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METHODS OF MAKING POROUS APPLICATOR STRUCTURES

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FIG. 1

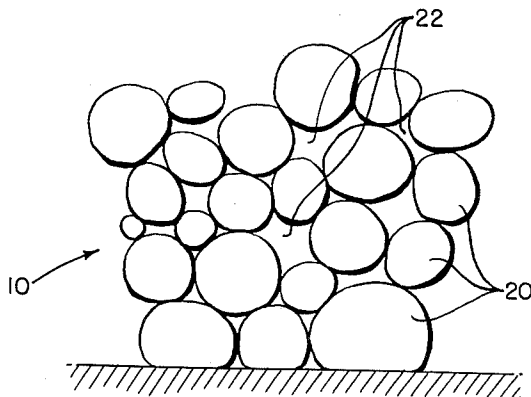
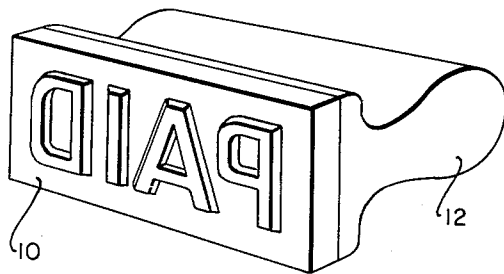


FIG. 2

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METHODS OF MAKING POROUS APPLICATOR STRUCTURES

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This invention relates to applicator structures of the type consisting of a porous resilient body containing a liquid which may be applied to a solid surface by pressing the applicator to the surface, and to compositions and methods of making such structures.

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 microporous 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. For best all-around purposes an applicator structure of this type should be easy to manufacture rapidly, as in a local stamp shop, and the final product should have as long a useful life as possible and should also be capable of having its supply or reservoir of liquid replenished from time to time.

The present invention provides a novel type of 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. This 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.

In general, the structures of this invention are formed of loosely packed, generally spherical particles of a re-

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silient material, preferably an elastomer, having a continuous interstitial phase consisting predominantly of the void that naturally occurs between packed spherical particles. This interstitial space is referred to herein by the term "intersphere region" and may occupy from about 15 to about 60 percent of the volume of the structure. In the applicator structure itself, the interstitial region will contain a supply or reservoir of liquid to be fed to the applicator surface. The intersphere region is accordingly of capillary dimensions which render it capable of retaining the liquid, but it may be visualized on a greatly magnified scale as being like the void space naturally occurring in a crate of oranges or apples imperfectly packed.

The structures of this invention are formed by causing particulate material consisting of generally spherical resilient particles to be combined into a porous solid in which the solid particles retain their generally spherical form, with the non-solid spaces being those naturally and inherently present between loosely packed generally spherical bodies. Preferably a slurry or paste of the solid particles in a substantially non-solvent liquid, which preferably contains a binder for the particles dissolved in the liquid, is formed and this is cast and molded to the desired shape and then caused to harden to an integrated body in which the resilient particles are adhered together. The porous solid structure thus formed is then saturated with the liquid intended for its use, but alternatively the liquid may have been included in the liquid phase of the slurry and retained within the product through the molding and curing steps.

The particulate material from which the structures of this invention are formed should be of a nature as to be wetted by the liquid to be dispersed and of such size, and size distribution, that when packed loosely under little or no pressure there exists an interparticle continuous intersphere region of suitable capillary dimensions capable of retaining the liquid and of being replenished when the liquid supply initially present has been depleted. The particles, however, should not be so fine as to form a network of colloidal dimensions as such would result in a loss of dimensional stability upon depletion of the liquid supply, and may not be readily replenished. For example, in preferred embodiments for ink stamps the particulate material is made up predominantly of particles larger than .001 inch diameter and less than .01 inch diameter. Their sizes may be distributed within these limits and by varying the size and size distribution, the texture of the printed image and the amount of void space may be varied, as is well understood in the art.

