Sept. 10, 1968 P. M. DAUGHERTY ET AL 3,400,998

FOUNTAIN PEN HAVING A POROUS ROD TYPE NIB

Filed May 17, 1965 2 Sheets-Sheet 1

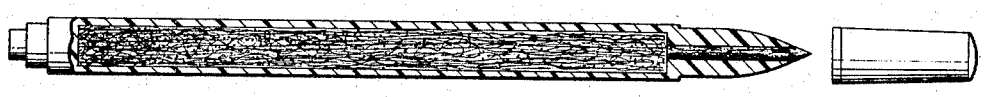

FIG. 1

FIG. 2

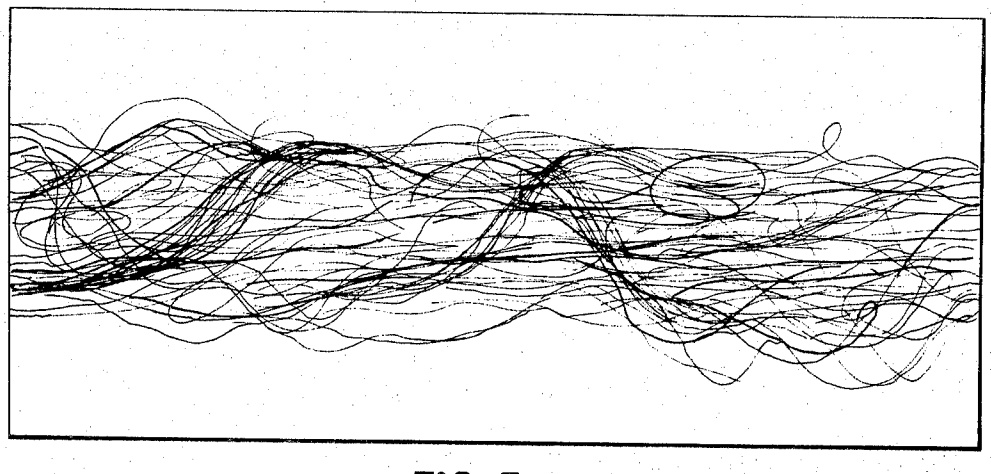

FIG. 3

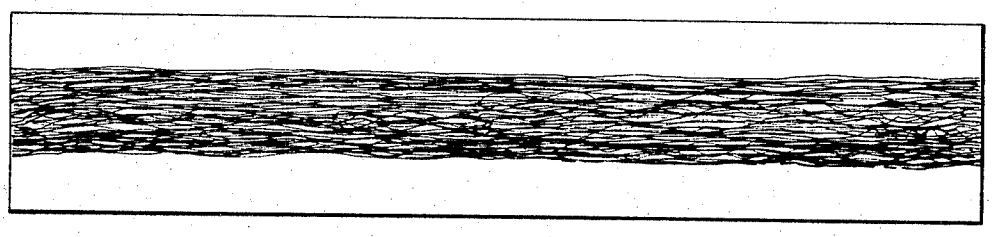

FIG. 4

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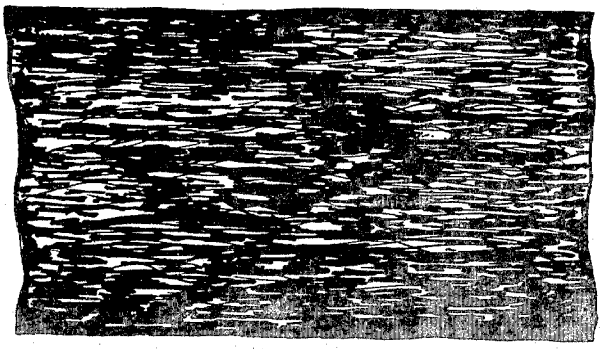

