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2,923,598

METHOD OF FORMING FILAMENTS EMBODYING POLYURETHANE RESINS

Filed June 30, 1954

2 Sheets-Sheet 1

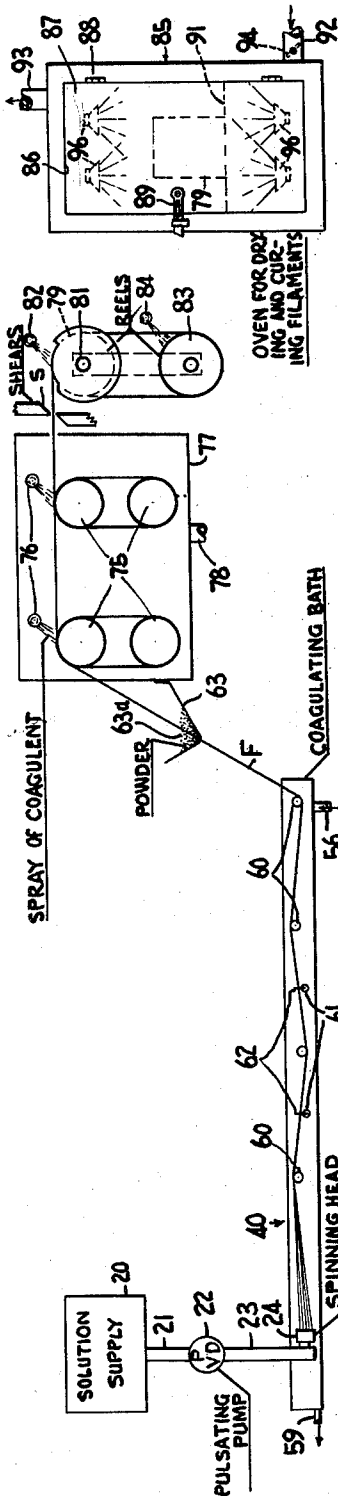


FIG. 1

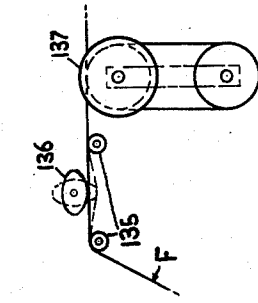


FIG. 2

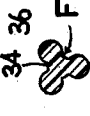


FIG. 7

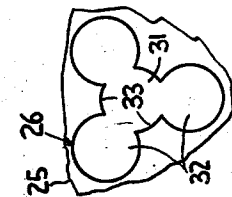


FIG. 5

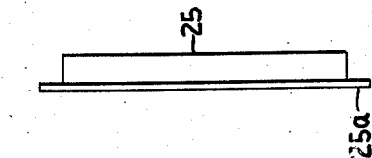


FIG. 4

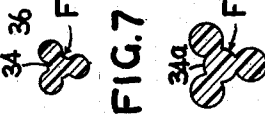


FIG. 8

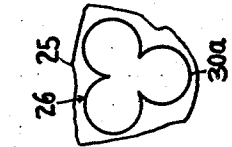


FIG. 6

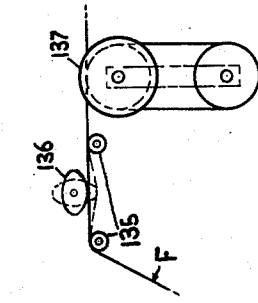


FIG. 17

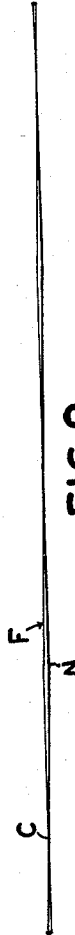


FIG. 9

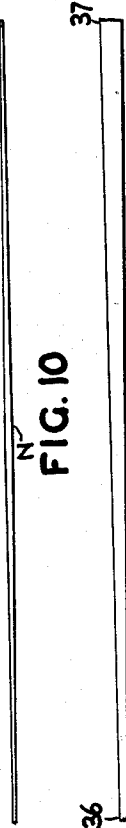


FIG. 10

FIG. 11

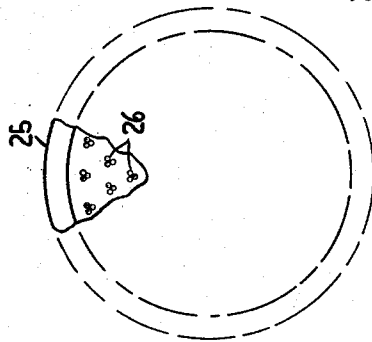


FIG. 3

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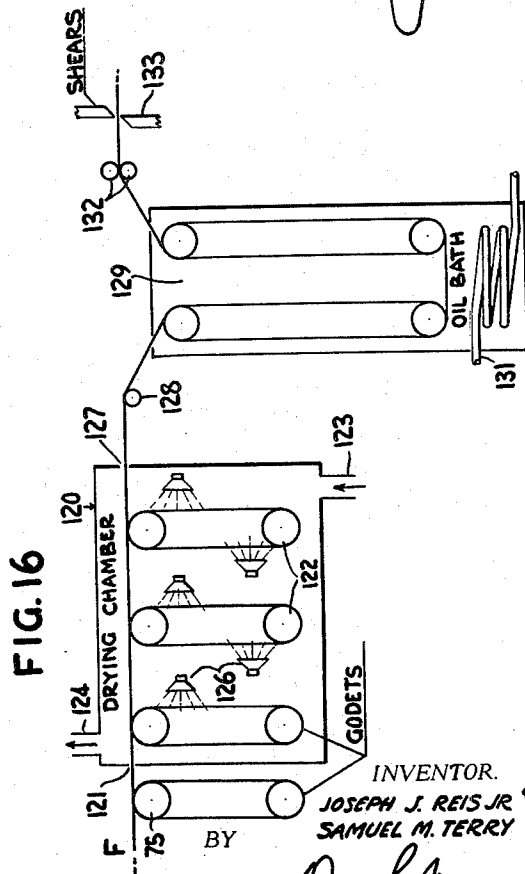
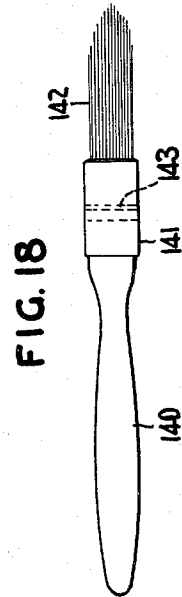
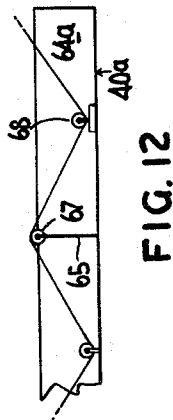
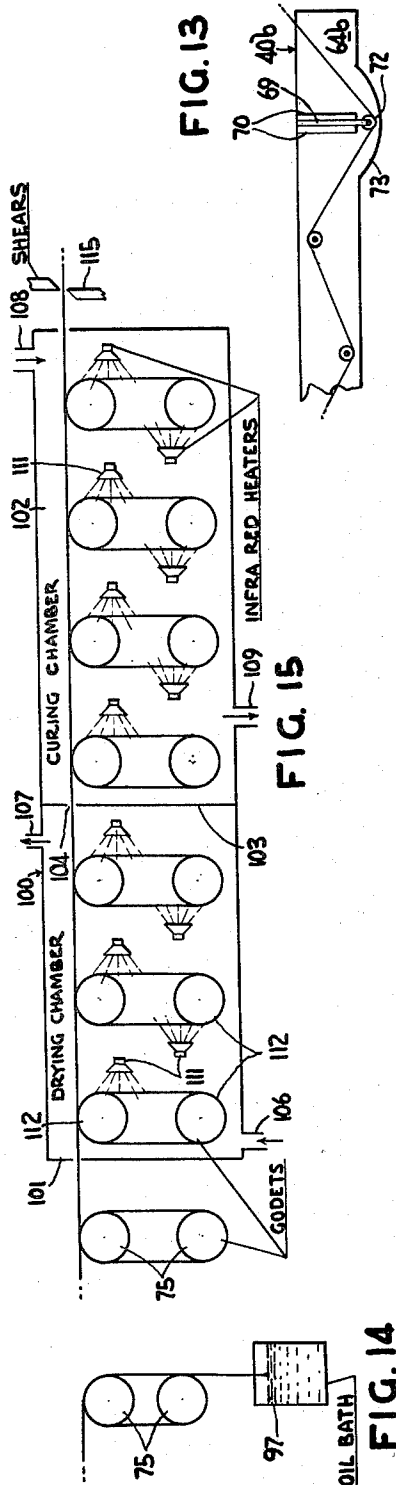
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2 Sheets-Sheet 2