Material suitable as the solid portion of applicator structures of this invention include in general rubber and rubber-like materials which are resilient, relatively unaffected by the liquid contained within them, and otherwise stable under actual conditions of use. When the materials are thermoplastic and of a generally tacky character, as in the case of unvulcanized rubbers, they may be combined into the desired microporous structure simply by their own self-adherent characteristics, and then may be cured to provide a durable, stable article. Alternatively, a binder, such as a compatible resin, may be combined with the particulate material to hold the structure together. In this respect the invention may employ any of numerous well-known rubbery or rubber-like materials alone or in combination with resinous binders, and is not predicated on particular materials or combinations of them, as those are well known in the art. The invention is rather predicated on the physical association of generally spherical particles to provide a solid structure having a reticulated continuous network of capillary dimensions, and to compositions and methods for making such structures. By way of example,

the spherical particle may comprise natural rubber, synthetic rubber, such as copolymers of butadiene and styrene and copolymers of butadiene and acrylonitrile, polychloroprene, as well as other materials having similar elasticity and resilience, all of which may be referred to as "rubber-like" materials.

The use of a slurry or paste of the particulate generally spherical particles simplifies the molding or casting operation in providing an essentially liquid premix well suited for casting and molding, and in providing for the uniform incorporation of a binder material which may conveniently be dissolved in the liquid phase. Suitable binders include such materials as phenolic resins, epoxy resins, and isocyanate resins, to name but a few that are compatible with rubber-like materials of the type described. Binders may however be omitted entirely, where the rubber-like material in itself possesses self-adhering properties, as in the case of unvulcanized rubbers, or where the liquid phase contains a solvent or semi-solvent capable of softening the rubber-like particles, but without destroying their essential generally spherical nature. The incorporation of such solvent or semi-solvent may be used in conjunction with a binder to reduce the amount of binder required. Best results for casting and molding porous stamps are realized when the solids content of the slurry (including dispersed particles and dissolved binder) is between about 30 percent and about 50 percent by weight. The casting or molding operation should not in any case be carried out under pressures sufficiently high as to compress the particles at the sacrifice of the intersphere region, and this range of solids content is well adapted to such processing. Following the casting operation, the composition is cured, as by heating, to cause the binder to harden or the particles otherwise to be combined together by the hardening action of heat, as through vulcanization or polymerization. The particles are, however, not fused, since that would impair the formation of the desired intersphere region which depends on the particles retaining their essentially solid and generally spherical character.

The particles of rubber-like material are referred to as being generally spherical but are not necessarily truly spherical. A microscopic examination of suitable particulate material shows numerous particles that depart from true spheres in being flattened, elongated, or pear-shaped, and such departures from true sphericity does not render the material unsuitable as long as the particles are of a generally rounded smooth contour capable of packing with a relatively large interconnected interstitial void space. The term "generally spherical" is used herein to denote such particles, and to distinguish them from particles in the form of shreds, flakes, crystalline structures, and rough particles of the type obtained when solid material is comminuted.

The invention is described below as it relates to the manufacture and use of an ink-containing stamp. Reference is made to the accompanying drawings in which:

FIG. 1 is a view from the bottom showing in perspective a typical stamp of the type in which this invention may be embodied; and

FIG. 2 is an enlarged cross-section showing the apparent structure, somewhat schematically, as viewed at a high magnification.

Ink-containing stamps made in accordance with this invention constitute one of its many uses and typify the numerous advantages which are provided.

The preferred stamp is formed of generally spherical particles of a butadiene acrylonitrile copolymer containing about 40 percent by weight of acrylonitrile and a compatible phenolic resin which serves as a binder. The use of phenolic resins in conjunction with butadiene acrylonitrile rubbers is well known in the art and the composition employed herein is, with regard to its particular components, one with which the art is generally familiar.

Example 1

The preferred embodiment of this invention makes use of the commercial rubber product known as Hycar 1411 sold by B. F. Goodrich Chemical Company, and the phenol formaldehyde resin known as Durez 12687 sold by Durez Plastics and Chemicals, Inc. The rubber as supplied by the manufacturer may contain some non-rubber solids which are preferably first removed as by screening air separation or washing. A solution of the resin binder in ethyl alcohol, containing about 10-20 percent by weight of resin, typically 15 percent resin, is then added to the rubber, in an amount such that there is the proportion of 25 parts of resin to 100 parts of rubber, along with enough liquid to form a slurry of from 15 to 50 percent by weight, preferably from 30-42 percent solids. The liquid phase of the slurry may consist entirely of alcohol, but may also include small quantities of solvents capable of swelling the rubber particles, such as acetone, the presence of which has a tendency to strengthen the final product, and to reduce the amount of resin binder needed for optimum strength.

