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METHOD OF MAKING RUBBERY ARTICLES

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This invention is concerned with a method of making rubbery articles and is particularly concerned with a method of making rubbery articles deposited directly from an aqueous dispersion of rubber-like material.

Many rubbery articles are made by depositing one or more layers of coagulum of rubbery material on a suitably shaped deposition form directly from an aqueous dispersion of rubber material. The deposition is preferably accomplished by associating with the surface of the form a coagulant for such aqueous dispersions and then immersing the form in an aqueous dispersion or latex comprising the desired rubbery material in order to build up a layer of coagulum on the surface of the form. If desired, the process may be repeated several times to build up a plurality of layers of coagulum. An article deposited in this fashion has coagulant-containing aqueous serum occluded in the deposit. Most or all of the water in the deposit must be removed before the article is vulcanized to avoid blistering of the article during vulcanization, and the coagulant must be removed before the vulcanization or the article will remain tacky or deteriorate rapidly on aging.

Prior to this invention, the coagulant was conventionally removed by washing the deposited article in water for extended periods of time. This removed the coagulant from the deposit but left the deposit containing a high percentage of interstitial water which had to be removed by drying the deposit slowly over an extended interval of time before vulcanization. The drying was conventionally carried out in air, either at room temperature or at elevated temperatures.

It is, therefore, an object of this invention to provide a method for making rubbery deposition articles in a much shorter time than was possible heretofore and particularly to provide a method for effectively leaching coagulant from a rubbery coagulum deposit in a short time without introducing a large amount of water into the deposit. Another object is to shorten or eliminate the drying step heretofore employed in making such articles. Another object is to combine the washing and drying steps, or the washing, drying, and vulcanizing steps into a single operation. Other objects will be apparent from the description which follows.

I have discovered that these objects may be accomplished by exposing the coagulum deposit to water vapor at a temperature of 100°–250° F. Under these conditions it is found that an aque-

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ous coagulant-containing liquid accumulates between the article and the form. The leaching or extraction of the coagulant is preferably accomplished with the article still on the deposition form and in such condition that the coagulant-containing efflux drains out from between the article and the deposition form during the leaching operation and the leaching is preferably carried out at substantially atmospheric pressure. The leached article contains very little interstitial water and may be readily dried, relatively thin articles such as balloons, finger cots and similar articles flash drying upon removal of the article from the vapor-laden atmosphere merely from the retained heat in the article and deposition form. Indeed, in many cases it has been found that no separate drying step need be employed before vulcanization, the vulcanization being brought about merely by retaining the article in the atmosphere of water vapor for a somewhat longer period than is required merely for leaching or extracting the coagulant.

The exact mechanism of the leaching in accordance with the invention is not fully understood and it is not intended to limit the scope of the invention by any theory which might be offered by way of explanation.

The leaching action is somewhat analogous to the osmotic effect obtained by dispersing a semi-permeable membrane between a salt solution and a solvent. In this case, however, the coagulant is also carried inwardly with the diluting water and although a little coagulant-containing serum appears on the outer surface of the article, most of it collects between the article and the form and drains therefrom. Furthermore, if the mechanism were purely osmosis, the leached deposit would be expected to contain a substantial percentage of retained water, whereas it has actually been found that the deposit is either substantially completely dry or contains at most only a very small proportion of water.

In contrast to the leaching action in accordance with this invention, it is found that when an article is leached by immersion in water, very little coagulant-containing serum collects between the article and the deposition form. The water must penetrate the deposit and carry the coagulant back out to the outer surface of the article. This leaves the pores of the deposit filled with water which must be removed before vulcanization is effected.

The leaching operation in accordance with this

invention is preferably carried out substantially at atmospheric pressure. Increased pressures hinder rather than aid the leaching action, and therefore offer no advantage. It has been found that the leaching is also preferably carried out at somewhat elevated temperatures, the temperature used preferably being lower, at least during the initial stages, than the vulcanization temperature of the rubbery composition being leached. The leaching is preferably carried out at 100°–212° F. at atmospheric pressure. The leaching may be carried out at somewhat higher temperatures, however, as for example up to 250° F. or higher or at slightly elevated pressures, if desired. Preferably, however, in the case of most rubbery articles, the leaching is carried out with vapor-saturated air maintained at 140°–180° F. since optimum results are obtained without premature vulcanization.