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2,923,598

METHOD OF FORMING FILAMENTS EMBODYING POLYURETHANE RESINS

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Application June 30, 1954, Serial No. 440,362

2 Claims. (Cl. 18—54)

This invention relates to synthetic brush bristles spun from a synthetic plastic material and it has particular relation to brush bristles which are spun from solutions of soluble addendum products of monomers containing $>C=CH_2$ groups.

It has long been customary to form brushes, such as are employed for spreading paints and for similar purposes, of natural hairs and bristles. Certain of the pig bristles are outstanding examples of these natural materials. The bristles of the domestic hogs of this country are seldom of much value as bristles for brushes; but those of certain species of swine raised in such countries as China and other Asiatic countries are long, springy, are naturally well tapered and have surface scales as well as tip flags which impart to them excellent capillarity. All of these characteristics are desiderata of a paint brush bristle and for these reasons, these bristles have long generally been accepted as being superior to all others. However, for a number of years owing to the world conditions, the supply has been very limited or nonexistent. Substitutes, such as horse hair or other hairs of relatively coarse, springy nature, have been employed but are lacking in such properties as taper and flagging at the tips, and for that reason are not very satisfactory substitutes for pig bristles.

Bristles such as are spun from synthetic plastics by extrusion operations have also been employed, but they have heretofore presented certain problems when incorporated into paint brushes. Thermoplastic resins, such as nylon, can be spun as a hot melt through fine spinneret openings into a chilling bath in such manner as to provide filaments periodically varying in denier. These filaments can then be cut into sections of a length equal to half the space between variations of denier so as to provide tapered bristle sections. When these bristles are assembled into brushes, they possess certain valuable properties, but they are also subject to certain important disadvantages. On the positive side, they possess high strength, flexibility, and are exceptionally resistant to wear. Upon the debit side they are characterized by high cost and the capillarity thereof with respect to many coating materials is poor, so that their retention of the coating material is relatively low. The charge which a brush of such bristles is capable of carrying without running or spattering is therefore small. Attempts have been made to overcome these defects by contacting the tips with high speed rotary knives to produce flagging.

Valuable synthetic bristles have also been spun from solutions of cellulosic materials, notably cellulose esters such as cellulose acetate. The latter material is inexpensive, and solutions thereof can be spun into filaments of periodically varying denier, which can be cut into sections at the proper points to provide tapered bristles. It is also possible to impart to them noncircular shapes of increased surface area. The capillarity of such bristles, when they are assembled into paint brushes is a substantial improvement over that of nylon. However, they are soluble in, or partly soluble in solvents of cellulose mate-

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rials such as may be employed in making up certain coating vehicles. In event that the coating materials contain these solvents of cellulose esters, bristles of cellulose acetate are unsatisfactory or even entirely inoperative. The bristles whether prepared from a polyamide (nylon) material or from cellulose acetate, where not subjected to a further curing operation after spinning in order to render them infusible and insoluble.

This invention is characterized by the provision of bristles which are often substantially cheaper than nylon bristles, which are of good flexibility and strength, which have high capillarity and which unlike the conventional cellulose acetate bristles are cured by a cross-linking agent to substantial insolubility in most of the solvents conventionally employed in the formulation of paints and other coating vehicles.

The invention is based upon the discovery that solutions of certain vinyl polymers can successfully be spun into filaments of variable denier and of a diameter appropriate for brush bristles. Such filaments can be stripped of solvents by application of appropriate techniques and the molecules of interpolymer comprising them can be cross-linked after the stripping operation by agents such as diisocyanates to render them tough, strong, resilient and relatively insoluble in all or most of the solvents employed in the vehicles of the paint industries. Subsequently, the filaments can be cut into lengths suitable for use as bristles in paint brushes and other brushes. The bristles so formed are less expensive than nylon bristles, are substantially infusible and likewise have better capillarity than the latter.

Ethylenically unsaturated monomers suitable for forming polymers which are plastic bodies that can be spun into bristle filaments in accordance with the provisions of this invention, preferably are fluid at normal atmospheric pressures, contain a terminal $>C=CH_2$ group attached to a negative radical and are polymerizable by addition reaction to a solid, plastic, but soluble state. Preferably they include hydroxyls in an amount to provide a reasonable number of points of functionality in the polymer chain. These points of functionality, admit of cross-linking of contiguous molecules with cross-linking agents such as diisocyanates to render them thermost and insoluble in all, or most of the solvents employed in the formulation of coating compositions.

It is preferred to interpolymerize vinyl chloride and vinyl acetate in well known manner to form mixed polymer molecules and then to hydrolyze the ester linkages of the ester component to provide a resin which is composed of about 2 to 5 percent of hydroxyls susceptible of subsequent cross-linking by such agents as the diisocyanates. One convenient material of this type is sold under the trade name of Vinylite VAGH.

