Feb. 25, 1947. I. V. HITT 2,416,390

FREE FALL FIBER

Filed Feb. 25, 1943 2 Sheets-Sheet 1

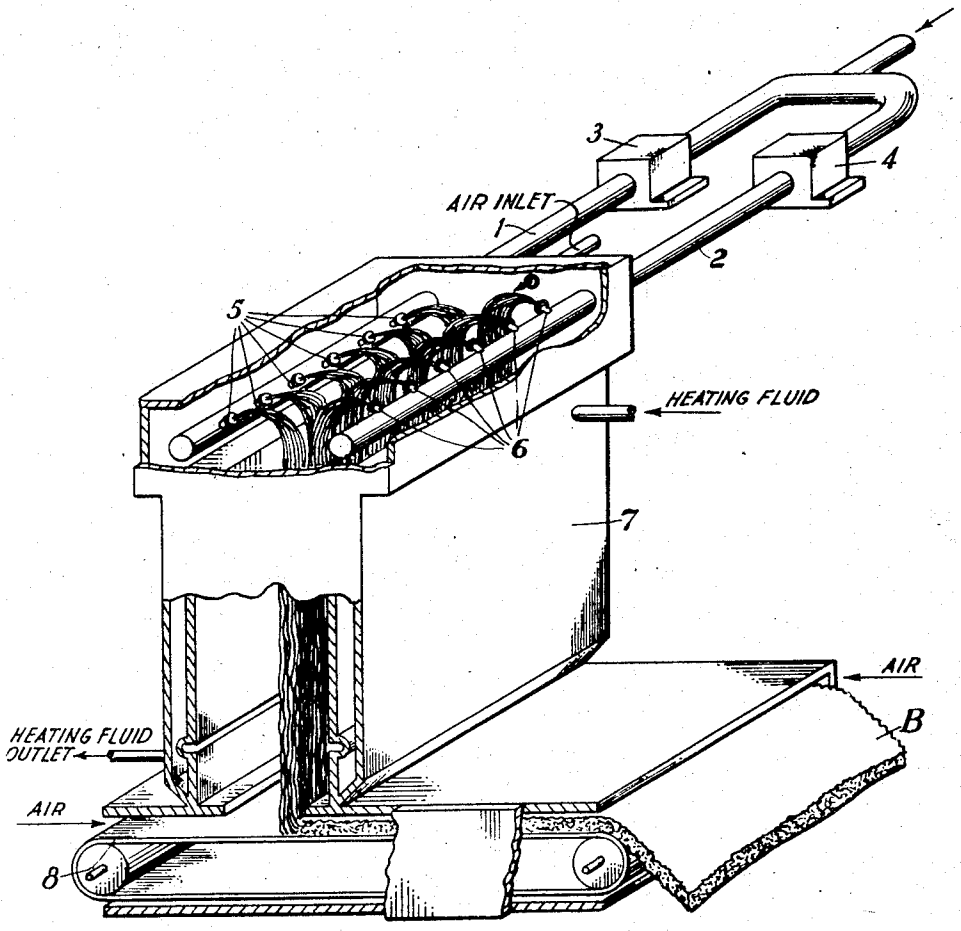


Fig. 1

Ira V. Hitt INVENTOR.

BY A. Ralph Snyder
ATTORNEY

Feb. 25, 1947. I. V. HITT 2,416,390

FREE FALL FIBER

Filed Feb. 25, 1943 2 Sheets-Sheet 2

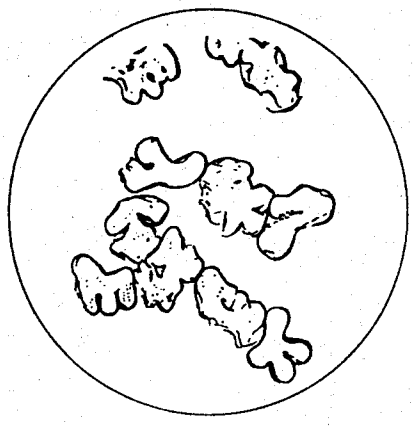


Fig. 2

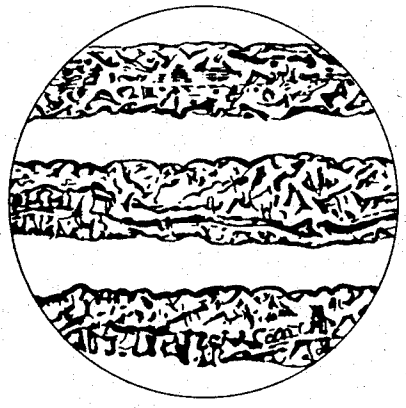


Fig. 3

Ira V. Hitt INVENTOR.