FIG. 5

FIG. 6

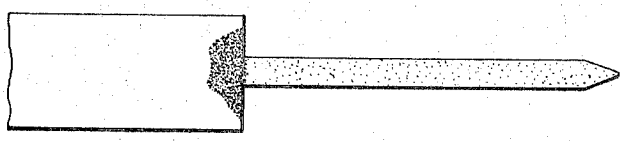

FIG. 7

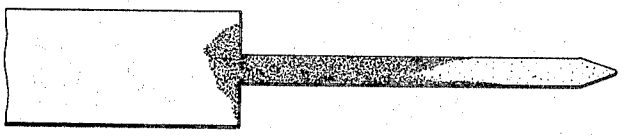

FIG. 8

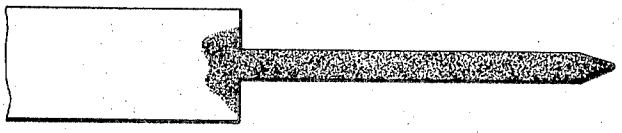

FIG. 9

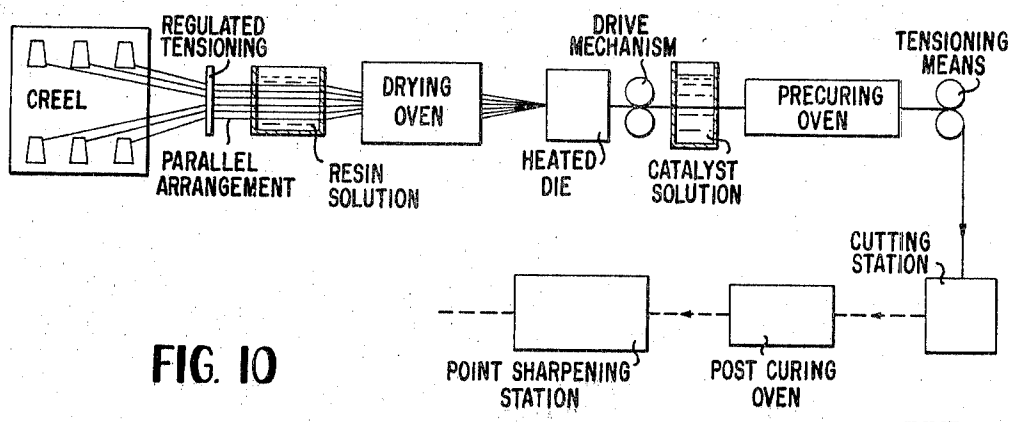

FIG. 10

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FOUNTAIN PEN HAVING A POROUS ROD TYPE NIB

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4 Claims. (Cl. 401—198)

This invention relates to writing instruments, and more particularly to a fountain pen having a barrel forming an ink reservoir and a nib extended from said barrel and communicating with said ink reservoir, wherein the nib is a porous substantially rigid rod made up of a bundle of longitudinally arranged tows of highly bulked, kinked and twisted polyester filaments bonded together with epoxy resin to form a micro-reticulated structure having substantially uniform interconnecting interstices of capillary dimensions for dispensing said ink to a writing surface.

The term "continuous filamentary, highly bulked tow" as used in this specification and the appended claims, means a material such as that which results when filaments spun from a plurality of spinnerets are brought together, bulked or textured, and combined preferably with filaments from other spinnerets, to form a continuous body of fibers "randomly oriented primarily in a longitudinal direction." The term "randomly oriented primarily in a longitudinal direction" as used in this specification and the appended claims, is intended to describe the condition of a body of fibers which are as a whole longitudinally aligned, and which are, in the aggregate, in a parallel orientation, but which have short portions running more or less at random in a non-parallel diverging and converging direction.

The nib structure is referred to as a fiber nib or fiber tip. Straight and textured filaments have been employed. The preferred filament, highly bulked polyester fiber, referred to commercially as "stretch" Dacron may be obtained from Madison Throwing Company, Madison, N.C. This highly bulked polyester fiber is used as received and it is known to contain approximately 3% of a lubricant. This lubricant is a proprietary material used to make the bulky fiber process more easy on textile machinery.

The preferred resin materials are those derived from bisphenol A and epichlorohydrin. These preferred epoxy resins are generally selected to have a molecular weight of 800 to 1500 and to possess both hydroxy and epoxide functional groups. The above refers to the uncured or raw meltable, resinous materials and not to the final thermoset resins that are produced upon curing, or hardening, in combination with the filaments during production of the rod.

The curing, or hardening, of the bonding epoxy resins within the fibrous structure can be brought about by means of polyfunctional amines, anhydrides and the like, but with the process to be described, the preferred agent to effect curing of the resin is boron trifluoride. The actual material employed is the complex formed by neutralizing the boron trifluoride with monoethylamine; the active boron trifluoride being released from the complex at the proper time during the process by the application of heat sufficient to decompose the complex and to rapidly effect cure of the resin.