This material is described in greater detail in a descriptive brochure entitled "Vinylite Resins," Technical Release Number 6, by the Bakelite Company, a division of the Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, New York. The material is understood to comprise approximately 91 percent vinyl chloride, 3 percent vinyl acetate and 2.3 percent hydroxyl. The latter calculated on the basis of equivalent vinyl acetate constitutes 6 percent. (Percentages as above quoted are by weight.) The material is understood to be prepared by interpolymerizing the vinyl chloride and vinyl acetate in accordance with well known procedures and subsequently hydrolyzing a portion of the ester linkages to provide hydroxyl groups. This material is soluble in many solvents but not in petroleum solvents such as those of low kauributanol value (K.B. value). Their solutions do not gel readily during storage. They dissolve cross-linking agents such as diisocyanates and when properly heated with the latter, they cure to the desired tough,

infusible, insoluble state at reasonable temperatures. The material gives good results in the fabrication of brush bristles in accordance with the provisions of this invention. However, it will be apparent that it is given by way of example. It may be replaced by other vinyl chloride interpolymers containing free hydroxyls adapted for reaction with cross-linking agents in such manner as to produce insolubility in the filaments spun therefrom.

In the spinning of filaments, the foregoing material is usually employed in the form of a solution in an appropriate solvent. Solvents may be selected from the following table.

Table I

Solvent:

Tetrahydrofuran	
n-Butanol	
n-Butyl acetate (98%)	
n-Butyl acetate (90%)	
Butyl Carbitol acetate	
Butyl Cellosolve solvent	
Carbitol solvent (low gravity)	
Cellosolve solvent	
Cellosolve acetate	
Diethyl Carbitol solvent	
Diisobutyl ketone	
Ethyl acetate (99%)	
Ethylene dichloride	
2-ethylhexyl acetate	
Methyl amyl acetate	
Methyl isobutyl ketone	
Methyl isobutyl ketone -----	25%
Isopropanol (anhydrous) -----	25%
Toluene -----	50%
Methyl isobutyl ketone -----	20%
Isopropanol (anhydrous) -----	30%
Toluene -----	50%
Methyl isobutyl ketone -----	15%
Isopropanol (anhydrous) -----	35%
Toluene -----	50%
Methyl isobutyl ketone -----	25%
Isopropanol (anhydrous) -----	25%
Toluene -----	25%
Trolooil -----	25%

Of these several solvents, tetrahydrofuran is presently regarded as being the most useful in the formation of a solution of the resin that can be spun into brush bristle filaments in accordance with the provisions of the present invention. Solutions of the resin and this solvent are stable and readily extrudable.

As previously indicated, the hydroxyl groups in the resinous material provide points of functionality where interaction can be effected with cross-linking agents in order to join or bridge contiguous polymer molecules and thus to attain insolubility of the filaments. In the preparation of the filaments, the cross-linking agent is usually incorporated into the solution of plastic material prior to the spinning operation. A number of cross-linking agents are presently available of which the following constitutes a partial list:

Table II

Dimethylol urea
Acid anhydrides such as—
Maleic anhydride
Phthalic anhydride
Acid halides such as—
Phthalyl chloride
Maleyl chloride
Formaldehyde
Glyoxal
Hexamethylene tetramine

Isocyanates containing the group —N=C=A where A is of the class consisting of oxygen and sulphur and being represented by:

Table III

Ethylene diisocyanate
1,4-tetramethylene diisocyanate
Cyclohexanediol diisocyanate
5 p-phenylene diisocyanate
2,4-tolylene diisocyanate
p,p'-Diisocyanato-di-phenylmethane
Hexamethylene diisocyanate
10 The corresponding diisothiocyanates where the oxygen is replaced by sulphur are also included.
Tetrahydrofuran solutions of hydrolyzable polyvinyl chloride-polyvinyl acetate interpolymer will tolerate substantial amounts of nonsolvent such as mineral spirits of
15 low kauri-butanol value without coagulation. It is often desirable to add an appreciable amount of the latter to the solutions employed in the spinning of synthetic bristles in order to reduce the stickiness of the filaments, when they are freshly spun from the solutions.
20 Appropriate solutions of hydrolyzed vinyl chloride-vinyl acetate interpolymer containing a cross-linking agent such as a diisocyanate, e.g. tolylene diisocyanate, may be of the following composition:
25 Resin (e.g. VAGH) ----- 115 to 140 parts by weight (preferably about 125 parts by weight).
Tetrahydrofuran ----- 140 parts by weight.
Mineral spirits (K.B. value 40 or less) ----- 0 to 35 parts by weight.
30 Diisocyanate (e.g. tolylene diisocyanate) ----- 10 to 25 parts by weight (preferably about 15 parts by weight).
35 Spinnable solutions of polyvinyl chloride containing hydroxyl groups for use in the practice of the present invention, when made into solution with a solvent such as tetrahydrofuran, preferably are of a viscosity of at least 60,000 centipoises and of course, should be under the gelled state. A range of about 70,000 to 120,000 is suggested as being appropriate. These viscosities were taken at approximately room temperature or 25° C.
40 In the extrusion of solutions of polyvinyl chloride containing hydroxyls in order to form filaments, the solutions preferably are squirted under pressure through small orifices or spinnerules of a size commensurate with the denier of the filaments. The orifices may also be appropriately shaped to impart lobed sections to the filaments whereby to increase the capacity of the latter to hold
45 liquids such as paints and other coating media.
50 The jets of solution from the spinnerets may be converted into hardened or gelled state, for example by projection into a heated medium such as air, or other gas which has a capacity of removing solvent by evaporation.
55 However, a preferred process involves projecting the jets into a liquid medium which is a nonsolvent for the plastic, but is adapted to extract out solvent from the plastic solution. One such class of media comprises the afore-mentioned liquid hydrocarbons such as aliphatic petroleum naphthas and ethers of a relatively low volatility, and K.B. value. A petroleum solvent having a low K.B. value, a minimum flash value of 38° C. and an initial boiling point beginning at about 149° C. is very satisfactory both
60 in the coagulating bath and as an additive to the solution to prevent sticking. In no event should the amount added to the solution be so great as to induce premature coagulation or gelling. Spinning is usually performed at a temperature of about 21° C. to 32° C. but other temperatures, higher or lower may be employed.
70 It will be recognized that the filaments as they enter coagulating bath, are relatively tacky and if they contact with each other at this stage, even while submerged, they may weld together. In order to obviate this tendency, the filaments should be maintained in spaced relationship until
75 as much as practicable of the solvent has been removed

by extraction in the coagulating medium. This spacing may be maintained by mechanical means such as by combs or other slotted or perforated devices providing separate reticulations through which the filaments of a tow can be allowed to glide without contact with respect to each other. It is found to be desirable to maintain the filaments in the coagulating bath for a substantial period of time, for example at least 30 seconds and preferably for a minute or two or more. This period can be regulated by control of the speed of spinning and/or by adjustment of the length of the bath.

In the coagulating bath, it will be recognized that solvent medium for the plastic is extracted out by contact with the filaments, thus producing gelling or setting of the latter to a substantial degree, and so permitting of the further handling of the filaments. However, the extraction is not always complete; residual solvent in the filaments reduces the softening point and in the absence of coagulant, renders them tacky. In order to carry the removal to completion or substantially to completion before final curing operations, it is often desirable to evaporate out the solvent at as low temperatures as practicable. If desired, the evaporation may also be promoted by the application of vacuum, or by rapid blowing with gaseous medium in order to speed up the evaporation without excessive increase of temperature.