BY C. Ralph Snyder
ATTORNEY

Patented Feb. 25, 1947 2,416,390

UNITED STATES PATENT OFFICE

2,416,390

FREE FALL FIBER

Ira V. Hitt, Waynesboro, Va., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application February 25, 1943, Serial No. 477,012

1 Claim. (Cl. 28—78)

1

This invention relates to the manufacture of new organic solvent-soluble thermoplastic filaments and fibers. More particularly, the invention relates to new organic solvent-soluble cellulose organic acid ester filamentous masses, and to novel processes of dry or evaporative spinning to produce these filamentous masses.

Thermoplastic filaments and fibers which are soluble in organic solvents, e. g., filaments and fibers of cellulose acetate, are most generally produced from solution by the dry or evaporate spinning process. In all modifications of the dry or evaporative spinning process heretofore known or practiced, the fine streams of spinning solution immediately on leaving the spinneret orifices and before any substantial solidification has taken place are subjected to a certain amount of tension imposed either by a positive drawing of the filaments from the spinneret or by the filaments falling under their own weight, which tension causes substantial elongation of the fine streams of spinning solution before and during transformation into self-sustaining filaments. The imposed tension and the internal strain set up in the filamentous structures at the time of their birth bring about substantial orientation of the molecules along the filament or fiber axis. The formed filaments are, therefore, inherently straight, and when drawn away and wound up into substantially parallel arrangement and twisted together to form a yarn, they are in a desirable form for use in the manufacture of fabrics and other textile goods where a reasonable amount of strength and elongation, uniformity and good running properties are needed.

However, when it is desired to produce crinkle or crimp in the filaments or fibers so as to produce more wool-like products which may be used to better advantage in subsequent processing alone or mixed with wool fibers, it has always been necessary to subject the substantially straight filaments or fibers to any of several after-treatments to produce the desired crinkle. For instance, the crinkle may be imposed mechanically by means of intermeshing gear-like elements, by means of a "stuffer box" type crinkler, or by twisting the yarns, setting the twist and then untwisting.

It has now been found possible to produce continuous, highly crinkled, thermoplastic filaments

2

in the form of a coherent filamentous mass of substantial width and thickness and in which there is no preferential orientation of the molecule in the direction of the filament or fiber axis.

It is, therefore, an object of this invention to provide novel filaments and fibers of organic solvent-soluble thermoplastics which are highly crinkled and which show no preferential orientation of the molecules along the fiber axis.

Another object of this invention is to provide a new process of spinning from solution in organic solvents thermoplastics so as to produce highly crinkled continuous filaments which exhibit no preferential molecular orientation along the filament axis, and collecting the same in the form of a coherent mass having substantial width and thickness.

A further object of this invention is to provide new composite structures comprised of highly crinkled filaments or fibers of an organic solvent-soluble thermoplastic, which filaments or fibers show no preferential orientation of the molecules.

A specific object of this invention is to provide a new process of spinning acetone-soluble cellulose acetate so as to produce highly crinkled continuous filaments which exhibit no preferential molecular orientation in the direction of the filament axis and which are collected as a coherent mass having substantial width and thickness.

Other objects will be apparent from the description that follows.

The novel filamentous products of this invention are produced by the dry or evaporative spinning process wherein a solution comprising essentially a thermoplastic filament-forming material dissolved in a volatile organic solvent or solvent mixture is extruded in the form of fine streams into an evaporative atmosphere under such conditions that the extruded material is subjected only to compressive force until it sets in the form of self-sustaining filaments, i. e., the spinning solution is extruded under (1) sufficient pressure or at a sufficiently high jet velocity that the filaments formed are pushed away from the extrusion zone by subsequently extruded material issuing from the jets, and (2) in the absence of any tension on the freshly formed filaments until they are substantially set.