It has been found advantageous to employ quantities of phenolic material, such as bisphenol A, as accelerators and to use certain modifiers in the system. Modifiers include, for example, tertiary amines containing hydroxyl groups which have been used to promote polymerization and crosslinking of the resin. A specific hydroxyl containing tertiary amine that has been found useful is N,N,N',N' tetrakis (2-hydroxypropyl) ethylene diamine.

The features of the writing instrument of the present invention having a porous rigid rod type nib and the method of producing same are illustrated in the accompanying drawings, in which:

FIG. 1 is a photograph of the cross section of the writing instrument of the present invention with the cap removed;

FIG. 2 is an enlarged photograph of the porous rigid rod type nib;

FIG. 3 is a 15 power photomicrograph of a tow of highly bulked, kinked polyester filaments in a relaxed state;

FIG. 4 is a 54 power photomicrograph of a tow of highly bulked, kinked polyester filaments placed under tension;

FIG. 5 is a partial longitudinal cross section of the porous rigid rod type nib;

FIG. 6 is a transverse cross section of the porous rigid rod type nib showing the micro-reticulated structure having substantially uniform interconnecting interstices of capillary dimension;

FIG. 7 is a dry porous rigid nib in initial contact with the capillary element of the writing instrument containing a liquid ink supply;

FIG. 8 shows the progressive travel of the ink through the porous nib due to the capillary action;

FIG. 9 shows the fibrous nib fully saturated with liquid ink; and,

FIG. 10 is a flow chart showing the method of producing the porous rod of the present invention.

In reference to FIG. 10, which illustrates the flow chart incident to the process of producing the nib material of the present invention, it will be seen that the process consists of arranging a plurality of continuous kinked and twisted filamentary highly bulked polyester tows in substantially parallel arrangement, from a suitable creel and then placing said parallel tows under a regulated tension and impregnating said tows with a solution of an epoxy resin, a preferred epoxy solution containing a resin having a molecular weight of 875, a hydroxyl functionality of 6, and epoxide equivalent weight ranging between 450 and 525.

The use of a solution serves to insure a uniform application of a limited quantity of the resin binder to the surface of the filaments. The "soaked" filaments are pulled vertically upward from the resin solution and passed as a loose bundle through a drying oven where the major portion of the solvents employed to dissolve the resin is removed. The bundle of filaments are then pulled through a heated die which effects fusion of the resin and compacts the "stretch" filament material into the desired rod shape. The rod-like structure then passes through an aqueous solution of the catalyst, BF_3—$C_2H_5NH_2$, wherein the capillary structure absorbs the catalyst solution. The rod, saturated with the catalyst solution, then passes through the pre-curing oven. The elevated temperature in the pre-curing oven removes the moisture that was absorbed during the passage through the catalyst bath and releases the boron trifluoride which in turn promotes the cure of the epoxy resin to a rigid matrix. A tension mechanism operates at the base of the curing oven to maintain the rod in a straight configuration as it passes through the oven. The partially cured rod, at this point, is quite strong and can be easily handled. The strength and rigidity at this point permit the rod-like structure to be cut to convenient lengths for post curing to obtain its ultimate strength.

As mentioned previously the preferred epoxy resin has a molecular weight range of about 800 to 1500 and possesses both hydroxyl and epoxy functional groups. The concentration of the resin used is interdependent upon the number of ends of the filament used and upon the

diameter of the rod desired. For purposes of illustration it will be assumed that the desired rod size is to be 0.060 inch in diameter. The resin concentration should then be chosen to fall within the range of 2.0 to 10.0 percent. This solution is maintained at ambient temperature.

The number of ends for the production of a 0.060 inch diameter rod will be selected from the range 40 to 60 for the 2 x 100 denier, 34 filament "Dacron" yarn. This solution is maintained at ambient temperature.

The temperature at which the dryer is operated will range between 100° F.–180° F., provided the speed at which the material is passed through the system is held between 7 and 10 inches per minute. It is desirable not to obtain complete dryness of the fibers as they pass through this portion of the system as trace amounts of the solvents aid in lubricating the molten resin-fiber combination as it passes through the die. Too much solvent remaining in the fibers, however, will interfere with proper absorption of the catalyst solution at the next stage of the process. At speeds higher than 10 inches per minute it is desirable to use drier temperatures of up to 220° F. to obtain optimum drying. It should be apparent that the actual temperature required will be dependent upon the construction of the drier as well as upon the rate of passage of the fiber.

