July 18, 1944. R. G. CHOLLAR 2,353,877

PROCESS FOR MAKING RESILIENT POROUS PRODUCTS

Filed Jan. 19, 1942

FIG. 1

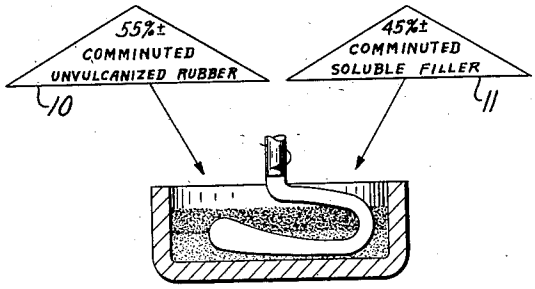


FIG. 2

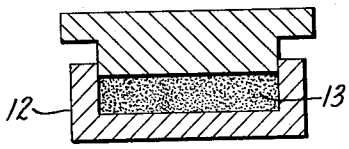


FIG. 3

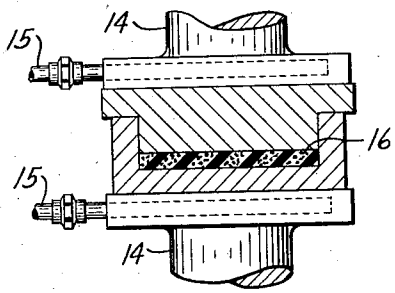


FIG. 4

FIG. 5

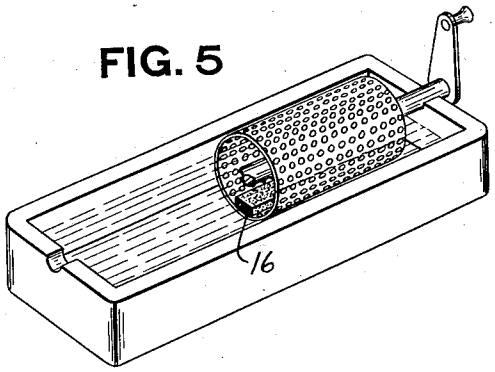
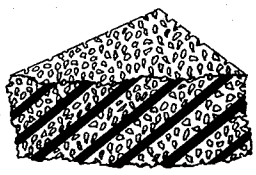


FIG. 6



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PROCESS FOR MAKING RESILIENT POROUS PRODUCTS

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10 Claims. (Cl. 18—53)

This invention relates to a process for making micro-porous rubber-like products and more particularly pertains to the making of rubber-like webs having interconnecting microscopic pores.

Although the invention is principally directed to a process for making micro-porous rubber webs for use in making ink-containing and ink-conducting printing plates, or inking webs, having the printing characters in relief thereon or in intaglio therein, the product is eminently suitable for other uses where micro-porous material of uniform pore size and having rubber-like qualities is required, such as, for instance, for filtering webs, for resilient porous partitions, for liquid passing separators more or less electrically and chemically inert, for wicks, or for porous fabricating material.

The process disclosed herein being directed principally to the making of printing plates or inking webs, the preferred rubber-like materials specified are the oil resisting butadiene co-polymers, which are chosen because of their resistance to attack by ink, particularly dye inks containing oily substances, but the invention is not to be deemed restricted to such particular materials, as other materials of a rubber-like nature having different characteristics may be used in accordance with the use to which the porous product is put.

Therefore, it is the principal object of this invention to provide a process for the making of micro-porous rubber-like webs having interconnecting pores.

Another object of the invention is to provide a process for the making of micro-porous resilient webs.

Another object of the invention is to provide a process for the making of micro-porous resilient printing plates.

Another object of the invention is to provide a micro-porous rubber-like printing plate resistant to corrosion or distortion by printing inks containing oily substances.

Another object of the invention is to provide a rubber-like printing plate having microscopic pores therein which constitute approximately 45% or more, by volume, of the plate as a whole.

With these and incidental objects in view, the invention includes certain novel features, the essential elements of which are set forth in the preferred embodiment to be described in conjunction with the drawing and in appended claims.

In the drawing:

Fig. 1 shows the mixing of the comminuted ingredients.

Fig. 2 shows the mixed ingredients in a molding die.

Fig. 3 shows the molding die in position in a steam-heated press.

Fig. 4 shows the molded and vulcanized article before removal of the filler.

Fig. 5 shows a method of washing out the filler.

Fig. 6 shows an enlarged fragment of the porous rubber web.

General description

Although the process to be described is available for any product using any moldable rubber-like raw materials, the process will be described particularly with reference to printing plates made with the synthetic rubber-like materials of the butadiene co-polymer class containing vulcanizing ingredients, as those materials are resistant to the disintegrating action of dye inks, particularly those containing oleic acid or other oily vehicles or wetting agents.