The filaments so produced are characterized by a combination of properties unique in the art

of artificial thermoplastic organic solvent-soluble filaments. They are strongly but irregularly crinkled, the crimps extending in three dimensions as distinct from most mechanically imposed crimps produced heretofore which lie in but one plane. When viewed under high magnification, the filaments exhibit rough, unsymmetrical surfaces characterized by deeply cut, irregular, disconnected pits or channels not found in any other synthetic filament bodies (see Figures 2 and 3). These cuts or channels may extend halfway or more through the cross-section of the filament, and when two or more of these channels occur in a given section along the length of the filament, as is often the case, there results a sharp change in the diameter of the filament at these points. For example, the diameter of a typical 12 denier filament of this invention will vary abruptly from a minimum of about 30 microns to a maximum of about 55 microns at frequent intervals along the length of the filament, and the surface will have a plurality of pits or channels about half of which will be about 5 microns deep and the remainder 15 microns deep. Cuts as deep as 25 to 30 microns have been observed. This unique surface structure is accomplished by a very distinct, though irregular crinkle. At intervals along the length of the filament, web-like formations are found which appear to be composed of one or more loops in the fiber. These physical characteristics have marked effects on the properties of individual filaments as well as on the properties of bundles or masses of filaments. Thus, surface irregularities give rise to nearly complete loss of luster or sparkle. The effect of crinkle on bundles of filaments is to give a surprisingly stable mass that maintains its shape under any reasonable stress. At the same time, such a mass is soft and yielding and has considerable resilience. Tensile strength, as usually measured on a per denier basis, is apparently much lower than usual for cellulose acetate filaments; e. g., where a highly lustrous cellulose acetate filament of relatively uniform cross-section produced by the conventional dry-spinning method has a tensile strength of about 1.4 grams per denier and an elongation of about 25%, a filament from the same spinneret operated in accordance with the principles of my invention (hence, a filament of the same average denier) will have a strength of only 0.7 gram per denier and an elongation of 20%. This is explained by the fact that in measuring the strength of filaments the breaking load registers the strength at the weakest point, i. e. the smallest section of the filament, whereas the denier determination on which the strength per unit size is reported is based on the total weight of the filament tested. The lower strength of my novel filament, then, is due to the diameter reductions caused by the deep channels, and the low apparent tenacity and low apparent elongation are in effect a measure of the characteristic unevenness in cross-sectional area of the filaments. The filaments of this invention are further distinguished by their X-ray diffraction pattern which shows a complete random distribution of the molecules with no preferential molecular orientation along the filament or fiber axis.

The invention may be applied to the spinning of any organic solvent-soluble, thermoplastic, filament-forming substance by the dry spinning technique, so long as the filaments are subjected only to compressive force until they become set to a self-sustaining state.

The jet velocity of the liquid streams being extruded must be sufficient to project them a substantial distance before their momentum is entirely lost. High jet velocity is most conveniently achieved by the use of relatively small spinneret orifices and by feeding the filament-forming solution to the spinneret at a high rate of speed.

Jet velocities sufficiently high to project the liquid streams at least 4 inches from the face of the spinneret are preferred. If the filamentous streams are projected against a counter-flowing fluid stream such as air, the jet velocity need not be so great nor the distance of travel before the filaments reach a self-sustaining state. This minimum distance may be further varied by the rate of formation of the self-sustaining filaments and will be affected not only by the viscosity and concentration of the solution but also by the rate of solvent evaporation and by the size of the filaments being spun. In general, this distance will be found to lie between 2 inches and 10 inches. Spinnerets having orifices of the order of 0.04 mm. diameter in combination with a rate of metering or solution delivery to give the stream a velocity of about 25,000 to 30,000 inches per minute as it leaves the orifice are preferred. However, larger orifices, for instance 0.05 mm. diameter, may be used and jet velocities may be varied from 20,000 inches per minute to 50,000 inches per minute.

In the preferred practice of this invention, absence of tension in the filaments before they become self-sustaining is secured by projecting the liquid stream of filament-forming solution in a direction which may range anywhere between the horizontal and 90° above the horizontal, but which is preferably at an angle of from 10° to 60° above the horizontal, and allowing the formed filaments to drop freely to a suitable collector.

