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POLYPROPYLENE FIBERS AND METHOD FOR PREPARING SAME

Catherine S. H. Chen, Stamford, Evalyn F. Hosterman, Greenwich, and Robert F. Stamm, Stamford, Conn., assignors to American Cyanamid Company, New York, N.Y., a corporation of Maine

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The present invention relates to a novel, light-stable, thermally-stable, chemically modified, preformed polypropylene fiber. More particularly it relates to a novel, light-stable, thermally-stable, preformed, vinyl-grafted, dyeable polypropylene fiber possessing a spongy structure, and to methods for preparing the same. Still more particularly, it is concerned with a thermally-stable, light-stable, preformed, chloromethylstyrene-grafted polypropylene fiber compatible with wool, cotton and other fibers and capable of being uniformly dyed, as well as with dyed fibers of the latter and with methods for preparing the same.

It is known that preformed polypropylene fibers of high average molecular weight in the range of from about 100,000 to about 500,000 are manifestly unsuited as a textile fiber. They possess a low sticking temperature of about 140° C. and are found to be heat-unstable, waxy to the touch, non-dyeable and, in general, relatively inert to all after-treatments. For instance, when such fibers are subjected to moderate heat as that developed during ironing of a fabric prepared therefrom, the fibers either discolor, partially fuse or melt. In view of the increased demand for readily dyeable, light-stable, heat-stable, high sticking temperature-polypropylene fibers, it would be highly desirable to provide such fibers.

It is, therefore, a principal object of the present invention to provide a readily dyeable, heat-stable, light-stable, preformed, colorless, vinyl-grafted polypropylene fiber of good tensile strength possessing a spongy structure with attendant extremely fine pores or channels therein. It is a further object to provide a novel method for obtaining a dyeable, heat-stable, light-stable, preformed fiber of good tensile strength. It is still a further object to provide a dyed, preformed, heat-stable, light-stable, colorless polypropylene fiber of good tensile strength and a good sticking temperature. Other objects will be apparent to those skilled in the art from a consideration of the detailed description herein.

To this end, a heat-stable, light-stable, colorless, dyeable, preformed polypropylene fiber of high tensile strength and good sticking temperature is provided utilizing an over-all straightforward method in its preparation. In its broadest aspects, the method involves irradiating a chloromethylstyrene-swollen, preformed polypropylene fiber in the solid state. Fiber so modified is rendered readily dyeable. Reaction of the fiber with a nucleophilic reagent can occur swiftly prior to the dyeing operation.

According to the over-all process of the invention, preformed polypropylene fiber is initially irradiated while causing the fiber to be contacted with a chloromethylstyrene monomer. Dyeing of such treated fiber can be carried out in the presence of dyestuffs in a suitable organic medium. Alternatively, dyeing can occur in an aqueous medium, in the absence of an organic solvent, usually at temperatures ranging from about 15° C. to about 150° C., when the so-treated fiber is subjected to a prior treatment with a nucleophilic reagent, such as an amine, ammonia, an alkali metal sulfite, and alkali metal bisulfite, or an alkali metal sulfide.

The preformed polypropylene fiber to be treated is a high molecular-weight, linear, isotactic polymer of weight-average molecular weight equal to form about 100,000 to about 1,000,000 and, preferably, from about 250,000 to about 750,000. In general, such untreated fibers possess a "waxy" hand and are insoluble in most organic solvents.

In order to render the preformed polypropylene fiber amenable to dyeing and to impart the above-noted properties thereto, it has been found that the fiber can be modified utilizing any one of several techniques. The modification in essence involves the grafting of a chloromethylstyrene to the fiber. One method involves the simultaneous contact of a chloromethylstyrene and the preformed polypropylene fiber in the substantial absence of oxygen while subjecting the fibers so-swollen with a chloromethylstyrene to ionizing irradiation. Another method for achieving modification of the fiber is to irradiate initially the preformed fiber by means of ionizing radiation to form free radicals throughout the fiber and then to immerse the so-irradiated polymer in a chloromethylstyrene monomer. This latter technique is similarly conducted in the absence of oxygen. Still another method is to irradiate the preformed polymeric fiber in the presence of oxygen-containing gas (e.g., air) to form a mixture of hydroperoxides and peroxides on the fiber, and then to heat the fiber in the presence of a chloromethylstyrene and in the absence of oxygen so as to graft the chloromethylstyrene onto the polymeric molecules throughout the fiber.