The slurry thus formed is molded by pouring it into an appropriate mold in which it is held under low pressure. The excess solvent is expressed from the slurry and the residual solvent is then dried from the slurry, and the molded article is finally cured in an oven at a temperature sufficient to combine the rubber and resin into a durable product, preferably after being removed from the mold. The Hycar-Durez composition described above may be cured sufficiently for practical purposes by heating it to about 300° F. for about 15 minutes, but longer and shorter periods of time at correspondingly lower and higher temperatures are also effective. In actual operation the still wet molded product is conveniently cured by placing it in an oven for one-half hour at 310° F.

After curing the molded stamp, it is inked conveniently by immersing it in a suitable ink, e.g. Carter's No. 1080, preferably heated, e.g. to 140° F., for about 2 hours.

The final product made as described above is exemplified in FIG. 1, which shows the ink-containing stamp applicator structure 10, with molded raised letters forming the word PAID as the stamp image. The letters are formed during the molding operation by using a mold having the reverse of the image on its bottom surface. A base 12, to which the stamp structure is mounted, provides a means for handling the stamp. Slight pressure to a surface to be marked will cause a printing of the word PAID.

The useful life of a stamp structure of this type will depend in part on its dimensions, which govern the total quantity of ink. A stamp of the type shown, about one-quarter inch thick with plan dimensions of about 2" x 1" will deliver about 20,000 impressions on a single inking, and may be reinked to deliver upwards of 40,000 impressions. The shelf life of the stamps is adequate from a commercial point of view and appears to depend largely on the stability of the particular ink employed.

The resin-rubber slurry from which the stamp is molded is itself a useful product which may be supplied in bulk to local stamp shops for use in the manufacture of custom stamps. The slurry composition is extremely stable and may be stored for a year or more prior to use.

The molding operation requires only simple stamp molding equipment, basically an open mold having a bottom formed to correspond with the desired insignia. The slurry is molded under low pressure, and, indeed, should not be compressed appreciably during molding lest the space between the particles be compressed and the ink retaining capacity be diminished. Sufficient pressure to assure adequate molding may be provided by pressing the slurry in the mold for a short period of time, and then releasing the pressure. A pressure between 5 and 10 pounds per square inch applied for 10-15 seconds is generally adequate to mold the slurry and express excess

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liquid. Higher pressures for short periods of time may be applied particularly if released prior to curing to permit recovery of the particles. As a general rule, it can be said that the pressure must not be sufficient to reduce substantially the volume of the space between the solid particles nor to disrupt their generally spherical character.

The foregoing formulation may be modified considerably, for instance compositions having proportions within the following range are entirely satisfactory:

	Parts by weight
Hycar (generally spherical particles)-----	100
Durez phenolic resin 2687-----	10-30
Alcohol -----	125-250

Ethanol is the preferred alcohol, but methanol and isopropanol, or mixtures of them, and other proprietary grades of alcohols, may also be used. Acetone and similar ketones may also be included as part of the solvent in small amounts, e.g. up to about 15 percent by weight based on total solvent. The presence of acetone tends to reduce the amount of resin required. The resin may also be reduced where less strength is required, for instance where the applicator structure of this invention is to be used as an ink pad for inking rubber stamps and the like, and may, in fact, be eliminated entirely.

In the following examples the use of various other rubber-like materials, with and without other resin binders, are illustrated. In each case the rubber-like material and resin (if any) are combined with the solvent to form a slurry. The slurry is then cast in a mold to form the stamp body which is cured by heating in an oven to the indicated temperature. In each case the rubber-like material was constituted predominantly, e.g. in excess of 90 percent by weight, of fine generally spherical particles between .001 and .01 inch in diameter.