While I do not limit myself to any particular theory of invention, it is my belief that during the very brief interval of time the projected streams of filament-forming material are free of tension, the self-sustaining filaments or fibers are born due to the elimination of the bulk of the solvent and during this period of travel under the impetus of the initial momentum, the fine streams of liquid, the semi-fluid filaments and finally the self-sustaining filaments are subjected only to a compression force which, if it tends to orient the molecules of the cellulose derivative at all, tends to orient them in directions other than along the fiber axis. Each infinitesimal section of the embryonic filament is pushed along by subsequent infinitesimal sections and as the momentum of an earlier formed section diminishes it is "bumped" from behind by the next succeeding section which naturally still has a higher momentum. Eventually, the velocity supplied to any one infinitesimal section drops to zero, since there is no force that tends to draw the section on at this stage, and this holds back the travel of the subsequent sections in the original direction of movement. At this point, then, there is a "piling up" of filament sections which causes severe undulation, crimp, or sharp folds to take place and when this point is suitably selected the filaments will thereafter be sufficiently set to be self-sustaining and can then be collected by any suitable means as a coherent mass having substantial width, thickness and length.

The filaments and fibers of this invention may be produced by any suitable evaporative spinning method for forming thermoplastic filaments from solutions in organic solvents. Thus the filaments

may be spun from a single spinneret and formed into a yarn, or a number of spinnerets may be grouped together to produce a coherent mass or batting of substantial thickness which has special utility as will be explained hereinafter.

Figure 1 of the accompanying drawing illustrates diagrammatically one mode of operation according to the principles of this invention, which mode of operation is preferred for its simplicity, ease of operation, and adaptability to present available equipment. Figure 2 is a copy of a highly magnified cross-sectional view of a plurality of filaments produced in accordance with this invention and shows the characteristic deep indentations. Figure 3 is a copy of a highly magnified side view of a plurality of filaments produced in accordance with this invention and shows the characteristic rough unsymmetrical surface of the filaments.

Referring to Figure 1, two horizontal parallel spinning solution pipes 1 and 2 are provided, each connected through suitable metering pumps 3 and 4 to a source of supply (not shown) of spinning solution. Each pipe has an equal number or nearly equal number of spinnerets 5 and 6 connected thereto and enclosed in the upper portion of a spinning cell 7 which is preferably jacketed in the usual fashion to permit accurate temperature control of the atmosphere within the cell and thus facilitate removal of solvent from the filaments. Pipes 1 and 2 are likewise suitably jacketed to permit heating of the spinning solution to the desired spinning temperature.

The two groups of spinnerets are arranged to face each other but are turned upwardly so as to eject the spinning solution at an angle above the horizontal. This angle formed by the line of projection of the spinning solution stream and the horizontal is preferably about 30°. The distance of the spinneret faces in one row with respect to the line of spinneret faces in the opposing row is selected so as to be very slightly more than twice the horizontal component of the travel of the spinning solution streams. Thus, the streams will have completely spent this initial momentum just before and without colliding with the opposing stream and the many self-sustaining filaments thus formed will drop together by the action of gravity as a more or less continuous batting.

A collector device, conveniently in the form of an endless belt 8, is located for practical purposes below the spinnerets at a distance of from 3 to 6 feet, although this "free fall" distance may be as much as 20 or 30 feet. By suitably regulating the rate of movement of belt 8, a coherent batting or mass B composed of highly crinkled continuous filaments and of any desired thickness, e. g. 0.5 inch to 10 inches, may be prepared which may be cut into slabs of suitable length or, if desired, processed in a continuous manner, for instance, by wetting, impregnating, finishing or otherwise treating with a fluid before cutting or winding up on a suitable core.

Removal of the solvent is effected in the usual way, i. e., by providing a constant flow of an evaporative atmosphere about the filaments. In the preferred arrangement air is introduced at the head of the spinning cell adjacent the spinnerets and at the bottom of the cell, and the solvent-laden air is removed at a point intermediate the top and bottom of the cell. To facilitate removal of residual solvent it is desirable to have the belt 8 quite long and enclosed by a low lying enclosure 9 beyond the point at which the filaments first contact it. Air is passed through the enclosure in a direction counter to the travel of the filaments. Any suitable alteration in the arrangement of air flow and heating expedients may of course be made as will be apparent to one skilled in the art.

The following specific examples further illustrate the invention. Parts are by weight unless otherwise indicated.