The leaching may be carried out in any gaseous atmosphere maintained at substantially 100% relative humidity or more. In some cases, it may be desirable to use an inert atmosphere such as nitrogen etc. or other gaseous atmosphere, with water being supplied thereto as by introducing steam therein. Preferably, however, the leaching is accomplished merely by circulating water vapor about the article being leached. In practice, this is suitably accomplished by disposing the article above a bath of boiling water or by blowing steam through a chamber containing the article, the amount of steam introduced being dependent upon the temperature desired.

The article being leached may be disposed in the water vapor in any position. The article, however, is preferably arranged so that the coagulant solution which collects between the article and the deposition form can continually drain out of the article rather than back up into the pores of the rubber. In the case of articles provided with an opening, such as balloons, finger cots, gloves, or the like, simple inversion of the form bearing the deposited coagulum to place the opening at the bottom will suffice; alternatively the article may be opened at the bottom before leaching so as to permit drainage therefrom.

The method is applicable for leaching coagulant from any unvulcanized rubbery article obtained by coagulating by known methods directly on a suitably shaped deposition form any desired aqueous dispersion or latex comprising any rubbery material which deposits in a coherent, continuous, flexible layer. Thus, the aqueous dispersion may include any vulcanizable rubber, whether natural or synthetic, which is or may be vulcanized in the presence of sulfur, sulfides, oxides and similar chemical vulcanizing agents, as well as rubbery polymeric materials such as vinyl polymers, pre-vulcanized rubber latices, etc. The latex may contain, in addition to the rubbery material, any of the commonly employed compounding ingredients for such dispersions such as stabilizers, emulsifying agents, fillers, reinforcing agents, antioxidants, vulcanizing agents and accelerators therefor, color pigments, and similar ingredients commonly employed in compounding such dispersions, the amounts and proportions of such ingredients being in accordance with conventional compounding techniques.

The coagulants which may be leached in accordance with this invention include any of the well-known coagulants for aqueous dispersions of rubber material, as for example, the water-soluble polyvalent metal salts of inorganic or organic acids, such as calcium nitrate or water-soluble

ionizable acids such as acetic acid or similar well-known water-soluble coagulants for rubber latices, which coagulants are usually employed in solution in a suitable solvent therefor which is preferably a volatile organic solvent miscible with water.

To illustrate the invention, the making of several articles will be detailed although it is not intended that the scope of the invention be limited thereby.

Example I

In making a balloon, a suitably shaped deposition form is coated with a coagulant for latex, as for example by spraying or dipping the form in a concentrated solution of calcium nitrate in acetone. The form may be of any desired material such as porous materials although the form preferably is made from aluminum, stainless steel, porcelain, or similar smooth impervious material.

The coagulant-coated form, which may be at least partially dried if desired, is then immersed in an aqueous dispersion or latex comprising natural rubber until a layer of coagulum of the desired thickness, e. g. 0.005" thickness, is deposited thereon. The form bearing the coagulum deposit is then removed from the latex and placed in a steam chamber in an inverted position so that the neck opening of the balloon is at the bottom. Steam is then blown through the chamber, which is open to the atmosphere, at a rate sufficient to maintain the temperature in the chamber at 140°–160° F. for 5 minutes.

After a few seconds in the chamber, a coagulant-containing efflux drains down from between the balloon and the form. At the end of the treatment, the efflux is substantially free of coagulant.

The leached article on the form is then removed from the steam chamber into the atmosphere whereupon the retained heat in the balloon and the form causes it to flash dry. The balloon is thereafter vulcanized in the usual manner without any further drying.

Example II

In the case of an article comprising a plurality of coagulum layers, it is desirable to vary the method somewhat to ensure optimum results.

