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3,427,277

METHOD OF MAKING PRESSURE-SENSITIVE LIQUID-DISPENSING DEVICE FROM POLYAMIDES AND ARTICLE THEREFROM**William J. Davis, Wyomissing, Pa., assignor to The Polymer Corporation, Reading, Pa., a corporation of Pennsylvania****No Drawing. Continuation-in-part of application Ser. No. 218,546, Aug. 22, 1962. This application Oct. 23, 1965, Ser. No. 504,218****U.S. Cl. 260—33.4****7 Claims****Int. Cl. C08g 51/66, 41/02; C09d 5/00****ABSTRACT OF THE DISCLOSURE**

Micro-porous gel-like irregular, unsymmetrical polyamide and liquid which is a non-solvent at room temperature and solvent at elevated temperature. Method of manufacture involves heating mixture to form a homogeneous liquid and cooling to gel. A substance to be dispensed from the gel, e.g., ink, is dispersed in the liquid.

This application is a continuation-in-part of my copending application Ser. No. 218,546, filed Aug. 22, 1962 now abandoned.

This invention relates to compositions, and methods for other manufacture, that have a self-contained supply of fluid material that will be expressed from the composition upon the application of pressure.

Compositions of this sort may be useful in dispensing numerous liquids such as inks, perfumes, deodorants, medicinal agents, and other like materials. While it should be understood that these devices may contain any such useful liquids, for simplicity, the invention will be described hereinafter with specific regard to ink filled materials that are particularly adapted for use as ink pads, ink rolls, marking stamps, printing platens, self-ink type, etc. It will be understood, however, that this is not done by way of limitation and that the invention is equally applicable to other liquid fillers which are intended to be included within the scope hereof.

Porous inking devices and structures are known to the prior art. Ordinarily, these devices are filled or impregnated with the inking medium only after they are in substantially finished form. It has also been proposed to produce inking devices having liquid-retaining regions, and with or without liquid ink present therein, with the aid of pore-forming agents. Further, vinyl plastisol and organosol compositions containing an incompatible inking vehicle in the fused state have also been used to produce a fused inking device.

In contrast to the above prior art devices and methods I have discovered an extremely simple solution method of forming inking devices that avoids the use of both solid and liquid pore-forming agents, complicated fusion procedures, and the provision of filling or impregnating the structure with ink only after it has been formed. In my device, the ink supply is formed in situ concurrently with the formation of the inking device itself. Moreover, I have discovered that by using certain synthetic polyamides as the essential ingredient, the finished device or article not only will dispense ink on demand, but also will exhibit excellent wear and toughness characteristic of polyamides, thus giving an unexpectedly long life to the inking device.

An object of this invention is to provide a method of making a pressure-sensitive liquid-dispensing device.

Another object of this invention is to provide a polyamide inking device having a long useful life with controlled exudation of ink to give very sharp images.

A further object of this invention is to provide a method

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of making a composition, and the composition per se, with liquid-dispensing properties.

A further object of this invention is to provide a composition useful in making liquid-dispensing devices.

Other objects of the invention will appear from the detailed description given below.

Describing the invention more particularly, the method involves mixing a powdered polyamide with a liquid which is a non-solvent for the polyamide at room temperature, but which is a solvent for the polyamide at elevated temperatures, and with a dye or pigment soluble in or dispersible in the solvent; heating the mixture thus formed, with or without agitation, to a temperature and for a time sufficient to dissolve said polyamide and form a homogeneous liquid; then cooling the homogeneous liquid to room temperature to produce a micro-porous pressure-sensitive ink-containing and -exuding gel-like structure. The hot homogeneous liquid can be poured, extruded, injection molded, or otherwise formed into the desired shape and configuration prior to cooling.

The following examples illustrate typical embodiments which are for the purpose of illustrating the invention.

Example I

The following materials were used in this example:

Ethylene glycol	cc.	60
Methyl violet base A dye	gm.	2
61 nylon ¹	gm.	10
Nylon blend E ²	gm.	10

¹ 61 nylon is a polyamide interpolymer or copolymer of $\frac{1}{2}$ part hexamethylene adipamide, $\frac{1}{2}$ part hexamethylene sebacamide, and $\frac{1}{2}$ part caprolactam. This was used in the form of a finely divided powder.

² A finely powdered blend of 60% type 6/6 nylon and 40% type 6 nylon.

