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POROUS APPLICATOR PREPARED BY BONDING THERMOPLASTIC FIBROUS FLOCK PARTICLES AT POINT OF CONTACT WITH THE AID OF A PLASTICIZER

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ABSTRACT OF THE DISCLOSURE

The invention is a pad or porous body consisting of an assembly of non-oriented thermoplastic, flock fibers, the body having interstitial voids of capillary dimensions, the fibers carrying a plasticizer bonding them into a cohesive bibulous body, and liquid in the voids and wetting the fibers, the liquid being dispensable from said body to a contacting surface.

This invention relates to porous liquid-containing applicator structures by which liquid may be applied to a solid surface by pressure between the surface and the applicator structure, and to compositons and methods for making such structure.

Applicator structures are generally useful wherever a liquid is to be applied to a solid surface in limited amounts as in the application of water to a remoistenable adhesive layer on labels, stamps, envelope flaps and the like; the application of medicaments or lotions to the body; the application of ink to printing devices; and the application of ink directly to an article or sheet to be marked as with an ordinary ink stamp. Porous applicator printing devices containing a supply of ink are commonly used as stamps, stamp pads and for similar printing purposes. Such devices generally consist of a resilient porous body having a surface corresponding to the character to be printed, and contain a reservoir of ink which is conducted to the surface through the porous structure. The present invention is particularly suited to the manufacture of such devices. Heretofore the manufacture of ink-containing printing, structures has generally involved the molding of a suitable resilient solid material in the presence of material such as a filler, blowing agent or liquid, which imparts a reticulated network of voids throughout the structure. Typical techniques are described in U.S. Patents 2,353,877 2,777,824 and 2,763,208.

The present invention provides a novel type applicator structure capable of retaining a relatively large quantity of liquid which may be delivered from the surface in controlled amounts and in which the supply of liquid may be replenished. The structure is durable to the extent of lasting many tens of thousands of applications and is both inexpensive and easy to manufacture. It differs in its basic structure from prior art devices in that the liquid-retaining regions are formed without the aid of any additional pore-forming material. The invention also includes within its scope a moldable composition from which applicator structures embodying the invention may be made, and the process of manufacture.

The applicator structures of this invention accordingly represent significant advances over those heretofore known in being easily and rapidly formed under low pressures. This factor alone represents a considerable saving in the equipment required for processing, and in the simplification of the manufacturing process in avoiding high pressure operations and subsequent processing steps such as extraction of pore-forming material. The structures themselves are also superior to many in retaining the liquid well within the structure, with little at the surface, and in requiring a positive pressure beyond mere contact to deliver the liquid. The feature is particularly desirable in inked stamps where controlled amounts of ink are to be delivered, and excessive draining upon prolonged contact is to be avoided.

Applicator structures having many of the advantageous characteristics set forth above and described in Clancy, et al., U.S. Patent 3,019,201, which is owned by the assignee of this application. The present invention represents a continuation of the work of Clancy, et al., and presents improvements in several of the characteristics of this earlier structure. Specifically, the applicator structures of this invention will hold and retain several times the amount of liquid, is more readily replenished with liquid, and is less subject to deterioration with age and repeated usage.

The structure of this invention consists in general of a solid mat or pad made up of short thermoplastic fibers which are bonded together by a fusion together of fiber to fiber junctions brought about by means of a plasticizer for the thermoplastic. The fibers are of the type commonly used for flocking and may be composed of any of numerous plasticizable thermoplastic materials, such as cellulose acetate, nylon, Vinyon (copolymer of vinylchloride and vinylacetate), Dynel (copolymer of vinylchloride and acrylonitrile), or Orlon (acrylic fiber). Preferably the particular fiber will be of a material that is wetted by the liquid to be retained, and the plasticizer will be a liquid that is miscible with the liquid to be retained. In many cases the plasticizer will be of the secondary type, capable of swelling but not dissolving the thermoplastic material, and will itself constitute the vehicle for the liquid to be retained. For instance, in the application of this invention to ink pads, the coloring material may be dissolved in the secondary plasticizer, or alternatively the coloring material may be carried by a solvent which is miscible with the secondary plasticizer.