During the evaporation of the liquids, it is obvious that the temperature should be sufficiently low to prevent undue softening of the freshly formed, but partially solvated filament. Usually, temperatures up to about 50° C. or 80° C. can be tolerated after the filaments leave the coagulating bath, but this temperature range may sometimes be exceeded, especially in those instances where the filaments can be supported without contact with other filaments or a single filament is not looped upon itself in such manner as to afford points of contact.

A filament, after evaporation of the solvent or substantial evaporation of the same, can be handled and stored at normal atmospheric temperatures without danger of cohesion at points of contact between contiguous strands or loops. However, it is to be recognized that at this stage, the filaments are still soluble and consist largely of a polymer of vinyl chloride containing components such as polyvinyl alcohol having hydroxyls capable of reacting with cross-linking agents such as tolyenediisocyanate. To a limited extent, cross-linking may already be initiated, but usually is still incomplete.

Partial or even complete cross-linking of hydroxyls in the plastic material with the diisocyanate can be effected over a long period of time by storing the filaments at a moderate temperature until cross-linking has progressed sufficiently far. However, the cross-linking can be greatly speeded up by the application of heat. By test, it has been determined that the rate of cross-linking is approximately doubled for each 10 degrees centigrade rise in the temperature at which the filaments are maintained. Temperatures of about 150° C. to 250° C. are suitable. The time of curing will vary from about 5 hours to about 4 or 5 minutes, dependent on the curing temperature, the degree of hardness and insolubility desired in the filaments and such like factors.

It is a characteristic of bristles of polyvinyl chloride-polyvinyl alcohol interpolymers that if excessively heated, they tend to become brittle. An appropriate schedule for curing the filaments whereby such embrittlement is avoided is previously described in this specification. However, it will be recognized that the formation of brushes by one common method comprises setting a bunch of bristles partway in a band or ferrule, pouring a rubber cement on the butts of the bristles in the ferrule and heating the resultant assembly for several hours at a relatively high temperature in order to cure or set the cement. With bristles of polyvinyl chloride-polyvinyl alcohol interpolymer containing a cross-linking agent such as a diisocyanate, this produces embrittlement and is objectionable.

To avoid this trouble, it is desirable to employ with the bristles of this invention a cold curing cement such as a glycidyl polyether such as may be obtained by reacting isopropylidenediphenol with epichlorohydrin in the presence of alkali to produce a liquid polyether of rather short chain length. This material, when treated with a hardening agent can be introduced into brush ferrules and can be cured at such temperatures as do not embrittle the bristles herein disclosed. It will be recognized that other cements than the one above described which are adapted to cure at low temperatures, below the embrittlement point of the bristles, may be employed.

This invention also includes the setting of bristles as herein disclosed before the curing or cross-linking operation, but after drying, in ferrules, applying a cement which requires a temperature within the range required for curing the bristles in order to effect hardening and then heating the resultant assembly simultaneously to cure the cement and also to effect cross-linking of the plastic in the bristles to obtain toughness and insolubility of the latter.

While it is possible to spin filaments susceptible of being cut into bristle sections on various embodiments of apparatus, conventional or otherwise, and the use of such embodiments is contemplated as being within the scope of the present invention, embodiments which have been developed by the applicants and which include a number of useful features are shown in the appended drawings in which like numerals refer to like parts throughout.

In the drawings:

Fig. 1 is a diagrammatical view of an appropriate embodiment of apparatus for use in the practice of the invention.

Fig. 2 is a diagrammatical view of an oven suitable for use in drying the filaments preparatory to the final curing operation, or for effecting the ultimate cure.

Fig. 3 is a fragmentary plan view of a spinneret plate suitable for use in the extrusion of filaments in accordance with the provisions of this invention.

Fig. 4 is a side elevational view of the plate shown in Fig. 3.

Fig. 5 is a fragmentary view showing in greater detail one of the spinneret openings in the plate shown in Figs. 3 and 4.

Fig. 6 is a fragmentary view of a modified form of spinneret opening.

Fig. 7 is a sectional view showing on an enlarged scale a section through a filament at the point of minimum denier.

Fig. 8 is a sectional view of the same filament but taken through a thickened portion thereof.

Fig. 9 is a fragmentary portion of a filament showing the periodically variable denier.

Fig. 10 is a view illustrating a single double end brush bristle element.

Fig. 11 illustrates a brush bristle element having a single tapered tip portion.

Fig. 12 is a fragmentary diagrammatical view illustrating means for applying a suspension of finely divided material to filaments after they have passed through the coagulating bath.

Fig. 13 is a fragmentary diagrammatical view of a modified form of apparatus for applying a suspension of finely divided material to the filaments.

Fig. 14 is a diagrammatical view of an alternative form of apparatus for receiving the freshly set filaments preparatory to drying and curing.

Fig. 15 is a diagrammatical view of a continuous oven for drying and curing the filaments.

Fig. 16 is a similar view of modified apparatus for continuously drying and curing the filaments.

Fig. 17 is a diagrammatic view of means to vary the taper of filaments by varying the rate of take up.

Fig. 18 is a side view of a brush assembled from bristles formed in accordance with this invention.

In the embodiments of apparatus, as illustrated diagrammatically in Fig. 1 of the drawings, a solution of plasticized material, is charged into a container 20 which preferably is disposed in somewhat elevated position, to provide a hydrostatic head in feed conduit 21.

For purposes of obtaining periodically variable denier in the filaments spun from the solution, the conduit 21 is provided with a variable delivery pumping mechanism which is indicated diagrammatically at 22. The solution of plastic is discharged from the pump under pulsating pressure corresponding to the desired variations in denier in the filaments through a conduit 23 which is illustrated as a single line, but in actual practice may comprise any desired number of branches in order to accommodate a desired number of spinning heads 24. These are essentially of conventional construction and the only element thereof illustrated in any detail embodies the spinning plate 25 containing the spinneret openings formed therein. In the embodiment of apparatus shown, spinning plate 25 is cupped or hat-shaped and is provided with an attaching rim 25a, by means of which it may be secured in position on the spinning head. The plate as illustrated in Fig. 3 is provided with a series of orifices 26. These may be of any convenient shape or sections, but for purposes of illustration, they embody the modified trefoil section illustrated in our copending application Ser. No. 364,302, filed June 26, 1953, now Pat. No. 2,746,839. The shape of this orifice is best illustrated in Fig. 5 of the drawings and the shape of the filaments obtained therefrom is illustrated in Figs. 7 and 8. A modification of the construction is illustrated in Fig. 6 of the drawings. In the embodiments shown in Fig. 5, a central opening 31 is drilled in the plate for each of the orifices and a plurality of equally spaced openings 32 are drilled at uniform distances from the central opening in such manner that the circumferences of the side openings intersect the circumference of the central openings. Lands 33, of considerable width are provided between the contiguous circular lobes of the resultant modified trefoil section. The lands provide grooves in the filaments as indicated at 34 and 34a in Figs. 7 and 8 and these grooves are substantially V-shaped at the intersection between the central opening and the lobes at their points of intersection. This construction is especially desirable, in as much as a maximum amount of liquid will be retained in the capillary channel 34—34a of the brush bristles formed from such filaments. Also the shape facilitates the drawing or spinning operation in forming the filaments in as much as any tendency of the lobes to merge or to run together as the liquid is drawn out of the orifices is reduced to the minimum. In the simpler, though somewhat less desirable modification, illustrated in Fig. 6 of the drawings, the orifices are of true trefoil section and the lobes 30a intersect each other. The grooves so formed in the filaments which are spun through the orifices, have longitudinally extending grooves which help to increase the capillary attraction of the filaments for liquid compositions.