The ethylene glycol was poured into a beaker and the methyl violet dye was stirred into it. The 61 nylon was then added to the beaker and stirred until wetted out, then the nylon blend E was added and stirred until wetted out. The contents of the beaker were then heated to 350° F. and occasionally stirred until a free-pouring homogeneous liquid resulted. This was then poured into several ink pad trays or molds and allowed to cool to room temperature under ambient conditions to form a gel. One of the trays was preheated to approximately 150° F. prior to pouring. After cooling, the resulting ink pads were used with conventional rubber stamps having molded raised letters and numerals. The transfer of ink from the ink pad to the rubber stamp was quite smoothly and easily accomplished with only slight application of pressure and the rubber stamp produced good, clear impressions. The stamp pad made in the preheated mold produced a slightly better ink pad. The pore size of the ink pads was in the range of from about 1 to about 3 microns.

Example II

The procedure and composition described in Example I were employed in this example with the exception that 72 cc. of ethylene glycol were used instead of 60 cc. and 3 gms. of methyl violet dye used instead of the previous 2 gms. The resulting ink pads were tough, had a pore size of about 1 to about 3 microns, and readily transferred ink to a stamp when applied against the surface of the ink pad. The stamp produced excellent impressions and imprints on many different grades of paper.

Example III

The following materials were used in this example:

Ethylene glycol	cc.	36
Propylene glycol	cc.	36
Methyl violet base A dye	gms.	8
61 nylon	gms.	10
Nylon blend E	gms.	20

The ethylene glycol and propylene glycol were placed in a beaker together with the dye and stirred until the dye was wetted out. The powdered nylons were then added with continued stirring until they were wetted out. The mixture was heated to approximately 350° F. and stirring continued until all lumps disappeared and a resulting free-flowing, homogeneous liquid was produced. This liquid was then poured into preheated roll molds and then cooled to form a gel.

This procedure produced an ink or inking roller which is useful for printing names and addresses or other indicia on sales slips or the like with a printing apparatus of the type shown in U.S. Patent 2,620,730. In this type of printing apparatus, a portable printing plate having raised characters is supported by one of two opposed members, the inking roller being carried by the other of said opposed members. A sales slip or the like, with or without a plurality of carbons, is interposed between the opposed members and the roller is then moved in a path substantially contiguous with the raised characters are imprinted upon the sales slip with one or more carbons also being produced, if desired.

The inking roller of Example III exuded ink from its surface only in those areas corresponding to the raised characters of the printing plate thereby giving a clear, legible impression without smearing or blotting.

In the above examples and in the claims, the term "homogeneous liquid" is intended to cover and include true molecular solutions as well as colloidal dispersions.

It is also noted that in the examples given above, the cooling operation may be carried out in molds which are at room temperature or with moderately preheated molds, e.g., preheated to a temperature of about 120–180° F.

While the exact theoretical basis for this invention is not fully understood, it would seem reasonable to suggest that something approaching a true solution is formed when the polyamide and solvent are first heated, and that upon subsequent cooling, a gel-like structure results. By definition, it can be understood that some intermolecular forces between polyamide chains are overcome during solution and the chains will have relatively complete mobility with respect to each other. Upon cooling, however, the solvation power of the solvent is reduced and intermolecular forces, particularly at the amide linkages, reassert themselves and tend to cause the polymeric chains to assume a somewhat fixed spatial relationship or orientation with respect to each other. If at this time solvent material is included within the orienting molecules, a gel-like structure will be formed in accordance with this invention. If, on the other hand, the intermolecular forces are sufficiently great to express or occlude the solvent from between adjacent molecules, the polyamide may precipitate from solution in the form of a fine powder.

From the above, it will be appreciated that the formation of a proper gel-like structure will depend to a major extent upon the selection of a suitable polyamide. As a generalization, it may be stated that the more uniform, symmetrical, straight chained polyamides with narrow molecular weight distributions have such strong intermolecular forces that it is difficult to form the gel-like structures of this invention. On the other hand, irregular, unsymmetrical polyamides, both branched and cross-linked, that have a wide molecular weight distribution are particularly suitable for use in the formation of these gels. The latter preferred polyamides are readily identifiable since they will generally exhibit characteristics of low crystallinity and a broad softening or melting point range.