Example 2

	Parts by weight
Hycar (generally spherical particles)-----	100
Epoxy resin—Bakelite EKRB 2002-----	30
Alcohol (methyl, ethyl or isopropanol)-----	125-250
Ketone (acetone, methyl ethyl ketone, cyclohexanone)-----	20-40
Curing temperature: 85-90° C. for 15 minutes.	

Example 3

	Parts by weight
Hycar (generally spherical particles)-----	100
Alcohol -----	250
Vinyl resin (Bakelite VAGH, VYHH mixture)-----	15
Vinyl resin solvent, 40/60 acetone-toluol mixture----	15

The vinyl resin dissolved in the solvent is added to the slurry of the Hycar in alcohol with vigorous agitation. The slurry is then molded, dried, and cured at 180-220° F. The product is relatively rigid and may be used advantageously as an ink pad, after being saturated with ink.

Example 4

	Parts by weight
Hycar (generally spherical particles)-----	100
Blocked isocyanate resin-----	9
Resin solvent 50/50 acetone-ethyl acetate mixture----	20
Curing temperature 140° C. for ½ hour.	

Example 5

	Parts by weight
Vulcanized generally spherical rubber particles ¹ precipitated from natural latex-----	100
Epoxy resin (Shell Epon 562, liquid)-----	10
Ethylene glycol-----	50
Curing temperature 80° C. for 10 minutes.	

¹ The precipitant for the latex contained an amine accelerator (dimethylolurea) for the epoxy resin.

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Example 6

	Parts by weight
Hycar (generally spherical particles)-----	100
Alcohol (commercial SD 30) -----	150
Acetone -----	15

The Hycar is dispersed in the alcohol-acetone mixture, by mixing in a Waring blender, and is then filtered out to form a filter cake, which is pressed with a flat disc. The cake is then dried at 80° C. for about 10 hours, and is finally impregnated with ink, for use, for instance, as a stamp pad.

Example 7

	Parts by weight
Hycar -----	50
Epoxy resin (Shell Epon 562, liquid) -----	10
Black stamp pad ink (Carter's No. 1080) -----	20-40
Curing temperature 80° C. for 15 minutes.	

Example 8

	Parts by weight
Vulcanized rubber particles precipitated from natural latex-----	10
Epoxy resin (Shell Epon 1001, 30% solution in acetone) -----	10
Black stamp pad ink (Carter's No. 1080) -----	2
Versamide 125, catalyst -----	1
Curing temperature 100-110° C. for 15-20 minutes.	

In the foregoing examples, the epoxy resins referred to in Examples 2, 5, 7, and 8 are reaction products of bisphenol and epichlorohydrin; the vinyl resins referred to in Example 3 are partially hydrolyzed copolymers of vinyl chloride and vinyl acetate; the blocked isocyanate resin referred to in Example 4 is a phenol blocked diisocyanate; and the Versamide used in Example 8 is a polyamide condensation product of fatty acids and a polyamine, useful as a curing agent for epoxy resins.

The microscopic details of structure of this invention are shown in a general way in FIG. 2, which is based on photomicrographs of actual specimens of the product of this invention. The drawing, however, indicates structure which is not clearly seen in the photomicrographs but is visualized as being present from the known character of the components and it should accordingly be viewed as presenting a schematic, rather than actual, representation of the details of the structure. What is shown is a porous solid lattice formed of the generally spherical particles 20, these being in mutual adherent contact by which physical integrity is imparted. Between these particles, and constituting from about 15-60 percent of the value of the structure, is the intersphere region containing the ink 22 or other liquid. In particular, it is noted that the intersphere region is completely and originally defined as the void, or non-solid, region which occurs between the loosely packed spherical bodies 20, and is not dependent on the presence of any other pore forming material. Even where the ink is originally present in the slurry and during the curing step, as shown in Examples 7 and 8, its presence does not contribute to the porosity of the structure. Its presence is a convenience that obviates subsequent inking but does not itself alter the form and orientation of the rubber-like particles. In this connection it should be noted that the solid spherical character of the particles is retained throughout the curing step without substantial change of form and without causing actual melting of the particles.