It is also contemplated to flag or otherwise to roughen the tip portions of the bristles after they are spun and cured by contacting them with rapidly revolving knives, or to point or to roughen them by contacting them with sanding belts or discs in well known manner in order to increase capillarity. Such operations may be performed on the bristles regardless of cross-sectional shapes.

It will be understood that in those instances where high capillarity of the filaments is not essential, as for instance where the filaments are used to form bristles for dusters and other forms of brushes which are not required to carry liquids, they may be spun through round orifices or any other suitable shape which may be convenient.

It is a feature of the present invention that the solutions of vinyl chloride containing hydroxyls and a cross-linking agent such as one of the diisocyanates, when properly

spun, will carry a cross-section conforming to that of the spinning orifice even when the solutions are spun with the rapidly varying pressures desirable to impart periodically variable denier approximating the taper of pig bristles. This cross-section is also carried by the filaments during any subsequent stages of drying in order to free them of solvents, coagulating liquid and the like, as well as during the subsequent stages of heating for purposes of attaining cross-linking action by the diisocyanate in solution in the plastic material. It is noteworthy that in the curing operation the filaments are initially softened and plastically extended by the action of the heat at curing temperatures, but as the cross-linking attending the latter operation progresses, they tend to return to their original length. It is the more surprising that the original section is maintained during these changes in length.

A filament F, as illustrated in Fig. 9 of the drawings, when spun from an orifice under periodically varying pressure has alternating constructions (anti-nodes) C and expansions of nodes N which correspond respectively to the points and the butt portions of bristles which are ultimately formed by severing the filaments at the proper points. Filaments spun from the orifices illustrated in Fig. 5 are trefoil or modified trefoil section throughout their length. A section corresponding to a single brush bristle element, as illustrated in Fig. 11 of the drawings, has the same shape at tip 36 and butt 37 though of course the shape is on a different scale at the respective points.

Variable pump 22 and riving mechanism for operating the same, may be of any convenient construction and may be, for example, of the form illustrated in our copending application Ser. No. 364,302, now Patent No. 2,746,839. If desired however, a constant delivery pumping mechanism may be substituted for the variable delivery mechanism and for purposes of attaining periodical variation in the denier of the filaments being spun, a suitable variable speed take-up mechanism may be employed. Such take-up device will be more fully discussed hereinafter.

The apparatus for forming filaments as illustrated in Fig. 1 of the drawings comprises a coagulating bath of petroleum hydrocarbon or other nonsolvent medium, contained in a trough 40. Coagulant may be admitted to the trough by a conduit 56 and may be withdrawn, after it becomes mixed with solvent, through a conduit 59 disposed preferably in spaced relationship with respect to the conduit 56.

A number of filaments are formed simultaneously and are drawn through the bath in a so-called "tow." For purposes of maintaining the filaments being set in the bath in relatively spaced relationship with respect to each other, a series of cross-bars 60 may be provided and the filaments are passed alternately over and under them. The bars may have smooth surfaces, or if desired, they may be provided with transverse grooves spaced to provide slots through which the filaments can glide without actual contact between contiguous filaments.

The bars 60 may be formed of various materials. However, it is desirable that they be of a material which will not tend unduly to adhere to the freshly formed filaments. Of the various materials which have been tested for use in the formation of the bars, polymers of tetrafluoroethylene have been found to be the most satisfactory. One such material is sold under the trade name of Teflon. The spacing of the filaments on the bars 60 may also be maintained by provision of intermediate combs 61 having spaced teeth adapted to be inserted between the filaments. The teeth 62 of the combs may be formed of Teflon or other suitable material.

In the spinning of solutions of polyvinyl chloride containing hydroxyl groups and a cross-linking agent, it is usually desirable that the spinning head 24 and the first of the series of bars 60 be substantially spaced with respect to each other in order to provide a considerable free run in which the freshly formed filaments are not

brought into contact with any solid surface. A reach, or space of at least 1 foot and preferably about 2 to 4 feet, is suggested as being satisfactory. In the interval between emergence of the filaments from the spinneret openings and the first contact with the solid surface of the first of the transverse bars, a sufficient interval is provided for the appreciable hardening of the surface of the filaments so that the latter can pass over the bars without undue distortion.

The filaments should be in contact with the coagulating bath in trough 40 for a substantial period of time (at least 30 seconds and preferably longer, e.g. 1 to 5 minutes). If the rate of spinning of the filaments averages 10 feet per minute, it will be apparent that a bath of 10 feet length will provide for a one minute immersion. The bath may be extended to any practicable limit in order to assure more thorough removal of solvent by the coagulating medium, but 5 feet (assuming a spinning speed of 10 feet per minute) would appear to be near the minimum.

The filaments, upon emergence from the coagulating bath, are solid, at least in their outer shell, and may be handled as for example by training them about conventionally driven Godet rollers, or other devices prior to the subsequent steps of drying and ultimate heating for purposes of effecting cross-linking action between the polymer and the cross-linking agent. However, it is often desirable to apply to the surfaces of the filaments, an appropriate liquid or pulverulent parting agent. This parting agent may be a pigmentary substance such as carbon black, titanium dioxide, or pigmentary silica such as the product sold under the trade name of Hi-Sil by the Pittsburgh Plate Glass Company. Liquid coating media such as solutions of cellulose acetate or waxes are not precluded. Carnauba wax or paraffin wax in a volatile solvent such as benzene constitute examples of wax coating agents designed to act as parting agents on the filaments.

The parting agent, if pigmentary in nature, may be applied by a dusting operation or by passing the filaments through a suitable orifice in the bottom of a dusting hopper indicated at 63 in the drawings. A bed 63a of pulverulent material in the hopper contacting with the surfaces of the filaments, applies a thin coating of pigmentary material which assures that in subsequent contacts of the filaments with each other, there will be little or no tendency of the contacting surfaces to weld together. A closed chamber having apposed slots for passage of filaments and containing powder as an air borne dust could be substituted for hopper 63.

It is also within the purview of the invention to apply a pigmentary material such as carbon black to the filaments as a dispersion in a suitable medium such as a lubricating oil, or in the hydrocarbon medium employed in the coagulating bath in trough 40. For example, carbon black or lamp black may be dispersed in the bath, a dispersing agent such as lecithin being employed to promote the dispersion. The finely divided black carried in the bath will cling to the filaments being spun and as the coagulating medium dries, will be deposited upon the surfaces of the filaments. The black so deposited will prevent cohesion between surfaces in contact with each other even in the complete absence of coagulating medium and at relatively elevated temperatures.