Example I

A cellulose acetate spinning solution is prepared by dissolving 25 parts of air-dry cellulose acetate, in which the combined acetic acid content is about 54.5% and which is of medium viscosity, in 75 parts of acetone containing 2% of water. After thoroughly mixing, deaerating and filtering, the solution is spun using the arrangement or apparatus shown in the accompanying drawing. Twelve spinnerets are used arranged in two groups of six spinnerets each, and each spinneret has 36 orifices of 0.04 mm. diameter. A metering pump is provided for each group of six spinnerets and is operated to give an average delivery through each spinneret of 30 grams of spinning solution per minute, which means that the average jet velocity for each orifice is about 30,000 inches per minute. Under these conditions, with the jets of solution directed at 30° above the horizontal, the opposing rows of spinneret faces are spaced 13 inches apart inasmuch as the horizontal component of the stream or filament travel due solely to the initial velocity imparted thereto is approximately 6 inches. The spinning solution is heated at the time of extrusion and sufficient air is brought into the vicinity of the spinnerets (as is shown in the accompanying drawing) so that the filament streams are substantially set or formed into self-sustaining filaments by the time the action of gravity begins to noticeably take effect. Five feet below the level of the spinneret orifices is located the top surface of an endless belt. Air at room temperature is brought into the spinning chamber above and along the upper surface of the endless belt on which the formed filaments are carried and is discharged, laden with solvent, through a suitable aspiration pipe. The movement of the belt is adjusted to a speed of 0.1 foot per minute and the partially dried filament mass or batting discharged therefrom is about 24 inches wide and 5 inches thick and has a density of about 0.04.

Example II

A cellulose acetate solution composed of 25% cellulose acetate (combined acetic acid content being about 54.5%), 72% acetone and 3% water is heated to 58° C. and extruded through a spinneret into the atmosphere of an open room. The rate of extrusion is 30 grams per minute through 36 orifices 0.04 mm. in diameter, or at an average jet velocity of about 30,000 inches per minute. The spinneret is directed at an angle of 30° above the horizontal, and 4 feet below the spinneret a clean surface was prepared on which the filaments that dropped were collected to form in the course of about 10 minutes a coherent mass of highly crinkled filaments. The mass formed in 10 minutes amounted to approximately 0.17 pound, occupied a volume of 152 cubic inches and had a density of 0.03.

These coherent masses or battings collected at the spinning machine are composed of highly crinkled filaments continuously extruded and therefore of extremely long lengths. While substantially endless filaments comprise the coherent

mass, they are so intimately associated with each other that separation of very long lengths is difficult. It is undoubtedly for this reason that the structure so tenaciously holds together and affords an excellent starting material for felting, compressing, or otherwise working into strong compacted forms as will be related hereinafter.

Although the invention has been described specifically with reference to the spinning of acetone-soluble cellulose acetate, it is applicable to the spinning of any thermoplastic filament-forming substance soluble in organic solvent, such as other cellulose acetates, cellulose propionate, cellulose butyrate, cellulose aceto propionate, cellulose aceto butyrate, or the like; organic solvent-soluble cellulose ethers such as methyl cellulose, ethyl cellulose, benzyl cellulose, or the like; mixed cellulose ether-esters such as methyl cellulose acetate, ethyl cellulose propionate, etc.; vinyl polymers such as vinyl esters, for example vinyl acetate, vinyl ethers such as vinyl acetals; copolymers of vinyl chloride and vinyl acetate such as "Vinylite V," copolymers of vinylidene chloride and vinyl chloride such as "Saran," polystyrene, nylon, methacrylate polymers, and the like. Any suitable organic solvent or combination of solvents may be used, depending of course upon the specific thermoplastic material being spun. Needless to say, in view of the commercial importance of acetone-soluble cellulose acetate, this invention is of greatest immediate value when applied to the production of this type of filaments and fibers.

The filaments produced by following the spinning processes described in Examples I and II are from 8 to 10 denier in size and strongly but somewhat irregularly crinkled. Filament sizes may be produced in accordance with this invention ranging from 4 or 5 denier or less up to 20 or 30 or more, and the number of crimps or crinkles per inch and the magnitude of the undulation will, of course, vary a great deal depending on the filament denier, the spinneret hole size, the jet velocity, the angle of extrusion, and other spinning conditions.