The article is prepared in the conventional manner by several successive immersions of the form first in coagulant solution and then in a suitable rubber latex. After the last coagulum layer has been deposited, the form bearing the article is removed from the latex and at least partially dried, as for example by heating the deposit in hot air from 1–30 minutes at 140°–180° F., causing the coagulum layers to adhere together and prevent the formation of large pockets of coagulant solution between the plies during the leaching operation. The partially dried deposit is then leached by subjecting it at atmospheric pressure to water vapor maintained at 100°–212° F. until the efflux from the article is substantially free of coagulant.

The leaching time necessary in the case of a multiple ply article will, of course, depend upon the thickness of the article and may be as long as 3 hours or longer in some cases. The pre-drying step prevents blistering and separation of the layers of the article. The multiple layer articles, because of their thickness, usually do not flash dry upon removal from the moisture-laden atmosphere but must be dried further in hot air. The total drying time, however, is much less

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than that necessary in drying a multiple layer article washed in the conventional manner. For example, the total drying time is reduced by more than 50 hours in the case of a 3-layer bulb.

The leaching method employed in practising this invention presents a further advantage. Deposition articles commonly shrink considerably upon drying particularly when the article is removed from the deposition form before drying and allowed to undergo free shrinkage. In the case of articles prepared in accordance with this invention, however, the shrinkage is much less pronounced than in the case of water washed articles, the shrinkage of vapor leached articles commonly being less than half the shrinkage of a water washed article. This reduced shrinkage also results in sharper definition of detail in the finished article.

Example III

In making a toe rubber, a single layer of rubbery coagulum is deposited on a suitably shaped porcelain form in the usual manner by first dipping the form in a solution of calcium nitrate in acetone and then dipping it in a suitable compounded rubber latex, such as a latex of a rubbery copolymer of butadiene-1,3 and styrene. The processing of the article thereafter proceeds as shown in the following table for the old method which involves water washing and the new method of vapor leaching in accordance with this invention.

	Old Method	New Method
Wash.....	2 hrs. at 70° F. in water.	15 min. at 160° F. in water vapor. Flashes dry.
Dry in air.....	30 min. at 170° F.	30 min. at 170° F.
Roll bead.....		
Dry in air.....	3 hrs. at 170° F.	
Strip from form.....		
Dry on tray.....	24 hrs. at 140° F. in air.	Not necessary.
Vulcanization.....	1 hr. at 220° F.	1 hr. at 220° F.

The second drying step is largely precautionary in the case of the vapor leached article, and may be omitted if desired.

Under the old method involving a water wash, the article is on the form for 5½ hours after deposition. In the case of an article leached in accordance with this invention, the article is on the form only 45 minutes. Therefore, the number of deposition forms necessary for producing a specified number of articles in a day is less than one-fifth the number necessary heretofore. Furthermore, the total time of making the article by this method is 1¾ hours as contrasted to 30½ hours using conventional methods.

Example IV

In making single layer corrugated tubing, the article is deposited on a suitably shaped form in the manner described hereinabove for making balloons by a single dip in a rubber latex. A comparison of the processing, up to the vulcanization step, of the water-wash method and the method of this invention is as follows:

	Old Method	New Method
Wash.....	4 hrs. at 70° F. in water.	15 min. in water vapor.
Dry in air.....	6 hrs. at 170° F.	Flash dry.

Example V

In making multiple dip deposition articles, the additional step of partially pre-drying the arti-

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cle before leaching is desirable to advance adherence between the successive layers to prevent blistering of the article.

A typical example of a multiple ply article is a rubber syringe bulb prepared by successive dips in coagulant and latex to build up a 3-layer deposit of about ⅛" thickness. The bulb is then inverted, or if the finished bulb is to be open at both ends, the bottom of the bulb is slit to allow drainage and the processing thereupon proceeds as follows:

	Old Method	New Method
Pre-dry in air.....	3 min. at 160° F.	30 min. at 160° F.
Wash.....	6 hrs. in water at 90° F.	3 hrs. at 140° F. in water vapor.
Dry in air.....	4 hrs. at 140° F.	4½ hrs. at 160° F.
Do.....	6 hrs. at 170° F.	None.
Strip from form.....		
Wash in water.....	4 hrs. at 90° F.	30 min. at 180° F.
Dry in air.....	1 hr. at 170° F.	1 hr. at 170° F.
Do.....	48 hrs. at 140° F.	None.
Vulcanization.....	1 hr. at 220° F.	1 hr. at 220° F.