A preferred class of polyamides that may be mentioned as being particularly suitable for use in this invention are those that are prepared by the amidization of polyfunctional amines, which preferably are at least trifunctional, and may be aliphatic, alicyclic or aromatic, and a mixture of di- and trifunctional acids that have been produced from unsaturated fatty acids or their esters by reductive oligomerization. Other of the known polyamides of at

least moderate molecular weight and mixtures thereof may be useful in this invention, and their initial selection may be based upon the above noted characteristics of low crystallinity and a wide softening or melting point range. The final choice of the particular polyamide used will depend upon the hardness and other properties desired in the final product.

Another group of preferred polyamides are copolymers and interpolymers. One such commercially available polyamide is prepared from approximately equal portions of hexamethylene adipamide, hexamethylene sebacamide and caprolactam (sold under the trade designation nylon 61 by DuPont).

The selection of a suitable solvent for use with a particular polyamide in forming the gel may also be of importance. Generally, the solvent is selected for its ability to solvate the polyamide at elevated temperatures as well as for its ability to form a relatively strong, stable gel. In some instances, it may be advantageous to use a mixture of solvents to obtain the advantages of both. As examples of solvents that are suitable for use in the practice of this invention, there may be mentioned alcohols, and especially the polyhydric alcohols such as ethylene, propylene and hexylene glycol, glycerine, and especially triethylene glycol. Also, while perhaps not solvents in the true sense, swelling agents such as epoxies and dioctylphthalate may be used effectively in some instances.

The proportion of solvent to polymer can be varied over wide limits depending upon the physical characteristics desired of the finished device. Generally, the proportions of polyhydric alcohol solvent will vary from 25 to 75% by weight of the entire composition.

In addition to the polyamide and solvent, it is contemplated that high boiling alcohols, low molecular weight polymers thereof, and various other suitable solvents may be added, as well as certain non-reactive additives to stabilize ink exudation and to control the hardness of the finished product. It is further contemplated that the finished product may be more suitable for use if supplied in a cross-linked state, either throughout the structure or merely a surface cross-linking, and to that end, minor amounts of known polyamide cross-linking agents may be employed.

In addition to dyes which may be used as the coloring or inking material, for example, methyl violet, methylene blue, methylene green, etc., it is also possible to use pigments dispersible in the polyhydric alcohol, e.g., carbon black, ultramarine blues and violets, chrome oxide greens, etc.

As mentioned above, it is also contemplated that the device of the present invention can be used to exude or transfer ingredients other than ink. For example, instead of incorporating ink or coloring material in the device, it is within the scope of this invention to include other ingredients dispersible or soluble in the polyhydric alcohol solvent, e.g., perfumes, deodorants, medicinal agents, etc.

I claim:

1. A method of forming a pressure-sensitive liquid-dispensing device that has a self-contained reservoir of a first liquid which comprises:

mixing a powdered synthetic irregular unsymmetrical polyamide with the first liquid and a second liquid, the second liquid being a nonsolvent for the polyamide at room temperature and a solvent for the polyamide at elevated temperatures;

heating the mixture at a temperature and for a period of time sufficient to form a homogenous liquid; and cooling the homogenous liquid to form a stable gel-like structure.

2. A method according to claim 1 wherein the first liquid is a marking fluid.

3. A method according to claim 2 wherein the marking fluid contains methyl violet.

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4. A method according to claim 1 wherein the second liquid is a polyhydric alcohol.

5. A method according to claim 1 wherein the polyhydric alcohol is ethylene glycol, propylene glycol, triethylene glycol, glycerine, or mixtures thereof.

6. A method according to claim 1 wherein the polyamide is an interpolymer consisting essentially of the polymerization product of hexamethylene adipamide, hexamethylene sebacamide, and caprolactam.

7. A form stable, pressure-sensitive, liquid-dispensing, gel-like structure comprised of a polyamide and a liquid that is a solvent for the polyamide at elevated temperatures and a nonsolvent at room temperatures wherein the polyamide is an interpolymer consisting essentially of the polymerization product of approximately equal

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molar portions of hexamethylene adipamide, hexamethylene sebacamide and caprolactam.

References Cited

UNITED STATES PATENTS

2,639,278	5/1953	Stott et al. -----	260—33.4
3,022,542	2/1962	Davis -----	260—2.5
3,055,297	9/1962	Leeds -----	260—33.4

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260—2.5, 37; 15—104.93

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,427,277

February 11, 1969

William J. Davis

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 3, the claim reference numeral "1" should read -- 4 --.

Signed and sealed this 24th day of March 1970.

(SEAL)

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