The process consists essentially of the step of intermlingling intimately certain proportions of vulcanizable comminuted rubber-like material with an equally comminuted filler substance in certain proportions; the step of molding the material under pressure; the step of vulcanizing the molded product either in the mold or after it has been released from the mold; and the step of removing the filler from the molded product, leaving interconnecting pores which the filler formerly occupied. In general, it may be said that the proportion of the rubber-like substance to the filler should be about 55% by volume of the rubber-like substance to about 45% by volume of the filler substance. The proportions mentioned assure a bonding of the rubber-like material in molding, yet leave the spaces, which were occupied by the filler before it is removed, interconnecting. The filler is of such a material that it may be removed by means which will not destroy the rubber-like part of the molded structure.

The molding step

In the preferred embodiment, a synthetic rubber, of the type of the butadiene co-polymers, containing standard vulcanizing ingredients, is comminuted so that the particles are uniformly more or less of a size, which size may be selected from a range of particle sizes between those that pass 25 mesh and those that pass 325 mesh to the inch, according to the coarseness or fineness of the porosity desired in the final structure. The comminuted rubber 10 (Fig. 1) is intermingled with a filler 11 of preferably the same or smaller

particle size, which filler is inert to the rubber-like material, dry, non-volatile under pressure and vulcanizing heat, and practically incompressible. It is to be noted that the filler may be compounded with the rubber and the compounded mass comminuted instead of comminuting the rubber-like material and the filler separately, although such compounding, by coating the filler particles with rubber, prevents a complete removal of the filler. The filler must be removable by means that does not adversely affect the rubber after it has been molded.

The preferred filler for the butadiene co-polymers is sodium nitrate, but other fillers which are easily removable from the molded product by dissolving them out by liquids inert to the rubber-like material may be used, suggested substances being sodium carbonate, ammonium sulphate, zinc, and poly-vinyl alcohol. The list of materials given for fillers is not to be deemed exhaustive. Some of the named materials such as zinc, the carbonates, and the nitrates may be dissolved out of the molded product by hydrochloric acid or dilute nitric acid. The sodium nitrate may also be dissolved out of the molded product with hot water, preferably having contained therein a wetting agent such as one of the soaps, or one of the sulfonated fatty alcohols, or salts of the aliphatic penetrates. The materials, after being intimately mixed, are placed in a die mold 12 (Fig. 2), preferably of the positive pressure type, in a layer 13 of from $^{2}/_{1000}$ of an inch in thickness to $^{150}/_{1000}$ of an inch in thickness, depending upon the mesh size of the ingredients. The finer the mesh size of the ingredients used, the more difficult it is for the filler solvents to penetrate through the entire molded web. For a 325 mesh mix, for instance, $^{2}/_{1000}$ of an inch will be the maximum thickness of a web from which the filler can be readily dissolved by washing, whereas the coarser 100 mesh mix web may be $^{100}/_{1000}$ of an inch thick. Thicker webs may be cleared of filler by washing and manipulating the piece, thus working the filler out and the solvent in.

If the product is to be a printing plate, the mold may be supplied with a suitable matrix. For making any other surface configuration, or for making a web of other than a plane configuration, ordinary molding practices are followed. A pressure of from 250 pounds to over 6,000 pounds per square inch may be used (Fig. 3). A vulcanizing temperature of approximately 307 degrees Fahrenheit for the butadiene co-polymers, or a standard vulcanizing temperature for any other of the rubber-like materials that may be used, may be applied during the molding in a press 14, as shown in Fig. 3, by steam supplied to the press through pipes 15, after the molding, or after the removal of the molded product from the mold. The matrix placed in the die may be Bakelite or other incompressible substance inert to the pressure and heat used.

Removal of the filler

In the preferred form or embodiment, the filler of sodium nitrate is removed from the molded web 16 (Fig. 4) by washing it in hot water, for example, as shown in Fig. 5, with a wetting agent mixed therein if desired, as long as is necessary to completely remove said filler. The time required for removing sodium nitrate from a web $^{1}/_{1000}$ of an inch thick and of 250 mesh particle size, by swirling it in hot water, is about two hours. Thicker webs and finer pore structure require a longer time and some manipulation. For other fillers than those specified, common laboratory methods for removing dissolvable materials may be used.

While the process herein described is admirably adapted to fulfill the objects primary stated, it is to be understood that it is not intended to confine the invention to the preferred form or embodiment herein disclosed, for it is susceptible of embodiment in various forms, choices of ingredients, operating conditions, and processing conditions, all coming within the scope of the claims which follow.