The catalyst solution is maintained at a concentration of about 3 to 6 percent boron trifluoride-ethylamine and it is advantageous, but not entirely necessary, to include small quantities of a wetting agent in the catalyst solution. Amounts up to about 1.0 percent of a non-ionic wetting agent is adequate for proper absorption of the catalyst. A suitable wetting agent is an alkylphenoxy polyethoxyethanol, commercially available as Triton X–100, manufactured by Rohm & Haas Company, Philadelphia, Pa.

The catalyst uptake should be regulated so that the catalyst solution is used at a rate equivalent to 0.1 to 0.3 the rate of depletion of the resin solution, if the concentration of the boron trifluoride complex is in the range lasted above. This regulation is obtained by adjusting the amount of wetting agent utilized and by adjusting the degree of drying of the fibers as they pass through the dryer tube.

The catalyst solution is maintained at room temperature.

The die (in the case being considered the die is 0.059 inch in diameter) may be constructed of a number of materials and is conveniently a brass block with an insert of hardened steel. The selection of a hardened steel insert was made because of the ease of obtaining a highly polished, hard wearing surface. The temperature of the die is maintained at 430° F. to 460° F. Below 430° F. the rod produced may not be sufficiently bonded to maintain a cylindrical configuration while passing through the drive mechanism. Above 460° F. it is difficult to maintain continuous operation because at this high die temperature the "Dacron" fibers lose strength with the result that the material is frequently pulled apart in the die.

The drive mechanism is adjusted to give a flow of material through the system of about 7 to 10 inches per minute. This rate of production is intended to provide a basis for example and is not meant to imply that this is the optimum rate of flow of material through this system.

The pre-curing oven is operated at approximately 300° F. to 450° F. and the residual time of the material in the oven should be of the order of at least 10 to 12 minutes. Under these conditions the rod structure should be sufficiently sturdy to permit cutting to convenient lengths for post curing.

The tension device which maintains the straight configuration of the material as it passes through to pre-curing oven is adjustable so that a very slight "tugging" effect is initiated when any movement (of the rod-like material) other than vertical is detected.

The post curing of the rod, usually cut to approximately the final desired length, is accomplished by heating at 350° F. to 475° F. for periods of 1 to 2 hours. It should be obvious to one cognizant with curing or hardening of epoxy resins that lower temperatures for greater periods of time could be used to effect this post cure. Temperatures significantly higher than the above range will not be beneficial and, in fact, may be detrimental to the structural strength of the final fiber nib.

After post curing the rod-like material may be pointed by dry or wet grinding; for example, with a coarse silicone carbide grinding wheel. Microscopic examinations of the fiber nib structure are shown in FIGS. 5 and 6.

It should be noted that the one drive mechanism serves both to pull the rod through the system to a point beyond the die and to push the formed rod throughout the remainder of the system.

Recall that the resin solution used was previously described as being dissolved in an organic solvent mixture. The solvent mixture used may not be critical, however, it has been found that mixtures of solvents containing:

	Parts
Xylene	40–60
Methyl ethyl ketone	40–60
"Carbitol" (monoethyl ether of diethylene glycol)	0–10

are useful with most epoxy resins of the desired molecular weight range, and in addition, such mixtures serve well to dissolve the additional materials, e.g., bisphenol A, that are also used.

Typical formulations of epoxy resin binder system that are useful:

	Parts
Xylene	45–48
Methyl ethyl ketone	45–48
Monoethyl ether of diethylene glycol	1–6
Bisphenol A	0.1–0.2
Epoxy resin (average molecular weight of 875, hydroxyl functionality of 6, epoxide equivalent weight of 450–525)	2–4

Typical catalyst solution to be used with the above formulation is:

	Parts
Deionized water	93–87
Boron trifluoride-ethylamine complex	3–6
Alkylphenoxy polyoxyethanol	.1–1

Microscopic examinations of the fiber nib structures so prepared as shown in FIGS. 5 and 6 show that the resulting structure is uniform in cross section and devoid of any large areas of accumulated resin and is remarkably free of any gross open areas. Sections cut longitudinally from the fiber nib structure show that the "bulked" texture of the original fibers is retained to a degree. This retention of the texture is believed to account in part for the uniformity of ink flow through the nib.