Radiation utilized in the process of the invention can be of several types. One type is particulate radiation, such as α-particles and β-radiation (electrons), obtained from radioactive nuclei or high-energy electrons from machine sources. Another type of radiation may be electromagnetic radiation, such as gamma-rays or X-rays. However, the preferred source of radiation is a beam of high-energy electrons possessing energies in the range of from about 0.02 mev. to 20 mev., and preferably in the energy range of from about 0.05 mev. to 4 mev. For optimum operation, a beam of electrons of 0.5 mev. has been found to be eminently satisfactory for the treatment of most thicknesses of carded staple fiber, tow fiber or even woven fabric.

It has been observed that for ionizing radiation a total dose as low as 5000 rads and as high as 20,000,000 rads can be effectively tolerated. Optimum results, however, are obtained when from 7,500 to 1,000,000 rads are absorbed to render the fiber substantially free from a "waxy" hand as well as to impart good dyeability with little or no attendant loss of mechanical strength.

In general, the chloromethylstyrene monomer reactant may be either ortho-, meta- or para-chloromethylstyrene or mixtures of the same in various proportions. Although chloromethylstyrene is exemplified herein, it is understood that a wide variety of other styrenes, such as bromomethylstyrene, chloromethylstyrene with other substituents such as halogen, alkyl or aryl groups on the ring, as well as α-halo- or α-alkyl-substituted chloromethylstyrenes may be used in the practice of the invention.

Sufficient chloromethylstyrene monomer is added to the fiber. The monomer swells the fiber and simultaneously provides a graft within the range of from between 1% and 50%, and preferably between 5% and 25% by weight. When the stated range is maintained, a wool-like hand, improved sticking temperature, improved color fastness to washing, improved water-retention, improved anti-static behavior of the fiber as well as uniform dyeability to deep, intense shades are surprisingly achieved.

Extremely short periods are advantageously required for delivering ionizing radiation in the form of high-energy electrons. It has been found that an exposure time in the range of from about 0.06 to about 0.6 second is

sufficient for delivering the necessary dose of ionizing radiation in the form of electrons. However, longer periods are usually required when using ionizing radiation in the form of electromagnetic waves. Thus, unless unusually large sources should become available which are able to supply very high dose rates, some ten to fifteen minutes may be required where X-rays or gamma-rays are used. When employing such ionization techniques, a broad range of temperatures, usually between about 70° C. and 150° C., can be employed to accomplish such modification.

In general, the grafting step is carried out heterogeneously in the absence of oxygen. A solid, preformed polypropylene fiber and a liquid chloromethylstyrene monomer are contacted in such oxygen-free environment. Swelling of the fiber by the monomer is most readily induced by employing increased temperatures, usually between 40° C. and 120° C. However, the use of pressure employing an inert gas such as nitrogen or any of the rare gases to expedite the penetration of the monomer into the fiber is also contemplated. Alternatively, the grafting reaction may be carried out heterogeneously by contacting the polypropylene fiber with a chloromethylstyrene in the vapor phase. In so-proceeding, a multiplicity of short grafts spaced at fairly regular intervals along the polypropylene chain appears to occur. So-grafted, preformed, colorless polypropylene fibers possessing high tensile strength and good dyeability, may be dyed in an organic medium, such as dimethylformamide. Alternatively, the fibers may be dyed in a conventional aqueous environment by causing a nucleophilic or electron-donating reagent in the solid, liquid or gaseous state to react with them and thereafter subjecting resultant fibers to dyeing at temperatures in the range of from about 20° C. to about 150° C., and preferably from about 25° C. to about 100° C.

The nucleophilic reagent can be added to chloromethylstyrenated, preformed polypropylene fiber. Alternatively, the latter fiber can be added to the nucleophilic reagent, if desired. Where the nucleophilic reagent is a normally solid material, such as alkali metal sulfides or sulfites, a solvent therefor is employed as a carrier. For instance, dimethylformamide can be used for such purpose. Where the nucleophilic reagent is a liquid, such as certain tertiary amines, diamines, hydroxyamines, pyridines and the like, the latter can be used without any diluent. However, where the nucleophilic reagent is a gas such as ammonia or trimethylamine, either superatmospheric pressure or an appropriate solvent can be employed.