In order to effectuate adequate bonding of the thermoplastic fibers, the plasticizer should have sufficient solvent action to soften the fibers to the point where they will adhere to each other. At the other extreme, the plasticizer should not be so much a solvent for the thermoplastic material as to dissolve it completely, or swell it excessively, as that would destroy the integrity of the individual fibers. Accordingly, a plasticizer may be selected on the basis of its activity, which for any particular thermoplastic material is known or readily determined by those skilled in the art. Alternatively, primary, or solvent type, plasticizers may be blended with secondary, non-solvent type, plasticizers to produce the desired and necessary softening of the fibers. The bonding together of thermoplastic materials by plasticization is known to the art and does not of itself constitute the novelty of this invention. See, e.g., Berger, U.S. Patent No. 3,095,343.

Flock particles of thermoplastic fibers, which may be up to three millimeters in length and preferably between one-half and two and one-half millimeters, and less than one mil in diameter, e.g., of 1–35 denier, combined together in the manner in this invention provide a porous body having a continuous interstial volume of capillary dimensions which will retain between about twenty-five percent and five hundred percent of liquid based on the net solid volume. The structures are smooth surfaced, resilient and dimensionally stable, and are thus well suited for applying liquid to a contacting surface, in such uses as stamp pads and ink containing stamps. Their resiliency permits accommodation of surface irregularities without, however, smearing the ink beyond the confines of the character face. The capillary dimensions of the ink-containing interstitial region provides for uniform feeding of ink to the surface of the article, and also distributes

the ink into the body of the structure when ink is added for replenishment.

The structures in many ways resemble paper, in being composed of short fibers, but are quite different in presenting a much greater proportion of interstitial volume, in being far stronger in tensile and compression, and in being far more flexible than a paper product of comparable thickness.

The product of this invention may accordingly be characterized as a pad or porous body consisting of an unoriented assembly of thermoplastic fibrous flock particles, having interstitial voids of capillary dimensions, the particles carrying a plasticizer bonding them into a cohesive bibulous body, and an absorbed liquid wetting the particles and dispensable from said body to a contacting surface.

In general, the structures of this invention are manufactured by mixing the flock particles with from two to eight times their weight of a liquid which comprises a plasticizer and may also include the liquid to be dispensed. The slurry that is formed is molded to the desired shape and is then heated for a time and to a temperature sufficient to activate the plasticizer to cause the flock particles to stick together. As the plasticizer is predominately a secondary plasticizer, with only sufficient primary plasticizers, if any, to augment the plasticizing effect of the secondary plasticizer, and of limited solvent action, the excess, upon cooling, will be retained without being absorbed by the thermoplastic, and it may constitute the vehicle of liquid to be dispensed.

The following examples set forth preferred and representative embodiments of this invention as it may be practiced in the manufacture of stamp pads.

EXAMPLE I

Forty parts by weight of bright cellulose acetate flock, 3 denier, uncrimped, was mixed with 60 parts by weight of a liquid consisting of:

Plasticizers:	Parts by weight
Triethyl citrate	25
Glycol diacetate	25
Dye vehicle: Ricinoleic acid	10
Dye: Methyl violet base	5

The mixture was poured into a pan, the surface smoothed, and was then heated in an oven at 325° F. for two minutes. After removal and cooling, the pad thus formed served ideally as a stamp pad.

EXAMPLE II

A series of nylon base applicators was prepared using a mixture of primary and secondary plasticizers, in various proportions of liquid to solid.

The plasticizers consisted of:

Primary—10 percent solution of $CaCl_2$ in methanol [1]

Secondary:	Parts by weight
Nonylphenol	10
Dibutyl phthalate	50
Santicizer 8	50
(O and P-toluene ethylsulfonamide).	

[1] A calcium chloride methanol complex.

combined in the ratio of four parts by weight of Primary to 11 parts of Secondary.

The plasticizer mixture was mixed with nylon flock, (Nylon 66) in the proportions of 1.5, 3, 4, and 6 parts of plasticizer to one part of nylon by weight, and each mixture was heated for from 1–3 minutes at 150°–350° C. to cause the flock fibers to bind together.

EXAMPLE II–A

A similar composition was prepared containing a solid resin dissolved in the secondary plasticizer to act as a thickener. Higher liquid ratios could be employed.

The secondary plasticizer was the same as in Example II, but contained additionally 90 parts by weight of Santolite MHP (an aryl sulfonamide formaldehyde resin, described in U.S. Patent 2,938,292, column 4, lines 6–14.

Primary and secondary plasticizers (including the dissolved resin) were combined in the weight ratio of 4 to 20, and mixed with nylon in the ratios of 6 and 8 parts liquid (including dissolved resin) per part solid. The mixture was caused to bond into a porous pad in the same manner as described in Example II.