Since the nature of the resin coated "Dacron" fibers present in fiber nibs is such that there is a tendency for water to be repelled rather than attracted into the capillary structure, it has been found advantageous to utilize specially prepared inks for use with these nibs.

Typical formulations are:

Vehicle:	Parts
Water, deionized	100
Salicylic acid	0.01–0.10
70% sorbitol solution	0.5–2.5
An alkyl phenoxy polyethoxyethanol (wetting agent)	0.1–1.0

To this vehicle is added water soluble dyestuffs; the amount depending upon the intensity and shade required. Suitable dyes included:

Blue fluids.—2 to 8 pts. C.I. Acid Blue 93 added to 100 pts. of the above vehicle.

Red fluids.—2 to 8 pts. C.I. Acid Red 73 added to 100 pts. of the above vehicle.

Yellow fluids.—3 to 6 pts. C.I. Acid Yellow 23 added to the above vehicle.

Orange fluids.—4 to 8 pts. of a 1.5/3 mixture of C.I. Yellow 23 and C.I. Acid Red 18 added to the above vehicle.

Green fluids.—4 to 8 pts. of C.I. Acid Green 16 added to the above vehicle.

Purple fluids.—2 to 8 pts. of a 1/1 mixture of C.I. Acid Red 18 and C.I. Acid Blue 93 added to the above vehicle.

Brown fluids.—5 to 10 pts. of a 1/1.5/3 mixture of C.I. Acid Blue 95, C.I. Acid Yellow 23, and C.I. Acid Red 18 added to the above vehicle.

Black fluids.—8 to 12 pts. of a 4/2/3/2 mixture of C.I. Acid Blue 93, C.I. Acid Yellow 23, C.I. Acid Red 18 and C.I. Acid Green 16 added to the above vehicle, or, 7 to 10 pts. of a 3/6 mixture of C.I. Acid Blue 93 and C.I. Acid Black 2 added to the above vehicle, or, 5 to 9 pts. of a 3/1/0.75/0.5 mixture of C.I. Acid Black 41, C.I. Acid Violet 12, C.I. Acid Orange 7, and C.I. Acid Green 9 added to the above vehicle.

The fiber nib produced by this process has been found to function very well for transferring the above writing or marking fluids from a capillary type reservoir. A typical reservoir material is a loosely compacted, cemented, cellulose acetate capillary material similar to that commonly used for cigarette filters. To produce a writing or marking instrument, it is necessary only to contain the capillary material in a suitable pen barrel or holder, allow the writing fluid to be pulled into the reservoir by capillary action, and insert the fiber nib into the pen barrel so that it contacts the filled reservoir, all as shown in FIGS. 1, 7, 8 and 9. Alternately, of course, a predetermined quantity of the writing or marking fluid can be forced into the capillary reservoir by any convenient means.

The present invention has been described in detail above for purposes of illustration only, and is not intended to be limited by this description or otherwise, except as defined in the appended claims.

We claim:

1. In a fountain pen having a barrel forming an ink reservoir and a nib extending from said barrel and communicating with said reservoir, the improvement of said nib being a porous substantially rigid rod comprising a bundle of longitudinally arranged tows of highly bulked kinked and twisted linear polyester filaments bonded together with epoxy resin to form a micro-reticulate structure having substantially uniform interconnecting interstices of capillary dimensions.

2. In a fountain pen having a barrel forming an ink reservoir, a capillary element disposed within said reservoir, a supply of ink contained in said capillary element, and a porous substantially rigid rod type nib extending from said barrel and communicating with said ink supply, said nib comprising a bundle of longitudinally arranged tows of highly bulked kinked and twisted linear polyester filaments bonded together with epoxy resin to form a micro-reticulate structure having substantially uniform interconnecting interstices of capillary dimensions for dispensing said ink to a writing surface.

3. A fountain pen as claimed in claim 2 and further characterized in that said ink is an aqueous solution of soluble coloring materials containing a water soluble organic compound having an affinity for the resin coated fibrous surface of the micro-reticulate structure.

4. A fountain pen as claimed in claim 3, and further characterized in that said water soluble compound is an alkylphenoxy polyoxyethanol in a concentration of less than 1%.

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ROBERT W. MICHELL, *Primary Examiner*.