When the filaments of this invention are collected as a continuous batting as described in Example I, they may be converted into wool-like tows or laps, and by suitably drawing and blending, yarns possessing many of the desirable properties of wool yarns may be made. If desired, the continuous filament batting may be cut into staple lengths and the cut fibers worked up and processed alone or mixed with wool fibers or other synthetic fibers into many desirable spun products. The batting itself may be used as a stuffing or insulation material without altering its structure. For instance, it may be used in comforts, sleeping bags, as heat and sound insulation, etc. Also, the batting or other filamentous masses produced by the practice of this invention are admirably suited for felting and may be used alone or mixed with wool to produce felt suited for many purposes.

Not only do these highly crinkled filaments have the necessary characteristics to felt and tenaciously hang together when subjected to the usual felting steps, but they are astonishingly useful for many other purposes due to the fact that structures having a variety of densities may be formed by simply compacting the material. It is indeed surprising that even at pressures as low as 10 pounds per square inch, in combination with heating to an elevated temperature of from 30° to 100° C. below the softening point of the thermoplastic material, filamentous structures composed entirely of organic solvent-soluble cellulose derivatives can be produced which have excellent coherence, and without using any binding adhesive therewith, although in some cases it may be desirable to treat the filamentous mass with a solvent prior to pressing to cause the filaments to be solvent-welded together or to cause only the surface filaments to be solvent-welded. Again, by using pressures up to 10 or 15 tons per square inch or more, while the mass is maintained at room temperature or at temperatures only slightly thereabove, structures of varying degrees of hardness, denseness, and toughness may be formed which open up many fields of use. As previously stated, it is not at all necessary to completely fuse the filamentous mass to gain dense, tough, coherent structures. On the contrary, high toughness and other desirable physical properties are possessed by the pressed material only when the physical identity of the filaments or fibers is substantially maintained. Products possessing unusually desirable properties may be produced by hot pressing under such conditions that the identity of the filaments is apparently lost but is regeneratable; i. e., transparent or translucent products are formed but by rupturing the product the fibrous structure becomes evident. The process for converting the filamentous masses of this invention to highly compacted structures suitable for use in manufacturing structural plates and sheets, gears, pirns, bobbins, spools, machine parts, factory baskets, cannisters, grommets, washers, packings, tool handles, and a host of other articles useful in all branches of industry, is fully detailed in copending application Serial No. 491,125, filed June 17, 1943.

This invention then opens up vast new fields of use for organic solvent-soluble thermoplastic filamentous structures. In the field of textiles along the invention makes possible the manufacture of warm, light weight fabrics that have many desirable properties of natural wool. Also, the filaments and fibers of this invention when mixed, blended or otherwise combined with wool, produce very desirable effects which have not heretofore been attainable by using any other synthetic textile fibers. In compressed form, numerous articles having a wide variety of densities and varying degrees of hardness and toughness may be formed, and in use will be found to give unusually satisfactory service. Furthermore, the ease of conversion of the coherent mass of filaments of this invention into dense, tough structures which may be of any size or shape makes for ready adaptability without substantial alterations in machinery for making pressed fibrous articles.

It will be apparent from the above description of the process and products of this invention that they are susceptible to extensive modification without departing from the spirit of the invention, and it is therefore to be understood that the invention is not to be limited except as set forth in the following claim.

I claim:

A batting of substantial width, thickness and length comprised essentially of long lengths of filaments of acetone-soluble cellulose acetate, said filaments having crimps lying at random in three dimensions, having a surface characterized by deeply cut, irregular, disconnected pits

or channels, and having substantially no molecular orientation along the filament axis.

IRA V. HITT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,035,950	Dillingham et al.	Mar. 31, 1936
2,174,575	Forrest	Oct. 3, 1939
2,290,929	Whitehead	July 28, 1942
2,238,977	Jackson et al.	Apr. 22, 1941
2,264,415	Taylor et al.	Dec. 2, 1941
2,155,067	Ubbelohde	Apr. 18, 1939
2,197,896	Miles, Jr.	Apr. 23, 1940
2,185,789	Heinrich	Jan. 2, 1940
2,287,099	Hardy et al.	June 23, 1942
2,249,756	Finzel	July 22, 1941
2,185,789	Jacque	Jan. 2, 1940
2,216,810	Dreyfus	Oct. 8, 1940
2,242,988	Averns	May 20, 1941
2,249,745	Charch et al.	July 22, 1941
2,352,328	Kleine	June 27, 1944
2,370,112	Truitt	Feb. 20, 1945

FOREIGN PATENTS

Number	Country	Date
514,821	British	Nov. 29, 1939