Advantageously, a wide variety of nucleophilic reagents may be employed in the present invention. Illustrative reagents are: pyridine, α-picoline, β-picoline, γ-picoline or mixtures thereof, trimethylamine, triethylamine, tri-n-propylamine, N,N-dimethylamine, amino triacetic acid, tri-β-hydroxyethylamine, β-dimethylaminoethyl alcohol, N,N,-di-methyl-o- (or m-, or p-)toluidine, N,N-dimethylbenzylamine, dimethylaniline, N-ethyl-N-methylaniline, N,N-diethylaniline, quinoline, isoquinoline, di-nicotine, N,N-di-n-propylaniline, 6-methylquinoline, 2-phenylpyridine, N,N - dimethyl - α - (or β-)naphthylamine, N-benzyl-N-methylaniline, N-benzyl-N-ethylaniline and triethanolamine. Also contemplated are: methylamine, propylamine, hexylamine, benzylamine, iminodiacetic acid, trimethylene diamine, ammonia, hexamethylene tetramine, glycine, lycine, sodium sulfite, potassium bisulfite, sodium sulfide and equivalents thereof, mono-, di- or trisubstituted phosphines, phosphites or dithiophosphates.

Advantageously, so-grafted polymeric fibers can be dyed without prior nucleophilic reagent pre-treatment with acid and direct dyes at about 75° C. to 120° C. in a solvent such as dimethylformamide. Examples of the dyes employed are the following: Calcocid Brilliant Scarlet 3 RN (Acid Red 18, C.I. 16,255); Calcocid Fast Red A (Acid Red 88, C.I. 15,620); Calcocid Yellow MCG (Acid Yellow 23, C.I. 19,140); Calcocid Alizarin Green CGN (Acid Green 25, C.I. 61,570); Calcocid Alizarin Blue SAPG (Acid Blue 45, C.I. 63,010); Calcocid Red FC (Direct Red 1, C.I. 22,310); Calcocid Fast Orange 2R (Direct Orange 26, C.I. 29,150); Calcozine Violet N (Direct Violet 1, C.I. 22,570).

Alternatively, the grafted material may initially be treated with a nucleophilic reagent whereby the fibers are rendered dyeable in standard aqueous dye baths using either an acid or a direct dye. In addition to all the dyes enumerated above, the following dyes produce extremely deep shades of true colors: Calcocid Phloxine 2G (Acid Red 1, C.I. 18,050); Calcocid Green B Conc. (Acid Green 1, C.I. 30,280) and Calcodur Turquoise GL (Direct Blue 86, C.I. 74,180).

Similarly, the grafted fiber initially treated with a solubilized alkali metal sulfide or sulfite permits ready dyeability with basic dyestuffs. For instance, by dissolving salts such as sodium sulfite, sodium bisulfite or sodium sulfide in a solvent, such as dimethylformamide, the fiber material can be dyed with basic dyes of which the following is illustrative: Sevron Yellow R (C.I. 48,055).

For a clearer understanding of the invention, the following examples are presented for purposes of illustration. They are not intended to be construed as being limitative thereof. Unless otherwise specified, the parts given are by weight.

EXAMPLE 1

3.7 parts of 3 denier polypropylene tow are placed in a suitable glass ampoule reactor. The latter is attached to a high vacuum line and evacuated. Ten parts of chloromethylstyrene are distilled into the ampoule under reduced pressure of about 10^{-6} mm. Hg. The reactor is sealed off and its contents allowed to equilibrate over-night. Then the ampoule and contents are subjected to irradiation with 250 kiloelectronvolt, peak value (kevp.) X-rays to a total dose of 0.27 Mrad at a dose rate of 1.6 Mrad/hr. The contents are permitted to remain sealed overnight and are then removed from the glass ampoule by breaking the latter. The fiber is washed several times with toluene, then with methanol and dried in an oven at 100° C. A weight gain of 0.92 part indicates a graft of about 25% chloromethylstyrene based on the weight of the fiber. On electron microscopic examination, the fiber possesses a spongy structure.