The dimensions of the particles are important in that they determine the dimensions of the intersphere region, and must provide for proper capillary absorption of the liquid. Permissible limits to their size will accordingly depend to some extent on the properties of the particular liquid, and on the amount of liquid to be applied with each impression. Where applicator structures of this invention are used for printing, as in stamps and the like,

the particle size will also bear on the fineness of the printed character. Generally particles at the smaller end of the workable range are most suitable for porous inked stamp applicators.

In use, the applicator structures of this invention provide for the delivery of uniform films of liquid to a surface upon contact, and also incorporate a metering effect that is brought about by the pressure of contact. This effect results from the fact that on contacts the particles are distorted and the liquid is squeezed out of the intersphere region and caused to flow to the contacting surface. The pressure on the particles adjacent to the surface may also be sufficient to cause them to flatten, or spread out, and thereby cause the channels between them to be narrower. The supply of liquid that can be delivered may thus be restricted by this closing of the passages leading to the interior of the structure while pressure is maintained. This effect, it will be understood, may not always be made use of, since frequently pressures less than sufficient to restrict the flow to the surface will be employed.

Although this invention is described with particular reference to its application to ink-containing stamps, its usefulness extends to any applicator structure intended to supply a film or layer of liquid upon surface contact. Thus other liquids than ink may be incorporated within the structure, it being only necessary that the latter be formed of a resilient material inert to, but wetted by, the liquid, and that the particles of the resilient material provide an intersphere region having capillary attraction for the liquid. Thus it is contemplated that numerous modifications of the structures, compositions and processes set forth in this specification will readily occur to those skilled in the art and that such may be made without departing from the scope of this invention.

Having thus disclosed our invention, we claim and desire to secure by Letters Patent:

1. The method of making a porous applicator structure comprising forming a slurry of generally spherical particles of unvulcanized tacky rubberlike material of which at least 90 percent by weight is constituted of particles between 0.001 and 0.01 inch diameter, and a liquid which does not substantially coat with said particles to cause a change to their dimensions or shape, molding said slurry, removing the liquid from said slurry, and finally heating said particles to cause them to adhere and become an integrated solid structure under sufficiently low pressure and temperature that the particles maintain their generally spherical character and form between them an intersphere region of capillary dimensions.

2. The method of making a porous applicator structure comprising forming a slurry of generally spherical particles of unvulcanized tacky rubberlike material of which at least 90 percent by weight is constituted of particles between 0.001 and 0.01 inch diameter, and a liquid which does not substantially coat with said particles to cause a change to their dimensions or shape, molding said slurry, and finally heating said slurry to cause the

particles to adhere and become an integrated solid structure under sufficiently low pressure and temperature that the particles maintain their generally spherical character and form between them an intersphere region of capillary dimensions containing said liquid.

3. The method of making a porous applicator structure comprising forming a slurry of generally spherical particles of rubberlike material of which at least 90 percent by weight is constituted by particles between 0.001 and 0.01 inch diameter, and a liquid which does not substantially coat with said particles to cause a change to their dimensions or shape, said liquid including a binder for said material, molding said slurry, removing said liquid from said slurry leaving the binder therein, and finally heating said particles and binder to cause the particles to adhere and become an integrated solid structure under sufficiently low pressure and temperature that the particles maintain their generally spherical character and form between them an intersphere region of capillary dimensions.

4. The method defined by claim 3 wherein the rubberlike material is a copolymer of butadiene and acrylonitrile, containing about 40 percent by weight of acrylonitrile, and the binder is a phenol formaldehyde resin.

5. The method of making a porous applicator structure comprising forming a slurry of generally spherical particles of rubberlike material of which at least 90 percent by weight is constituted by particles between 0.001 and 0.01 inch diameter, and a liquid which does not substantially coat with said particles to cause a change to their dimensions or shape, said liquid including a binder for said material, molding said slurry, and finally heating said slurry to cause the particles to adhere and become an integrated solid structure under sufficiently low pressure and temperature that the particles maintain their generally spherical character and form between them an intersphere region of capillary dimensions containing said liquid.

6. The method defined by claim 5 wherein the rubberlike material is a copolymer butadiene and acrylonitrile, containing about 40 percent by weight of acrylonitrile, and the binder is a phenol formaldehyde resin.

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