Apparatus to apply a suspension of coating medium is shown in Figs. 12 and 13. The apparatus in these respectively comprise troughs 40a and 40b for the coagulant which are appropriately compartmentalized and one of the compartments, e.g. the terminal one 64a or 64b is employed as a container for a suspension of pigmentary material such as carbon black. In the embodiment shown in Fig. 12, a partition 65 is disposed near the forward end of the trough 40a to form the terminal compartment 64a. The upper edge of the partition may be provided with a guide bar 67 of Teflon or other material having

low cohesion with respect to the plastic filaments. This bar, along its upper edge, may be serrated to provide individual grooves in which the separate strands of the tow can pass without contact with their neighbors. A second bar 68 is disposed beneath the surface of the liquid and the strands are passed thereunder. Bar 68 may also be formed with serrations to guide the individual strands. The strands, after passing under the bar 68, are drawn upwardly to the winding mechanism subsequently to be described.

In the construction as disclosed in Fig. 13, the end compartment 64b of the trough 40b is separated from the main body by means of a vertically slidable partition 69, which is disposed between guides 70 on the sides of the trough. The lower edge of the slide is provided with a Teflon bar or coating as indicated at 72 which is disposed in a depression 73 in the bottom of the trough. This depression is filled with a liquid medium which is of higher density than the coagulant in the troughs and is a nonsolvent for the latter, as well as for the filaments and which provides a seal between compartments. One liquid, having an adequate density and being a nonsolvent for the other materials with which it is in contact in the bath, comprises mercury, but it may be replaced by other heavy, nonsolvent liquids. Needless to say, the liquid in the depression tends to wipe the filaments before they are contacted with the coating bath. The auxiliary baths, 64a or 64b if desired, may be heated to establish a temperature gradient designed partially to set the plastic by cross-linking, before it passes to the take-up mechanism to be described.

In any event, the terminal portion of the trough is sealed from the rear portion by the partition 69, and the liquid in the depression 73, whereby to provide a separate compartment for the suspension of the pigmentary material.

The filaments as they reach the forward extremity of the coagulating bath and the coating bath, are trained upwardly to a set of Godet rollers 75 of conventional design which are appropriately power driven at a rate which preferably is equal to or just slightly excess of the average rate of extrusion of the filaments as they emerge from the extruding head.

In those instances where it is desired to spin filaments without resort to application of coatings to prevent them from being sticky, upon power-driven Godet, a set of spray pipes 76 may be provided and these pipes are designed to spray coagulant continuously over the rollers. A drip pan 77 receives any coagulant which may drip from the rollers. The drip pan is also provided with a discharge outlet 78, providing means whereby the liquid collected can be drawn off and if desired, returned to the sprays 76. It will also be apparent that the sprays from the pipes 76 may be charged with pigmentary material such as suspended carbon black designed to coat the filaments. This system of coating may be employed as an alternative to or a supplement to the application of powder in the hopper 63a, or to the application of suspended black in the terminal portions of the troughs 40a and 40b.

As shown in Fig. 1, means to collect the filaments from the Godet rollers 75 comprises a spool or reel indicated at 79 and being supported upon a shaft 81 in such manner as to admit of ready removal and replacement.

A spray pipe 82 may also be disposed contiguous to the spool or reel, in position to direct a spray of coagulant upon the filaments as they are taken up from the Godet rollers. This spray may also be made to function as a vehicle for deposition of carbon black upon the filaments. For purposes of attaining continuity of operation in extruding filaments, a second driven roller 83 may be disposed contiguous to roller 79 in such manner that when the latter has been filled, the filaments may be severed by shears S and the ends immediately trans-

ferred to the rollers 83. Roller 83 may also be sprayed with coagulant by pipe 84 similar to 82.

It will be appreciated that the spools or reels, after they have been filled, may be stored for substantial periods of time and for purposes of promoting further removal of the solvent of vinyl chloride polymer during this storing operation, they may be immersed in a static or a flowing bath such as a bath of petroleum naphtha designed to extract out additional solvents. A shower of naphtha could also be applied to the filament. If desired the bath or shower of coagulant could be partly or completely saturated with diisocyanate to prevent migration of the latter from the filaments while the solvent is being extracted.

However, if preferred, the spools or reels containing the filament may be dried immediately and to this end, an oven 85 best shown in Fig. 2 is provided. For purposes of illustration, it has been indicated as comprising a chamber 86, having a door 87, upon hinges 88, and being secured by an appropriate latch mechanism 89. Within the oven is disposed a shelf or series of shelves or other appropriate racking mechanism 91, designed to support the spools or reels while they are being dried. For purposes of promoting the drying action, a warm gaseous medium such as air, or an inert gas such as carbon dioxide, may be circulated through the oven, as for example, through the inlet pipe 92 and outlet pipe 93. Manifestly the drying may also be promoted by the application of vacuum to the oven and to this end, pipe 92 is shown as being provided with an appropriate valve 94, by means of which the inlet 92 may be closed or at least partially closed to restrict the admission of gaseous medium to such rate as will admit of the maintenance of a desired degree of vacuum in the chamber. The chamber is also indicated as being provided with radiant heaters such as infrared bulbs 96 which may be used in the alternative or simultaneously with warm gases for maintenance of the desired temperature within the heating oven. During the operation of removing solvents and coagulents from the filaments, it is essential that the temperature be restricted to a moderate value to prevent cohesion between the layers of filament upon the spools or reels. Naturally, this permissible temperature will vary somewhat for different plastic materials, but it has been found in most instances, that if the temperature does not substantially exceed about 50° C. or 80° C. little or no permanent cohesion between layers is likely to occur.

After residual solvent and coagulant in the filaments has been sufficiently reduced or completely eliminated in the drying operation, the tendency of the filaments to cohere is greatly reduced so that if proper precautions are observed, they may be heated to a much higher temperature as for example about 150° C. to 200° C. or 225° C. to admit of attaining curing of the filaments through the esterification reaction between the hydroxyls in the polyvinyl chloride and the cross-linking agent. In many instances, adequate protection to prevent cohesion between the turns of the filaments during the curing operation is attained in the pigmentary coatings already referred to. However, in event that it is not desirable so to coat the filaments, or as a supplementary precaution the reels or spools containing the filaments may be immersed in a relatively nonvolatile, nonsolvent medium such as a mineral oil which can be heated to the curing temperature of the filaments without danger of undue evaporation or decomposition. To this end, the reels or spools may be introduced into containers appropriately charged with such oil in an amount to cover them. Subsequently, the containers can be heated in an oven to effect the curing operation. The oven may be the same as that employed in the drying operation, though of course at a higher temperature level such as is required to effect curing or cross-linking between the plastic material and the cross-linking agent such as one of the

diisocyanates. Preferably a separate oven is employed to permit concurrent drying and curing operations.

The time required for adequate curing will depend upon the degree of insolubility desired in the filaments and the temperature at which the curing operation is conducted. In any event, the cure should not be so prolonged as to attain an excessive degree of brittleness of the filaments. Usually curing can be completed in a period of about 5 minutes to 4 or 5 hours and the necessary time and temperature can be determined approximately by the application of the rule that the curing rate is approximately doubled for each 10 degrees in rise of the curing temperature between the limits of 150° C. to 200° C.