The washing step after stripping from the form is merely a superficial washing in water to thoroughly cleanse the surface of the article. It can be seen that by the old method, the article was on the form for slightly over 16 hrs.; while in the present method, the article is on the form not over 8 hrs. The total processing time, exclusive of the deposition of the article, in accordance with this invention is about 10½ hrs. as compared to about 70 hrs. for conventional processing.

Example VI

In the case of single dip articles such as balloons or finger cots, the process may be modified still further. Thus, a balloon may be formed by coagulant deposition on a suitably shaped form. The form bearing the article is inverted and placed in the steam chamber and treated with steam for 5 min. at 140° F. During this time, the coagulant-bearing serum drains out. The temperature of the chamber is thereafter immediately raised to vulcanizing temperature, e. g. 180°-220° F., and the treatment is continued for 10 min. more which serves to vulcanize the balloon. Upon removal of the balloon from the chamber, it flash dries and no further processing is necessary.

Example VII

In some cases, it may be desirable to use a so-called "prevulcanized" natural rubber latex. A finger cot deposited on a suitable deposition form using such a latex need only thereafter be leached with vapor-laden air at 160° F. for 10-15 minutes with the cot inverted. Upon removal of the finger cot from the chamber, it flash dries and no further drying or vulcanization is necessary.

Example VIII

The article which is leached in accordance with this invention may be prepared by a deposition process wherein a suitably shaped form is first dipped into a suitably compounded rubber latex, raised from the latex with an adhering latex film thereon and then dipped into a coagulant solution such as in dilute acetic acid to coagulate the latex film. The coagulated deposit may thereupon be washed if desired and the process may be repeated until a deposit of the desired thickness is obtained. This deposit is then vapor leached at 100-250° F. as described hereinabove, dried if necessary and vulcanized.

Example IX

The method of the invention may be varied somewhat in the case of thin single layer articles which leach quickly. A balloon form is coated with coagulant and dipped into suitably compounded natural rubber latex until a deposit of the desired thickness, as 0.005", is obtained. The article while still on the form is inverted and placed in a steam chamber. Steam is blown into the chamber at atmospheric pressure and at vulcanizing temperature, e. g. 180° F. The balloon begins to bleed coagulant solution almost immediately and at the same time begins to vulcanize. By the time the vulcanization has proceeded nearly to completion, the efflux from the balloon is free from coagulant and has almost ceased. As the vulcanization is completed the balloon becomes non-porous and the leaching stops altogether. The vulcanized balloon flashes dry on removal from the chamber and may be stripped from the form. Such a method takes but 7½ minutes from the coating of the form with coagulant to the stripping of the vulcanized balloon. Simultaneous leaching, draining and vulcanizing of such articles, although preferably carried out at 180° F., may be carried out at 180° F. to 250° F., or desirably 180°-212° F.

Obvious variations and modifications may be effected within the spirit and scope of the invention as defined in the appended claims.

I claim:

1. In the method of making a rubbery article comprising a single layer of deposited rubber material, the steps which comprise partially immersing in an aqueous dispersion of rubber material a suitably shaped form coated with coagulant for said dispersion to deposit thereon a continuous coagulum layer of rubber material having an opening at the top of said coagulum deposit, removing the coagulum-coated form from said dispersion, inverting the coagulum-coated form and subjecting the external surface thereof at atmospheric pressure to water vapor maintained at a temperature of 100°-212° F. to accumulate and drain an aqueous liquid from between said article and said form until the deposit is substantially free of coagulant, and thereafter drying said coagulum deposit.