The pads of Examples II and II–A were tested as follows:

Ink release: 2" x 2" pads were subjected to 100 p.s.i. pressure until essentially all of the expressible liquid was removed. From the weight loss, the percent of the total ink that was removed was calculated.

Tensile strength: Samples 1 inch wide were tested in a Scott tester. The results were converted to pounds per square inch.

Hardness: Shore A Durometer

Penetration: ASTM method D5–52 with a 50 gram weight, 10 seconds at 75° F. The results are given in tenths of a millimeter.

Flexibility: Samples were bent 180° around a series of mandrels, each one successively smaller, until fracture occurred. The results are given as diameter at failure and thickness of sample.

TABLE I.—TEST RESULTS

	Ink release	Tensile	Hardness	Penetration	Flexibility (mm.)	
					Mandrel	Sample
1.5:1	42	----------	12	----------	35.7	----------
3:1	77.5	81.6	76	15	14.3	2.8
4:1	79.3	118	72	9	12.8	2.7
6:1	83.3	82.3	65	3	7.9	3.4
With resin:						
6:1	78.5	70.5	61	20	15.7	3.2
8:1	80	79.5	50	26	22.3	3.6

EXAMPLE III

Nylon stamp pads were prepared by mixing four parts by weight of nylon flock (Nylon 66) with a liquid made up as follows:

Primary plasticizer:	Parts by weight
175 pts. methanol.	
50 pts. $CaCl_2$	3
Secondary plasticizer:	
Nonyl phenol	1
Santicizer 8	5
Dimethyl phtholate	5
Colorant: nigrosine base	1
Color developer: salicylic acid	1

The salicylic acid is dissolved in the secondary plasticizer mixture, and the nigrosine is then added, followed by the primary plasticizer. Solution is poured over the nylon flock, mixed thoroughly, placed in a pan and heated to about 150° C. for 1–3 minutes.

The following process was found to effect a smoother pad than that discussed above.

Holes 1/16" in diameter were punched in the bottom of a metal stamp pad container. A uniform slurry of nylon flock in methanol was prepared (approximately 200 grams methanol, 10 grams nylon flock (by mixing on a Waring Blendor. The slurry was then poured into the perforated container and smoothed under hand pressure. Subsequently, the filled container was dried at 100°C. The plasticizer-dye containing solution was poured on to the nylon in the container in the proper ratio (4 parts solution, 1 part nylon). The tin was heated to approximately 100° C. on a hotplate for approximately 3 minutes.

The plasticizer component in Example II–A includes a dissolved resin which serves to body or thicken the liquid component, which is present in a relatively high proportion. In general, in compositions which contain a high proportion of interstitial volume, the capillarity of the solid matrix is frequently diminished because of the relatively larger interstitial channels, and the incorporation of thickening agents and materials to increase the surface tension of the liquid may be advantageous.

Although this invention has been described with specific reference to its preferred embodiments, it is contemplated that obvious modifications will readily occur to those skilled in the art and familiar with the principles herein disclosed, and that such may be made without departing from the scope of this invention.

Having thus disclosed my invention, I claim and desire to secure by Letters Patent:

1. A porous applicator structure for applying liquid to a contracting surface under pressure characterized in that the supply of the liquid in the applicator may be replenished, comprising a porous fibrous body formed of an essentially unoriented assembly of thermoplastic fibrous flock particles and a plasticizer therefor causing said particles to become fused together at fiber to fiber junctions into a cohesive bibulous mass having interstitial voids of capillary dimensions in which the fibrous character of said particles is essentially preserved, and a liquid compatible with said thermoplastic particles including a plasticizer therefor in addition to that bonding said particles together within said interstitial voids and expressible from said body under the pressure of surface contact, said interstitial voids containing between about 25 percent and 500 percent of liquid based on the volume of solid particles and said solid particles being less than 3 mm. in length and 1 mil in diameter.

2. The applicator structure defined by claim **1** wherein the particles are nylon.

3. The applicator structure defined by claim **1** wherein the particles are selected from the group consisting of cellulose acetate, nylon, vinylchloride-vinylacetate-copolymer, vinylacetate polymer, and acrylic fiber.

References Cited

UNITED STATES PATENTS

2,297,248	9/1942	Rudolph.	
2,371,868	3/1945	Berg et al.	
2,777,824	1/1957	Leeds.	
2,688,380	9/1954	MacHenry	401—198
3,039,908	6/1962	Parmele	401—198
3,094,736	6/1963	Bunzl et al.	401—198
3,111,702	11/1963	Berger	401—198
3,126,009	3/1964	Mahoney et al.	131—265

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