As illustrated in Fig. 14, as an alternative to the use of the spools 79 and 83 for winding up the freshly spun and coagulated filaments, a container such as a can indicated at 97 may be disposed in such position that the filaments as they are taken off from the last of the Godet rollers 75 are allowed to drop therein. In order to reduce the possibilities of cohesion between the various convolutions of the filaments in the can, the latter may be filled with coagulant medium such as petroleum naphtha or with mineral oil. The filaments may be stored in the containers for some time in order to attain further removal of solvent medium by solution or if preferred, the filaments may be removed immediately upon the filling of the cans, for purposes of subjecting them to drying operations. In any event, the filaments either immediately or after an appropriate period of time, are wound upon spools or reels and are then subjected to a suitable drying operation and as for example in the oven indicated in Fig. 2. Ultimately the dried filaments are subjected to curing temperature in order to attain cross-linking with conversion of the plastic material into a tough insoluble state.

In event that it is desired to conduct the drying and curing operations upon the filaments in a continuous manner without recourse to spools or reels 79 or other collecting devices as an intermediate stage, an elongated, tunnel-like oven such as is indicated in Fig. 15 may be provided. This oven is indicated generally by the numerical 100, and is divided into a rear chamber 101 and a forward chamber 102 which are separated from each other by means of a suitable partition 103 having a slot 104 through which the tow of filaments can pass from one chamber to the other. The chamber 101 is provided with inlet conduit 106 and outlet conduit 107 by means of which gases at an appropriate temperature for drying the freshly spun and coagulated filaments can be circulated. Similarly the chamber 102 is provided with inlet and outlet conduits designated respectively as 108 and 109 for circulating a heating medium. It will be appreciated that the chamber 101 may be maintained under partial vacuum if so desired, in order to increase the rate of evaporation of solvents and coagulant which may be associated with the filaments. Concomitantly, or in the alternative to the application of heat to the filaments by contact with heated medium, the filaments may be heated by irradiation as for example by heating elements such as infrared lamps indicated diagrammatically at 111.

For purposes of admitting of shortening the length of the chambers 101 and 102 by providing a highly tortuous path for the filaments in their progress therethrough, a series of Godet rollers 112 is provided and filaments are trained back and forth between the rollers in such manner as to obtain a high degree of sinuosity of path. The number of rollers, and the total length of the oven should be so selected as to assure that at the working temperatures employed, the filaments will be adequately dried and subsequently cured by cross-linking action between the plastic and the cross-linking agent. The tendency of the filaments to elongate and then to contract while being cured, has already been mentioned. In

order to compensate for this tendency, it may be desirable to drive some of the Godet rollers at a faster peripheral speed than the others; for example, the first set or two of rollers in the curing oven may be speeded up enough to maintain reasonable tautness of the filaments at all times. Shears 115 provide means to cut the filaments into sections.

A further modification of apparatus for continuously drying and curing the filaments from the coagulating bath is shown in Fig. 16. This apparatus comprises a drying oven 120 disposable contiguously to Godet rollers 75 and being provided with slot 121 for entrance of the filaments. Godets 122 in the chamber carry the latter in a tortuous path through the chamber while they are dried by warm gases circulated through inlet 123 and outlet 124, or alternatively, by vacuum. Heating may be promoted by radiant heaters such as infrared lamps 126. The filaments may be drawn out of the chamber through slot 127.

They may be trained over a shoe or roller 128 down into a curing bath of oil or other medium heated to curing temperature and being confined in a vertically elongated chamber 129. The temperature of the bath is maintained at desired value by means such as tubular coils 131 through which a medium such as steam or a hot liquid may be circulated. Electrical heating coils might also be substituted for tubular coils 131.

The filaments in tough, insoluble cured state may be trained away from the bath by driven rollers 132. They may be severed into bristle lengths as they are cured by a set of shear blades 133. These are only diagrammatically indicated in the drawings and may manually be operated; but may also be fully automatic, as will be well understood. The shears 133 or 115 may embody the cutting and sensing mechanism as disclosed in Gregory Patent 2,356,841. If preferred, the filaments may be spooled up for cutting into bristle lengths in a subsequent operation.

In Fig. 17 is diagrammatically shown a simple mechanism by use of which the rate of take-up of the filaments may be varied periodically to produce nodes and anti-nodes in the filaments corresponding to the butts and tips of bristles. In this mechanism, the filaments pass over spaced shoes or rollers 135 between which rotate a driven cam roller 136 having peak portions which as the roller rotates, alternately increases and relaxes the pull on the filaments to produce the nodes and anti-nodes. The filaments pass over Godet rollers 137 to reels for drying or to a continuous dryer. With this embodiment of apparatus, the variable delivery pump mechanism 22 may be eliminated.

The preparation of an illustrative spinning solution of hydrolyzed interpolymer of vinyl chloride and vinyl acetate and the subsequent steps of converting the same into useful brush bristle stock will now be described. The interpolymer resin in this instance comprised so-called Vinylite VAGH already referred to and containing 91 percent vinyl chloride, 3 percent vinyl acetate and 2.3 percent hydroxyl. The latter was equivalent to 6 percent vinyl alcohol.

A spinnable solution was of the following composition:

Vinylite VAGH	125 grams.
Tetrahydrofuran	140 grams.
Mineral spirits	35 grams.
Toluene 2,4-diisocyanate	4.5 percent based upon the total mixture.

The mineral spirits employed was of a flash point of about 380° C., and had a boiling point of about 149° C. The K.B. value was below 40.

The solution of resin was prepared by wetting the latter with the mineral spirits and the toluene 2,4-diisocyanate. The latter agent could be added at a subsequent stage, if so desired. So long as it is not in the solution, there is no danger of premature gelling of the latter.

The tetrahydrofuran was added and the mixture was heated under its own vapor pressure at 50° C. for 7½ hours. A homogeneous, bubble free solution was obtained. Agitation was found convenient in dispersing any lumps of resin present in the solution. The solution was then allowed to stand over night at room temperature, and was ready for spinning.

In the spinning operation, the solution of resin was introduced into the tank 20. A pulsating pressure could be employed in spinning. The coagulating bath was charged with mineral spirits, such as that above described. The solution was extruded through orifices of the shape shown in Fig. 5 at a rate to form filaments of a length of 10 feet per minute. The solution during the extruding operation was at a temperature in a range of 21° C. to 32° C.

The filaments after emergence from the bath, were tacky and they were traveled for some distance in the air on the Godet rollers 75 in order to permit evaporation of some of the solvent, whereby to obtain a non-tacky state. Cohesion between convolutions of strands or between separate strands could be reduced if desired, by spraying the rollers as indicated with mineral spirits. In this particular instance the filaments from the Godet rollers were wound on metal reels and were allowed to air dry in order to eliminate mineral spirits and tetrahydrofuran in so far as was practicable. Subsequently the filaments were heated to a temperature of from 50° C. to 70° C. until all or substantially all of the solvents were eliminated.

