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J. J. MARX ET AL

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RUBBER FOOTWEAR

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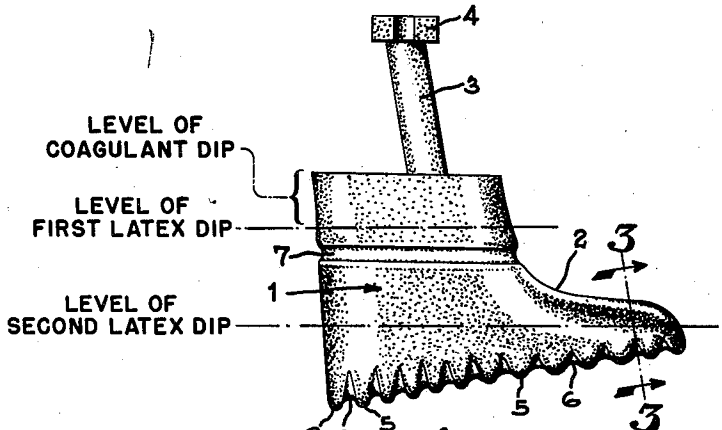

Fig. 1

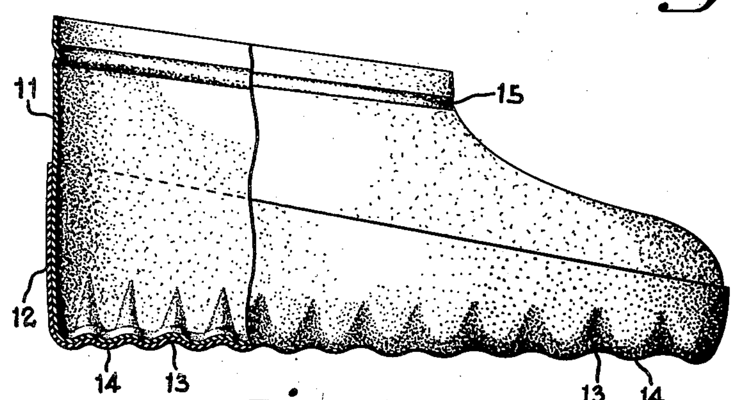

Fig. 2

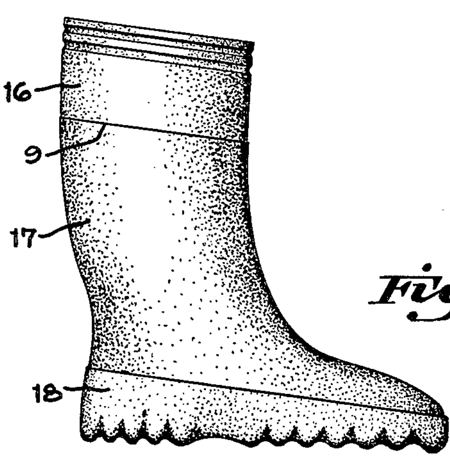

Fig. 4

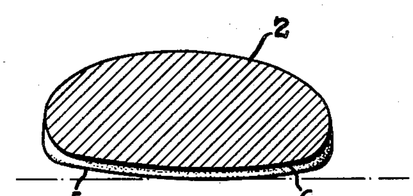

Fig. 3

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RUBBER FOOTWEAR

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1 Claim. (Cl. 36—7.3)

1

This invention relates to novel elastomeric footwear, particularly overshoes suitable for children, and to a process by which such footwear may be fabricated. The shoes of this invention are light, flexible, attractive in appearance and adapted to be manufactured by the dipping of forms in liquid latex compound. While elastomers other than natural latex may be used, the following disclosure will be made in relation to rubber overshoes so fabricated.

Broadly, and from the method point of view, the invention comprises dipping a form in coagulant, then dipping it two or more times in latex compound, the depth of each dip being progressively less. This technique produces an overshoe, the upper portion of which is constituted by a single rubber film of substantial flexibility to permit the top of the overshoe to be drawn over the foot. The lower or sole portion of the overshoe is constituted by two layers of film, that is, the inner layer which constitutes the upper and the outer layer which provides reinforcement over the sole portion of the overshoe.