2. The method of making a thin rubbery article such as a balloon and the like comprising a single layer of rubber material, which method comprises coating a suitably shaped form with a coagulant for aqueous dispersions of rubber material, partially immersing the coagulant-coated form in an aqueous dispersion of rubber material to deposit thereon a thin continuous coagulum layer of rubber material having an upwardly-directed neck opening, removing the form and coagulum layer from the aqueous dispersion, inverting the form and coagulum layer to direct said neck opening downwardly and subjecting the external surface of the coagulum layer at substantially atmospheric pressure to air maintained at 140°-180° F. and saturated with water vapor for 1-15 minutes to leach coagulant from said coagulum layer and allowing liquid material to drain from between said form and said layer of coagulum, removing the coagulum layer from the vapor saturated air and allowing residual water to evaporate, and thereafter vulcanizing the coagulum layer.

3. In the method of making a rubbery article comprising a plurality of coagulum layers of rubber material deposited on a deposition form directly from an aqueous dispersion of rubber ma-

terial by means of a coagulant for said dispersion, the steps which comprise partially drying the article after deposition to bind the layers thereof together and thereafter subjecting the external surface thereof at substantially atmospheric pressure to water vapor maintained at a temperature of 100°-212° F. to accumulate an aqueous liquid between said article and said form, and continually draining said liquid therefrom during exposure to said water vapor.

4. In the method of making a rubbery article comprising a plurality of coagulum layers of rubber material deposited directly on a deposition form by successive immersions in a coagulant for latices of rubber material and in a latex comprising rubber material, the steps which comprise heating the deposited article for 1-30 minutes at 140°-180° F. to advance adherence between the successive rubbery layers, thereafter arranging the article to permit drainage of liquid from between said article and said form, subjecting the outer surface thereof while still on the deposition form to air saturated with water vapor maintained at 140°-180° F. at atmospheric pressure to cause an efflux of an aqueous liquid from between the article and the form, and maintaining the article in said vapor until the efflux from the article is substantially free of coagulant.

5. In the method of making a rubbery article deposited on a suitably shaped form directly from an aqueous dispersion of rubber material by means of a coagulant therefor, the steps which comprise arranging the form having the deposited article thereon to permit drainage of liquid from between said article and said form, exposing the outer surface of said article while still on said form to water vapor maintained at 100°-212° F. and at atmospheric pressure to cause an efflux of coagulant solution from the article, maintaining the article in said heated water vapor until the efflux is substantially free of coagulant, removing the form bearing said article from the vapor, at least partially drying said article, stripping said article from the deposition form, and thereafter vulcanizing the rubbery article.

6. The method of making a rubbery article by direct deposition of coagulum of a prevulcanized rubber latex, which method comprises coating a suitably shaped form with a coagulant for said latex, at least partially immersing said form in an aqueous dispersion comprising prevulcanized rubber to deposit a coagulum layer comprising prevulcanized rubber on said form, and thereafter exposing the outer surface of said coagulum deposit while still on said form to water vapor at a temperature of 100°-212° F. and substantially atmospheric pressure to cause an aqueous liquid to accumulate between said form and said deposit, simultaneously draining said liquid therefrom, and thereafter drying said deposit and removing it from said form.

7. In the method of making a rubbery article deposited on a suitably shaped form directly from an aqueous dispersion of rubber material by means of a coagulant therefor, the steps which comprise exposing the outer face of said article while still on the deposition form to water vapor at 140°-180° F. and substantially atmospheric pressure, accumulating an aqueous liquid between said article and said form and simultaneously draining said liquid therefrom, and thereafter raising the temperature of said water vapor to 180°-250° F. to vulcanize said article.

8. In the method of making a rubbery article

deposited on a suitably shaped deposition form directly from an aqueous dispersion of vulcanizable rubber material by means of a coagulant therefor, the steps which comprise exposing the outer face of said article to water vapor at 180°-250° F. at substantially atmospheric pressure to accumulate an aqueous liquid between said article and said form and to vulcanize said article, and simultaneously draining said liquid from between said article and said form.

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