About 0.05 part of a sample is dyed with a solution of 0.005 part Calcocid Alizarin Blue SAPG (C.I. 63,010) in 25 parts (by volume) of dimethylformamide at 120° C. for one hour. The dyed sample is rinsed with water, then boiled in water for one hour and air dried. The fibers are dyed a dark blue shade.

A portion of these same dyed fibers is "potted" in polymethylmethacrylate. Several thin cross sections are next prepared by slicing the potted fibers on a microtome. Examination of the cross sections of the fibers by microscopic techniques reveals that 80% of the fibers are dyed completely to the center. The examination further reveals that fibers which are not dyed all through to the center, exhibit dye penetration to at least (or greater than) one-third the radius of each such fibers. Under dark-field illumination, it is seen that all the fibers possess channels or pores which are not present in the original fibers. The originally constituted solid structure surprisingly has been opened by the grafting procedure.

Another portion of the grafted, but undyed fibers is likewise "potted" and sectioned as above. These sections are examined by transmitted light in an ultraviolet microscope at wavelengths where polychloromethylstyrene absorbs strongly but where polypropylene is essentially transparent. It is observed that at least 75% to 80% are grafted all the way to the center. Those fibers which are not grafted all the way to the center exhibit transparent counter sections.

EXAMPLE 2

Polypropylene tow (4.1 parts) is placed in one ampoule of a suitable apparatus consisting of two ampoules connected at their necks with a tube which is attached to a high vacuum line. In the other ampoule are added 40 parts of chloromethylstyrene. The monomer is degassed by repeated freeze-evacuate-thaw cycles. The evacuated apparatus is sealed off and the fiber irradiated with 250 kevp. X-rays to a total dose of 1 Mrad at a dose rate of 1 Mrad/hr. During irradiation, the monomer is shielded from X-rays by one-half inch lead shield around the ampoule containing it. Thirty seconds after irradiation is terminated, the monomer is poured onto the fiber, completely immersing it, and allowed to stand overnight. The apparatus is opened, the fiber washed with toluene, then with methanol and dried in an oven at 100° C. A polypropylene-grafted fiber weight gain of 0.58 part shows at 14% graft of the chloromethylstyrene.

0.05 part of the grafted fiber is dyed a brilliant blue by 0.005 part Calcocid Alizarin Blue SAPG (C.I. 63,010) in 25 parts by volume of dimethylformamide at 120° C. for about one hour.

A sample of the original ungrafted fiber subjected to an identical dyeing procedure remained completely colorless. Further, the non-grafted fiber had a "wavy" hand.

EXAMPLE 3

This example illustrates the treatment of polypropylene powder.

One part of polypropylene powder is placed in a suitable ampoule attached to a high vacuum line. Two parts of chloromethylstyrene are vacuum distilled onto the powder. The ampoule is then sealed off under a reduced pressure of about 10^{-6} mm. Hg and subjected to irradiation with 250 kevp. X-rays to a does of 0.27 Mrad at a does rate of 1.6 Mrad/hr. Polypropylene powder with a 40% by weight graft of chloromethylstyrene is obtained. The grafted powder does not melt below 310° C. while the ungrafted polypropylene powder melts at about 165° C. Further, the grafted powder advantageously exhibits improved anti-static properties.

EXAMPLE 4

0.8 parts of polypropylene fiber is placed in the apparatus described in Example 2 above. The fiber is immersed in 50 parts of chloromethylstyrene, after the degassing and sealing-off procedure described in Example 2. Irradiation with 250 kevp. X-rays to a dose of 0.27 Mrad at a dose rate of 0.4 Mrad/hr. yields fiber with a 19% graft of chloromethylstyrene. Samples of grafted fiber each weighing 0.05 part are dyed in baths containing 25 parts (by volume) of dimethylformamide and 0.005 part of Calcocid Alizarin Blue SAPG (C.I. 63,010) dye. Dyeing is carried out at 118° C. for about one hour.

Upon infrared analysis of the dyed fiber chemical bonding between the sodium sulfonate group of the dye and the benzyl chloride in the grafted chloromethylstyrene appears to occur.

EXAMPLE 5

Polypropylene fibers (0.8 part) are carded, placed on a large fritted glass filter, and nitrogen is blown over them for one hour. They are then immersed under nitrogen in 50 parts of chloromethylstyrene. Nitrogen gas is bubbled through these fibers for one hour. The air-free mixture is contained in a suitable glass bottle. The bottle is tightly stoppered and irradiated with 250 kevp. X-rays to 0.27 Mrad at 0.4 Mrad/hr.