Preferably, the compound which deposits the outer layer is of composition different from the liquid which deposits the inner layer. If there be no difference other than that of color, a bright attractive two-tone appearance is provided. But it is within the contemplation of this invention that the outer layer should contain materials which enhance the resistance of the film to abrasion. While the sole portion of the overshoe may not be so flexible as the upper portion, substantial resistance to abrasion may be imparted to it without sacrificing flexibility unduly. Thus, this piece of footwear combines the wear-resistance so important in children's articles with an easily stretchable upper rim which can be pulled apart almost like a rubber band, even by younger children. Further, the expansible nature of the upper accommodates the overshoe to be worn for a long time without the child's outgrowing it. The overshoes are particularly well adapted to this children's market, especially when made in bright colors, although the method and the articles to be described are in no way limited to those suitable only for children.

The overshoe of this invention is sufficiently flexible that overshoes manufactured on a given form may be worn over shoes the sizes and shapes of which vary over considerable range. It is not necessary to have a form corresponding to each size and style of shoe of the prospective purchaser. This characteristic of the overshoe, which is in part determined by the method of its

2

fabrication, facilitates quantity production at reasonable cost.

It is desirable that an overshoe constituted by a smooth rubber film be provided with some sort of tread to prevent the wearer from slipping too easily. However, it is very difficult to provide a tread on the bottom of the form because of the tendency of the tread to entrap air in the dipping operation. On this account the configuration of the tread of the overshoe of this invention is fashioned in relation to the dipping problem and consists of alternating grooves and ridges running transversely of the overshoe and tapering from the central longitudinal line of the overshoe to the margins to form a slightly convex sole surface. These lateral treads permit air to escape to the sides when the form is being dipped. The toe portion of the overshoe upper presents a substantial area of horizontal surface, in addition to that of the sole itself. Therefore, to avoid the formation of air pockets along these surfaces and to facilitate drainage in the dipping operation, the form is turned downwardly at an angle from toe to heel so that as the sole is dipped from heel to toe, the air tends to escape forwardly. These angulations are of substantial importance to facilitate quantity production of the overshoes by the dipping technique without production of too much worthless scrap as a result of entrapment of air.

Since the latex compound deposits on the form by virtue of the exposure of the rubber in the latex compound to a coagulant on the form, it has been a problem to obtain a uniform and substantial deposit of rubber on the dips subsequent to the first dip. This problem has been surmounted by incorporating in the latex solution a stabilizer which imparts to the deposited film a permeability to the coagulant solution, whereby the coagulant migrates through the unhardened film after its deposition and becomes available to procure the deposition of a film of uniform and substantial thickness on the next dip.

An additional feature of the invention is the finish of the top rim of the overshoe. Obviously it is desirable that this finish be even and straight as trimming operations to obtain this result would be unduly expensive from the point of view of both the labor involved and the scrap resulting. We have found that if a coagulant solution possessed of the proper physical and chemical properties is utilized, and if the dipping is performed sufficiently slowly, then the first rubber film may be deposited with such evenness that no trimming operations are required. The straight, smooth edge which results not only eliminates this expense but helps prevent tears from making a start in the film. While the slow dipping of the forms in the latex compound tends to expose the bottom of the form to the solution for a longer period of time than the top of the form, any inherent unevenness of deposit thus produced tends to provide a thicker sole portion and a thinner, more flexible upper portion, both of which characteristics are desirable.

The invention will be better understood by reference to the following drawings, in which Figure 1 is a side elevation of a form upon which layers of an elastomeric compound may be built up, showing the angle at which it is to be held during the dipping operations and the levels of successive dips to produce an overshoe of the type shown in Figure 2.

Figure 2 is a side view, partly in cross section, showing an overshoe constituted of two layers and stripped from the form of Figure 1.

Figure 3 is a section of the form of Figure 1 taken along line 3—3 showing the slightly convex sole surface.

Figure 4 is a side elevation of a boot or galosh made by the process of this invention, after having been stripped from a form of corresponding configuration.

As disclosed in Figure 1, a metallic, porcelain or other suitable form indicated generally as 1 is provided with a dipping portion 2 and a stem 3 having a hanger stud 4 by which it may be attached to a dipping rack, which is not shown. The hanger stud is angulated with respect to the bottom of the form so that when it is attached to a rack in horizontal position, the bottom of the form slopes downwardly from front to back at an angle of substantially 5–10°. The bottom of the form is provided with ridges 5 separated by grooves 6. Preferably each groove slopes upwardly from the central longitudinal line of the shoe to the margins to facilitate the escape of air on dipping and avoid the entrapment of air in the grooves. The degree of this slope may also be substantially 5–10°. The grooves and ridges extend for a short distance up the vertical sides of the form to provide channels for escape of air bubbles when the form is immersed in liquid. This arrangement also provides for the finished product a distinctive appearance otherwise unavailable, for normally the overshoe is displayed with the sole obscured, yet the corrugations are visible because of these extensions. Spaced above the bottom of the form, that is, at the portion of the form corresponding to the ankle or just below, is a depression 7 extending about the form, adapted to provide a tension band above the instep or about the ankle of the wearer. Preferably the heel of the sole portion of the form terminates in a ridge rather than a groove to provide a drip edge 8 to prevent too great a latex layer build-up at this point. The overshoe itself, as the two dip products shown in Figure 2 comprises an inner and flexible film of rubber constituting an envelope 11 for the foot and instep of the wearer reinforced by an outer layer 12 of rubber over the sole portion of the overshoe, and extending up above the sole and heel portion of the shoe of the wearer of the overshoe. As indicated, this outer layer may be of color different from that of the inner layer and may be of composition resistant to abrasion.

Corrugations on the overshoe consist of grooves 13 and ridges 14 corresponding to grooves 5 and ridges 6 of the form. Tension band 15 conforms to depression 7 of the form.

The overshoe shown in Figure 4 is of the boot or galosh type and is constituted by three latex layers each progressively of lesser extent. In this form the inner layer of rubber constitutes an envelope 16 extended not only over the foot and instep portions but up the ankle to whatever length is desired. The second or intermediate thickness 17 of rubber covers the sole and instep portion of the first layer. The third or outer layer 18 of rubber reinforces the sole of the galosh and extends upwardly to a point slightly above the bottom, that is the sole and heel portion of the shoe.

The form itself is preferably fabricated from aluminum or aluminum alloy of the type commonly employed for forms to be dipped in latex. The coagulant may be any one of the many utilized for dipping forms in latex but should be chosen in respect to its capacity to penetrate a stabilized first film, in relation to its effect upon the strength and stability of the rubber films deposited over it and in relation to its immobility on the form. The coagulant film should be sufficiently immobile prior to the first dip to avoid downward drainage of the undipped coagulant which would mar the evenness of the top of the first deposited layer of rubber. A good coagulant of the following composition by weight has been found to be suitable for this purpose:

	Per cent
Anhydrous calcium chloride	27
Calcium nitrate, tetrahydrate	27
Zinc nitrate, hexahydrate	6
Wetting agent	1
Methanol—to make	100
Micronized talc (added to above)	5

The wetting agent utilized in the above formula is of the nonionic type, and may be a polymerized ethylene oxide condensation product. Such an item is manufactured under U. S. Patent Nos. 1,970,578 and 2,213,477 and is sold by the General Dyestuff Corporation of New York.

The latex compound in which the form is first dipped to deposit the envelope 11 for the foot and instep, that is, the sole and upper portion, is of a type low in sulfur and low in accelerator, thus requiring a low cure. Low percentages of these constituents contribute to a relatively high tear resistance. Preferably there is no zinc oxide in this latex solution, although there is enough zinc, as the nitrate, present in the coagulant to obtain proper aging characteristics for the film.

The latex compound used for the first dip is almost of pure gum stock in order to get a low modulus. This compound must contain a stabilizer which, in the quantity used, will permit the coagulant to penetrate the film deposited so that the proper reinforcing film may be deposited over the sole portion of the overshoe. A small percentage of the condensation product of cetyl alcohol with ethylene oxide performs this function satisfactorily.

A product of this type is manufactured by General Dyestuff Corporation of New York under U. S. Patent No. 1,970,578. This stabilizer produces a first coat, which is uniformly penetrated by coagulant to permit a second coat to build up uniformly.

We have found any of the following formulae for latex compounds suitable for obtaining the proper physical properties in the finished articles. The figures listed, as well as other similar references throughout this disclosure, represent parts by weight per 100 parts of dry rubber:

	Formula No. 1	Formula No. 2	Formula No. 3
Sulfur	1.2	1.2	1.2
Di-β-naphthyl paraphenylene diamine	0.5	0.5	0.5
Zinc diethyldithiocarbamate	0.25	-------	0.10
Zinc dimethyldithiocarbamate	-------	0.5	0.15
Mercaptobenzothiazole	0.75	0.5	-------
Tetramethylthiuram disulfide	-------	-------	0.75

The second latex solution is similar to the first except that a dyestuff, or a different dyestuff, is usually employed to give the overshoe a two-tone effect. The cetyl alcohol-ethylene oxide condensation product may be omitted from the second dip, for its use may cause the sole dip to creep up the first dip and no straight line would be formed at the top of the sole layer. Also it is preferable that the second dipping, if it is to constitute the outer layer of the sole of the overshoe, be more resistant to abrasion than the flexible inner layer. A suitable toughening material is colloidal silica dispersed in water at a concentration of 30% by weight and stabilized. Products of this type are manufactured by E. I. Du Pont de Nemours & Company of Wilmington, Delaware. As little as 5 parts of this material to 100 parts of rubber on a dry basis will increase abrasion resistance substantially 25%. It is recommended that substantially twice this amount of toughener be used. Alternatively, from 10 to 50 parts of colloidal clay may be added to the latex compound to impart toughness to the finished article.

In making up the abrasion resistant latex the almost pure gum latex compound is first mixed with one part of ethylamine in the form of a 35% aqueous solution per hundred parts of rubber. The purpose of the use of this material is the segregation of the natural proteins in the latex to prevent them from coming into contact with the silica which is to be added later and which would be precipitated thereby. Next, one-half part per hundred of potassium hydroxide is added in the form of a 25% aqueous solution. This further stabilizes the solution and tends to reduce skin formation in the dipping tank. Preferably these materials should be added to the latex at least 24 hours before adding the siliceous stabilizer. Although the amount of silica of the toughener may be varied depending upon the amount of abrasion resistance desired, good results are obtained by adding enough silica so that the relationship of the dry silica to the dry rubber is 1 to 10. Coloring material may be added at any stage of the mixing.

In manufacturing the overshoes the forms to be dipped are preferably cleansed in acid, then soap solution, particularly to remove any adhering particles of rubber remaining from prior dips. They are then rinsed in hot water and thoroughly dried. Next, the forms are disposed on racks and are heated to a temperature of substantially 120–180° F., for instance, 160° F. They are then dipped, while still hot, in the coagulant which has been stirred to maintain uniformity. Preferably the depth of this dipping is appreciably greater than the contemplated dip in the first latex solution, for example, beyond the dot-dash line shown in Figure 1. The forms need not be held in the coagulant for any definite period of time, but they are removed from the coagulant very slowly for over a period of approximately

two minutes and then are revolved in air or are blown with air until the coagulant evaporates to the consistency of a stiff syrup and the temperature of the forms is somewhere in the neighborhood of the latex temperature. This operation is of substantial importance in that it immobilizes the coagulant film on the form to a degree which precludes the coagulant running down the form during the first latex dip. If the latter were to occur, a shelf of latex would form about the overshoe upper rim and a straight line at the top of the overshoe would be impossible without hand trimming.

As an alternative, to dipping, a coating of coagulant may be established on the form by spraying, by impregnating a porous form with coagulant, or by any other conventional means.

The forms with the film of coagulant deposited thereon are next dipped into the first latex compound which is adapted to form the over-all envelope of the overshoe. The dipping is carried out very slowly to prevent trapping of air underneath the sole of the form. After the sole has been covered, the rate of immersion may be accelerated until maximum depth is reached. The form after being immersed to the dot-dash line indicated in Figure 1 is permitted to remain in the latex compound for a period of from 1 to 3 minutes depending upon the thickness of the coating desired. In general thicker coatings are desirable on the larger sizes of overshoes. The forms are then slowly withdrawn from the latex solution during a period of approximately 2 minutes. The relatively even drainage resulting from this slow withdrawal tends to provide a deposited film which is adequately even and uniform despite the irregularities of the form. On the other hand, this rate of withdrawal is sufficient to drain the latex from the vertical surfaces of the form to a thickness which is still permeable to coagulant. Drainage is not so uniform from the toe portion of the form, but the stabilizer in the latex compound is effective to render disproportionate thicknesses at this point penetrable by coagulant, thereby permitting further layer build-up on successive dips.

In the fabrication of the boot shown in Figure 4, the removal from the first dip may be interrupted at a level corresponding to the ledge indicated at 9. The form is held in this fixed position for several minutes to allow the establishment of an area of intermediate thickness terminating at the straight line ledge 9. Except for this two-stage withdrawal, the operation is identical with that for the overshoe of Figure 2.

After withdrawal from this latex solution, the forms are rocked several times to distribute any liquid latex which may be accumulated at the heel and then are allowed to set-up for a period of 3 or 4 minutes to permit relatively uniform penetration of the film by the underlying coagulant. Next the forms are dipped in the latex compound adapted to provide the outer layer to the level of the lowermost dot-dash line of Figure 1. This dip is performed in the same manner as the first dip, but the forms are allowed to dwell in the latex compound for a period of from 6 to 8 minutes, depending upon the thickness of deposit desired. The additional time is provided to allow for migration of coagulant into the second layer. The three thicknesses shown in Figure 4 may also be obtained by an intermediate dip in latex, the dip being preferably of less depth but slightly greater duration than the first dip.

After withdrawal from the final latex dip, the films on the forms are permitted to set up for approximately 15 minutes and are then leached in running water at a temperature of substantially 125° F., for approximately one minute for each thousandth inch of film thickness. The overshoes are then heat treated for a period of between 1½ and 1¾ hours at 160° F., depending upon film thickness and weather conditions. Next they are heated for substantially ¾ hour at a temperature of substantially 230° F. After this the overshoes are stripped from the forms, an operation which is greatly facilitated by the inclusion of talc in the coagulant. The overshoes are then given a chlorine treatment by being dipped for about 30 seconds in chlorine water containing substantially 300 parts of chlorine per million parts of water. Finally the overshoes are washed in running water and dried.

The chlorination imparts to the surfaces of the products a particularly smooth finish. This is important, for the inside of the article may thereby be more easily pulled over the shoe by the wearer.

Inasmuch as the composition of the rubber footwear just described is almost pure latex, the specific gravity of the finished article is only slightly greater than that of a pure gum product. Thus, overshoes may be fabricated as described to be light enough to float, even though filled with water. This is true as to all formulations described herein except that shoes with a substantial sole portion having colloidal clay as a toughener will not float; nor will an all-white product be light enough to float, for the white pigment, such as titanium dioxide, used in the composition is too dense. However, a two-tone shoe with either a white upper or sole portion and the other portion colored by dyestuffs can be made in the relative proportions shown and described and such a shoe will not sink.

Thus, rubber footwear produced by the method of our invention may not only be used as overshoes, but are peculiarly well-adapted to be used as beach shoes due to their buoyancy, the protection of the sole of the foot against sharp objects such as oyster shells, pebbles, etc., and the combinations of bright and attractive colors attainable. When such use is the main objective, the rubber shoes may preferably be supplied with a plurality of holes of varying sizes at various points of the vertical side portions or at or near the toe portion. These apertures act as ports to let air in and water out. The moistened interior of the beach shoes adheres more tightly to the bare skin of the wearer.

Having described our invention, we claim:

A light-weight protective overshoe comprising a flexible envelope composed solely of latex adapted to completely enclose the sole and heel and at least a substantial portion of the upper of the shoe to be protected, said envelope being longitudinally and transversely circumferentially continuous, except for a single top aperture through which the shoe is inserted, the entire upper portion of said envelope including that portion which is adjacent said aperture being of substantially uniform thickness and relatively thin, flexible and resilient in comparison with the lower portion of the envelope to facilitate stretching it over the shoe, the said lower portion of the envelope being of substantially uniform thickness and thicker than the upper portion and differentiated from said upper portion by a ridge extending continuously around the overshoe in an inclined plane which passes through the front of the overshoe somewhat above that portion thereof which embraces the forward edge of the sole of said shoe and which passes at a higher level through the rear of the overshoe at approximately the height of the top of that portion thereof which embraces the counter portion of said shoe, and the top edge of said envelope which joins its exterior and interior surfaces and defines said aperture, being a smooth, even and unserrated surface deposit of latex disposed in a plane parallel to the plane of said ridge.

JOE J. MARX.
EDWARD M. DAVIS.

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