What is claimed is:

1. The process of making a microscopically porous web, including the step of intermingling finely comminuted moldable resilient material with a comminuted non-resilient soluble filler; the step of molding the mingled substances under pressure into a web; and the step of removing the filler by dissolving it in a solvent to which the resilient material is relatively inert.

2. The process of making a micro-porous web, including the step of intermingling a comminuted rubber-like material having vulcanizable ingredients with a comminuted solid filler in the proportions of approximately 55% rubber and 45% filler; the step of molding the intermingled substances under pressure and heat in a die to form a vulcanized web; and the step of dissolving out the filler by a solvent not affecting the rubber-like material by temporary contact therewith.

3. The process of making a micro-porous rubber-like web, including the step of intermingling finely comminuted vulcanizable rubber-like material with a finely comminuted dry inert soluble non-resilient substance; the step of placing the intermingled substances in a mold and subjecting them to molding pressure and vulcanizing temperature; and the step of washing the vulcanized web in a solvent which dissolves and removes the non-resilient material but which does not dissolve and is chemically inert as to the rubber-like material.

4. The process of making a micro-porous web, including the step of comminuting, to a uniform particle size somewhere between 25 and 325 mesh to the inch, a butadiene co-polymer containing vulcanizing ingredients, and approximately 45% by volume of sodium nitrate; the step of subjecting the mixture to a molding pressure of between 250 pounds to the square inch and 6000 pounds to the square inch, and applying vulcanizing temperature to the molded web, either during the molding operation or after removal from the mold; and the step of washing said vulcanized web in hot water until the sodium nitrate is removed.

5. The process of making a micro-porous rubber product, including the step of comminuting vulcanizable rubber uniformly to a mesh size as selected between 25 mesh and 325 mesh to the inch; the step of intermingling the comminuted rubber with a filler comminuted so that the largest particle size does not exceed the largest particle size of the rubber, said filler being dry, chemically inert with the rubber under molding pressure and vulcanizing heat, and soluble apart from the rubber, in the proportion of 55 parts by volume of the rubber and 45 parts by volume of the filler; the step of molding said intermingled substances under pressure between 250 and 6000 pounds to the square inch; the step of vulcanizing the molded product in the mold or after removal from the mold; and the step

of washing the filler out with a dissolving agent that is inert as to the rubber.

6. The method of making a resilient porous product, including the step of comminuting a vulcanizable butadiene co-polymer to a uniform particle size somewhere between 25 mesh and 325 mesh to the inch; the step of comminuting a filler substance having the characteristics of relative incompressibility, of chemical inertness to the butadiene co-polymer, and of remaining dry and non-volatile under heat and pressure, to the same mesh size or smaller than the mesh size of the butadiene co-polymer; the step of intimately intermingling approximately 55% by volume of the butadiene co-polymer with 45% by volume of the filler; the step of molding the intermingled substances to the desired form under pressure somewhere between 250 pounds to the square inch and 6000 pounds to the square inch; the step of vulcanizing the molded product either while under pressure in the mold or after said molded product has been removed from the mold; and the step of dissolving out the filler from the molded product by a solvent which is inert to the butadiene co-polymer by washing.

7. A process for making a micro-porous resilient web, including the step of comminuting vulcanizable rubber or rubber-like material to a uniform particle size somewhere between 25 mesh and 325 mesh to the inch; the step of comminuting a dry, pressure-resisting, non-volatile, and non-compressible substance to a particle size at least as small as the particle size of the rubber or rubber-like material; the step of intimately intermingling to a uniform condition 55% of the comminuted rubber or rubber-like material by volume with 45% of the filler material by volume; the step of molding the material under pressure somewhere between 250 pounds to the square inch and 6000 pounds to the square inch; the step of vulcanizing the molded product either in or out of the mold; and the step of dissolving out the filler by a solvent which is inert chemically to the rubber or rubber-like material, said liquid containing a wetting agent of the group comprising soaps and aliphatic penetrates.

8. A process for making micro-porous rubber having the pores interconnecting and of uniform size, including the step of molding a mixture of moldable rubber of micro-fine particle size with a filler of particle size at least as fine as the rubber; and the step of dissolving out the filler from the molded product by a solvent inert as to the rubber.

9. A process for making micro-porous rubber having the pores interconnecting and of uniform size, including the step of molding a mixture of vulcanizable moldable rubber of micro-fine particle size with a filler of particle size at least as fine as the rubber; the step of vulcanizing the molded body; and the step of dissolving out the filler from the molded product by a solvent inert as to the rubber.

10. A process for making a micro-porous butadiene co-polymer having the pores interconnecting and of uniform size, including the step of molding a mixture of moldable resilient butadiene co-polymer of micro-fine particle size with a filler of particle size at least as fine as the butadiene co-polymer; and the step of dissolving out the filler from the molded product by a solvent inert as to the butadiene co-polymer.

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