Resultant fibers increase in weight demonstrating that a 24% graft is obtained. They have a soft-wooly feel and can be readily incorporated into wool and uniformly dyed.

Similar results are obtained when bromomethylstyrene is substituted for chloromethylstyrene in the above examples.

EXAMPLE 6

One part of polypropylene fiber is swept with nitrogen gas as in Example 5 above and then immersed in ten parts of chloromethylstyrene which has been purged with nitrogen. The fiber and monomer in a suitable glass container are warmed to 60° C. for thirty minutes and then irradiated with 3 mev. electrons from a Van de Graaff accelerator to a total dose of 0.51 Mrad.

A 20.1% graft of chloromethylstyrene is achieved rendering the fiber readily dyeable to intense deep colors in a dimethylformamide dye bath.

EXAMPLE 7

Repeating Example 6 in every material respect except that a total dose of only 0.26 Mrad yields a material with a 9.2% graft of chloromethylstyrene which is also dyeable under the above conditions.

EXAMPLE 8

The chloromethylstyrene grafted fiber prepared in accordance with the procedure set forth in Example 2 above, is immersed in pyridine at 60° C. to 70° C. for thirty minutes. The fiber is then washed with water and dried.

The sticking temperature of a portion of pyridine-treated fiber, which has been grafted with chloromethylstyrene, is increased from 140° C., the sticking temperature of the original untreated fiber, to 180° C.

Another portion of the fiber so-prepared is next dyed to deep shades in a series of standard aqueous dye baths employing either direct or acid dyes. Typical dyes so utilized are: Calcocid Brilliant Scarlet 3N (Acid Red 18, C.I. 16,255), Calcocid Phloxine 2G (Acid Red 1, C.I. 18,050), Calcomine Fast Orange (Direct Orange 26, C.I. 29,150), Calcocid Yellow MCG (Acid Yellow 23, C.I. 19,140), Calcocid Green B Conc. (Acid Green 1, C.I. 30,280), Calcodur Turquoise GL (Direct Blue 86, C.I. 74,180), Calcocid Alizarin Blue SAPG (Acid Blue 45, C.I. 63,010), and Calcozine Violet N Conc. (Direct Violet 1, C.I. 22,570).

Each of the fibers so-dyed is exposed simultaneously to heat and ultraviolet and visible light in a standard carbon arc fadeometer. Visual examination of each is next performed after 20, 40 and 80 hours. No fading is noticed after 40 hours exposure. Further, each dyed portion is rated in a fadeometer test. This is the same rating given to these specific dyes when they are dyed on wool to deep shades and exposed in the same manner.

Each of the dyed fiber samples is color-fast to washing for one hour at 160° F. with a 1% soap solution containing 0.1% sodium carbonate.

EXAMPLE 9

In a suitable glass bottle, carded polypropylene fiber (1.5 parts), through which nitrogen has been blown for about one hour, is immersed in 60 parts of chloromethylstyrene previously purged with nitrogen. The mixture is heated to 55° C. for one hour while nitrogen is bubbled through it to increase the amount of monomer imbibed by the fiber during the process of swelling. The bottle containing the fiber and monomer is tightly stoppered and irradiated with 3 mev. X-rays at a dose rate of 0.4 Mrad/hr. to a total dose of 0.2 Mrad. Weight gain after extraction of the fiber with toluene at room temperature shows a 37.5% graft. The fiber is readily dyeable to deep shades in dimethylformamide or in aqueous dye baths after treatment with pyridine.

So-grafted, pyridine-treated fiber is placed in an atmosphere of air at 23° C. and 50% relative humidity for 48 hours after which it is weighed. It is then placed in an oven at 105° C. and heated for two hours and next placed in a desiccator to cool, weighed, heated at 105° C., cooled and weighed again. The "percent (%) moisture regain" is defined as the maximum difference in weight observed, multiplied by 100 and divided by the "bone-dry" weight. Typical data are shown below which are to be compared

with the figure of 4.0% for the material cited in this example.