Doubtless, during this time the cross-linking between the vinyl resin and the diisocyanate had been initiated. However, it was found that continuance at a temperature of 50° C. for 24 hours was not sufficient to remove all tack from the filaments. In order to complete the cross-linking operation, the filaments on the reel were wet with mineral oil at room temperature or thereabouts, in order to eliminate tack during subsequent curing operations. For purposes of attaining a complete cure of the freshly formed filaments, the rack containing them was immersed in a mineral oil bath which was heated at 150° C. in an oven such as 85 for 4 hours in order to obtain a good cure in which the filaments were tough, flexible and resistant to the action of solvents. When curing was initiated, the threads or filaments relaxed or stretched to a substantial degree, but as curing progressed, they returned to their original length.

The filaments so spun were of an average diameter of about 0.005 to about 0.030 inch. Filaments of other diameters using the same apparatus and materials could be formed.

The filaments obtained could be cut into desired length for brush bristles.

As previously indicated, these bristles are heat sensitive at least to such temperatures and for such long periods of time as are conventionally employed in the vulcanization of rubber cements employed to bond conventional bristles in the brush ferrules. Accordingly, in the manufacture of brushes, a cement which was a polyether of isopropylidenediphenol and epichlorohydrin was employed. This cement was a commercial product of rather short chain length, sold under the commercial name of A5 Stabilizer. Before the cement was applied to the bristles, a hardening agent namely diethylene triamine in an amount of about 10 percent based on the mixture was added. The resultant material is capable of curing at room temperatures, or at least at very mild temperatures, so that the curing thereof does not result in embrittlement of the bristles.

A brush constructed as above described is illustrated in Fig. 19 and comprises handle 140, ferrule 141, and a bristle knot 142, of hydrolyzed vinyl chloride-vinyl acetate interpolymer bristles which have been rendered tough and insoluble by toluene diisocyanate. These bristles

may be tapered as for instance to a taper ratio in a range of about 1.3:1 to 2.5:1. The higher figures represent butt diameters, the lower ones are tip diameters. These are held firmly in place by cement layer 143 of the above mentioned cement. This to some extent permeates between the butt portions of the bristles.

The doubly tapered sections of the filaments illustrated in Fig. 10 may also be employed as for example in forming bristle strips or in annular brush sections where they are doubled about a filamentary core to lock them between suitable clamping walls.

While the filaments prepared by the techniques herein disclosed are particularly satisfactory in the formation of brush bristles, it is to be recognized that similar techniques may also be employed in the spinning of various fibers such as may be employed in the weaving of fabrics, for cordage and for many other applications. For example, the vinyl chloride-hydrolyzed vinyl acetate interpolymers as herein disclosed may be formed into solutions with cross-linking solutions such as the diisocyanates, e.g. tolylene diisocyanate, and employed to spin various fibers used in the weaving of fly screens and for many other purposes. Obviously, for these purposes, the use of fluctuating pressures or other means of creating variable denier in the fibers is not required. The fibers may also be of any desired shape, e.g., circular. Fibers containing the cross-linking agent such as tolylene diisocyanate regardless of the subsequent applications to which they are to be placed may successfully be heated to drive off solvents and subsequently cured by the techniques herein disclosed, to provide filamentary bodies of high toughness, strength and resistance to various chemical agents.

The forms of the invention as herein disclosed are to be regarded as being by way of illustration rather than limitations. It will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

We claim:

1. In the method of forming tough, insoluble filaments which are adapted to be cut into sections and used as brush bristles, the steps of forming in a solvent selected from the group consisting of:

Tetrahydrofuran
n-Butanol
n-Butyl acetate
Monobutyl ether of diethylene glycol
Acetate of monobutyl ether of diethylene glycol
Monobutyl ether of ethylene glycol
Monoethyl ether of diethylene glycol
Monoethyl ether of ethylene glycol
Acetate of monoethyl ether of ethylene glycol
Diethyl ether of diethylene glycol
Diisobutyl ketone
Ethyl acetate
Ethylene dichloride
2-ethylhexyl acetate

Methyl amyl acetate
Methyl isobutyl ketone

Mixture of:

Methyl isobutyl ketone ----- 25%
Isopropanol (anhydrous) ----- 25%
Toluene ----- 50%

Mixture of:

Methyl isobutyl ketone ----- 20%
Isopropanol (anhydrous) ----- 30%
Toluene ----- 50%

a solution of (1) tolylene diisocyanate, (2) an interpolymers, said interpolymers being of approximately 91 percent of vinyl chloride and approximately 3 percent of vinyl acetate, and being hydrolyzed to provide approximately 2 percent to 5 percent based upon the interpolymers of hydroxyl groups, the solution being of a viscosity of about 60,000 to 120,000 centipoises at 25° C., extruding the solution through spinneret orifices into a coagulating bath of mineral spirits to form a filament, withdrawing the filament from the bath, drying the filament and heating the same to a temperature of about 150° C. to about 225° C., whereby to effect curing thereof.

2. In the method of forming tough, insoluble filaments adapted to be cut into lengths to form synthetic brush bristles, the steps of forming a solution comprising (1) tolylene diisocyanate 10 to 25 parts by weight, interpolymers resin about 115 to about 140 parts by weight, said interpolymers resin being of about 91 percent of vinyl chloride and about 3 percent of vinyl acetate, and being hydrolyzed to provide about 2 percent to about 5 percent of hydroxyls, the tolylene diisocyanate and interpolymers resin being dissolved in about 140 parts by weight of tetrahydrofuran and from 0 to about 35 parts by weight of mineral spirits, said solution being of a viscosity of about 60,000 to about 120,000 centipoises at a temperature of about 25° C., extruding the solution through a spinneret orifice into a coagulating bath of mineral spirits to form a filament, withdrawing the filament from the bath, drying the filament and heating the same to a temperature of about 150° C. to about 225° C. to effect curing thereof to a tough, insoluble state.

References Cited in the file of this patent

UNITED STATES PATENTS

50	2,221,316	Shepherd -----	Nov. 12, 1940
	2,271,102	Lewis -----	Jan. 27, 1942
	2,277,083	Dorough -----	Mar. 24, 1942
	2,320,704	Peterson -----	June 1, 1943
	2,327,872	Dahle -----	Aug. 24, 1943
55	2,341,823	Smith -----	Feb. 15, 1944
	2,408,718	Haux -----	Oct. 1, 1946
	2,512,726	Penn -----	June 27, 1950
	2,605,509	Dreisbach -----	Aug. 5, 1952
	2,712,490	Stuchlik -----	July 5, 1955

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,923,598

February 2, 1960

Joseph J. Reis, Jr., et al.

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

Column 7, line 73, for "thta" read -- that --; column 8, line 18, for "spung" read -- spun --; line 19, for "constructions" read -- constrictions --; line 20, for "of" read -- or --; same column 8, line 29, for "andd riving" read -- and driving --; column 12, lines 42 and 43, for "numerical" read -- numeral --.

Signed and sealed this 3rd day of January 1961.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents