numbers__________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-26 and 29-35 drawn to a product classified in Class 524 Subclass 451 and to a process of forming the product classified in Class 264 Subclass 108.

II. Claims 27 and 28 drawn to a process of determining the size of particles which align classified in Class 264 Subclass 40.1.

1.☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone Practice

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.

<u>Attachment to Form PCT/ISA/210, Part IV. 1.</u>

Telephone approval:

$140 payment approved by Mr. Warren A. Sklar on 09 January 1989 for Group II; charge to Deposit Account No. 13-1070. Counsel advised that any protest must be filed no later than 15 days from the date of mailing of the search report (Form 210).

Reason for holding lack of unity of invention:

The invention as defined in Group I (claims 1-26 and 29-35) is drawn to a product which is classified in Class 524, Subclass 451 and to a process of forming a product which is classified in Class 264, Subclass 108. The product in Group I is independently distinct from the method defined in Group II (claims 27 and 28) which is classified in Class 264, Subclass 40.1 because the method of Group II does not produce the product of Group I. The process of Group I and the process of Group II lack unity under PCT Rule 13 since the combination (Group II) does not require the particulars of the subcombination (Group I process) for patentability because the method of forming the product requires the particulates having a size characteristic when they are aligned. Additionally, the subcombination has separate utility such as the method of determining the size requires different sizes of particulates.

Time limit for filing a protest:

Applicant is hereby given <u>15 days</u> from the mailing date of this Search Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 40.2 applicant may protest the holding of lack of unity <u>only</u> with respect to the