Table I

Material:	Percent moisture regain
Chloromethylstyrene-grafted pyridine-treated polypropylene	4.0
Acrylan acrylic fiber	1.7
Orlon acrylic fiber	0.9
Dacron polyester fiber	0.4
Dynel acrylic fiber	0.3
Polypropylene	0.0

EXAMPLE 10

0.5 part of polypropylene fiber containing a 7.2% graft of chloromethylstyrene is heated at 100° C. for one hour in a mixture of 500 parts of dimethylformamide and 1 part of sodium sulfite. The fiber samples are washed with water and dried at 100° C. They are then dyed in aqueous solutions of the following basic dye:

Sevron Yellow R (C.I. Basic Yellow 11, C.I. 48,055).

Dyeability is markedly improved over controls which consist of ungrafted, untreated polypropylene fiber and grafted but not treated polypropylene fiber.

Similar results are obtained when sodium bisulfite or sodium sulfide is substituted in lieu of the sodium sulfite in the above example.

EXAMPLE 11

In a suitable apparatus permitting semicontinuous operation, 3-denier polypropylene tow is pulled downward through a metal tube containing nitrogen gas flowing continuously counter-current to the fibers into a J-box containing liquid chloromethylstyrene monomer at approximately 25° C. while continuously bubbling nitrogen through the liquid which escapes from the liquid and passes vertically into both legs of said J-box. The fiber enters, passes through, and leaves from the quiescent portion of the monomer which is free from the bubbles, thereby avoiding entrainment of bubbles by the fiber. The tow moves at a linear speed of about 180 inches per minute and at this speed retains approximately 10% by weight of monomer (based on fiber plus liquid) which wets the fiber forming a thin layer on each fiber. The wetted tow carrying approximately 10% by weight of monomer and still in a nitrogen atmosphere saturated with monomer vapor, enters a hot zone with vertical pipe approximately 90 inches long maintained at a temperature of approximately 90° C. This zone is continuously supplied with hot nitrogen gas saturated with monomer vapor so that the fibers can be swollen very quickly at the elevated temperature without losing monomer. The tow then makes a 90° turn, and, passing horizontally through a continuation of the pipe still moving in a nitrogen atmosphere saturated with monomer vapor and now moving with a speed reduced by 10% in order not to squeeze monomer out of the fiber, enters another hot zone maintained at a temperature of approximately 115° C. and, while in this hot zone, passes under a beam of 3 mev. electrons directed vertically downward. (The top wall of the pipe is provided with a 0.0005 inch stainless steel window to admit the beam of electrons.)

During the passage of the tow under the electron beam, a given segment of fiber receives a dose of ionizing radiation of about 0.6 Mrad. The tow, still in a nitrogen atmosphere, is kept at a temperature of about 125° C. for an additional 60 seconds while moving horizontally, then after making a 90° turn, proceeds vertically downward through an unheated pipe and, at the original speed of 180 inches per minute, enters another J-box containing a nucleophilic reagent, in this case, liquid pyridine at a temperature of 40° C. On leaving the J-box and while ascending vertically upwards, now in air, the fibers carry with them approximately 5% by weight of pyridine which penetrates the fibers and reacts with the chloromethyl groups when proceeding through a hot zone, the atmosphere of which is saturated with pyridine vapor, maintained at a temperature of approximately 70° C. The residence time in this zone is approximately five minutes. The fibers are then washed with water at a temperature of 25° C. to 50° C. and are given a hot stretch in air at approximately 110° C. to increase the length by approximately 25%.

We claim:

1. A light-stable, heat-stable, colorless, chloromethylstyrene-grafted, preformed polypropylene fiber capable of being dyed and possessing good tensile strength, high sticking temperatures and spongy structure.

2. The fiber according to claim 1, in which the average molecular weight of the polypropylene falls within the range of from about 100,000 to about 1,000,000.

3. A heat-stable, deeply-dyed, chloromethylstyrene-grafted polypropylene fiber possessing good tensile strength, high sticking temperatures, good moisture regain, anti-static and color wash-fastness properties.

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NORMAN G. TORCHIN, *Primary Examiner.*

MURRAY TILLMAN, ABRAHAM H. WINKELSTEIN, *Examiners.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Catherine S. H. Chen et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 1, for "form" read -- from --; column 5, line 25, for '"wavy"' read -- "waxy" --.

Signed and sealed this 19th day of July 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents