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2,762,784

TEAR-RESISTANT POROUS PLASTIC SHEET MATERIAL COMPRISING POLYVINYLCHLORIDE AND A COPOLYMER OF BUTADIENE-ACRYLONITRILE

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1 Claim. (Cl. 260—2.5)

This invention relates to plastic sheet material and more particularly to improved resinous polymeric material in the form of micro-porous, tear-resistant sheets suitable for use in footwear, the material being particularly advantageous in the making of insoles.

A portion of the present disclosure is presented in the application for United States Letters Patent, Serial No. 41,726, filed July 30, 1948 in applicants' names and now abandoned.

Many materials have been considered and tested for use as insole materials in footwear. Leather has been satisfactory in such use and heretofore has been much preferred by many users but this preferred material is commonly known and understood to possess some characteristics which detract from its desirability. Leather deteriorates rapidly when subjected to the effects of moisture and foot perspiration. Its resilience is not sufficient to give proper or preferred cushioning beneath the foot of a wearer. Fabricated fibrous materials have also been used and with success. In many cases fibrous materials have been found preferable over leather for insole use but here again the materials do not completely satisfy the requirements of what is desired to give optimum satisfaction and increased comfort to the wearer.

Recently it has been determined that synthetic, resinous, polymeric materials including at least one vinyl resin, when properly sintered from an initial powder or particle form into integral micro-porous sheets, provide a resilient structure which is far superior to leather and fibrous materials in so far as insole use is concerned. This superiority has been proven in extensive and practical wear tests. Broadly, the technique of forming integral micro-porous plastic sheets is taught in the United States Letters Patent No. 2,371,868, granted March 20, 1945, to Herbert Berg and Martin Doriat. The porous material, assuming that a given shoe is of the proper size, does not "draw" the foot in any type of weather. It may be expected that the sensation of wearing rubber boots will be imparted to the wearer in the use of this material but wear tests have shown that the porous plastic insoles are actually cool in summer and are comfortably warm in winter. Moisture, in general use of the tested insoles, is adequately transferred from the foot and this characteristic of the plastic structure together with the resilient support the latter provides the foot gives comfort to the wearer heretofore not experienced. This comfort is accompanied by substantial protection of the foot against localized pressures occasioned by small stones and so forth met with in walking or by cramped spots on the foot due to improper or imperfect fitting of the shoe. Other softer or equally soft materials could be used as insole material but the micro-porous plastic material herein contemplated definitely sustains or resiliently supports the foot without losing its porosity or moisture transpiration characteristics either momentarily or permanently.

Despite the advantages of the porous plastic as an insole material, difficulty has been experienced in its use

because of its lack of strength in tear resistance especially when tension must be resisted or when stitching or sewing of the material is necessary or desirable. Sewing thread tends to pull or cut through the porous plastic and resistance of the porous polymeric material to such shearing or tearing by the thread has heretofore been negligible. The sintered products, as heretofore known, will crumble under the slightest strain such as induced by the material being subjected to a slight twist, especially in the absence of a plasticizer. With the plasticizer present, the material is improved but still leaves much to be desired in so far as stability, resilience and resistance against tension and tearing forces are concerned. As a result, the use of such material in insoles subject to tension and shear has been discouraged despite the attempted use of reinforcement means, such as fabric embedded in the plastic or a layer of stitch retaining material supplementing the plastic by adhesion.

Applicants have now found that an improved micro-porous plastic sheet material for insoles may be made which is very much stronger (2 to 20 times stronger dependent upon the specific formulation) in so far as rip-tear strength and resistance against tension stresses are concerned, this pronounced change in the physical characteristics not being accompanied by any objectionable loss in porosity. In some cases the increase in strength is accompanied by a definite and substantial increase in porosity. In all cases the desired combination of porosity, flexibility, and resilience may be had without objectionable rubberiness.

An object of the present invention is to provide improved micro-porous plastic sheet material for insoles, which material combines a high degree of porosity, proper firmness and resilience together with greatly increased tension and tear strength.

The term "micro-porous" is used herein to define a material having pores so small that they are not easily discernible with the naked eye but which permit the passage of air.

The customary definition of the word "sinter" as used hereinafter is as follows: To become or cause to become a coherent solid mass by heating without thoroughly melting. This meaning is adhered to herein but it is to be understood that the process disclosed and claimed is not such as to secure a solid or non-porous product—i. e.—although a sintering temperature is used, the pressure, temperature and time condition are controlled and are not imposed to such an extent as to solidify the particles into a mass of non-porous material.

In the production of the improved sheet material an intimate mixture of compatible thermoplastic polymers including at least one vinyl resin is blended and subsequently made into a powder each particle of which is made up of the blended polymers. A layer of such particles or powder is then sintered together with interstices being maintained between the particles yet with the latter so joined as to form a unitary article. The preferred resins are solid water insoluble non-tacky resins derived by polymerization of vinyl chloride or copolymerization of 95% to 99.5% of vinyl chloride with vinyl acetate monomers. These vinyl resins may be combined with from about 75% to about 100% of the weight of the resin of a copolymer of butadiene and acrylonitrile in the ratio of from about 33 to 40 parts of acrylonitrile to 67 to 60 parts of butadiene.

The ingredients may contain a vulcanization agent, a filler, and an accelerator. During the process of sintering, the resins, to some extent, must be thermoplastic and compatible. A thermoset resin may be added, however, and this would act as a type of filler.

A mere mixture of particles of several compatible polymers—i. e.—one polymer only in each particle—will

not serve in the present invention. It is essential, if the necessary characteristics are to be secured in the sintered product, that each particle of the powder to be sintered be made up of a polymeric blend comprising at least one of the polymeric resins as set forth above.

In preparing the blend of resins a solid or liquid plasticizer is used. If a solid plasticizer is employed, the ingredients may be fluxed on a hot two-roll rubber mill. The resultant sheet is chilled, coarsely subdivided and then ground to a fine powder. If the plasticizer selected is a liquid, the latter may be stirred together with the resin or resins at some temperature below the fusion point and the product is subsequently finely subdivided. Another way of obtaining a sufficiently intimate mixture of the resins is by precipitation of the polymers from a colloidal dispersion of them and with a subsequently division into fine particles.

In sintering a given layer of the plastic particles heat is applied during the pressure molding process and this heat may be derived from heated platens of a press or by high frequency heating. Heat applied from an outside source (heated platens) results in satisfactory sintering and increased tear and tension resistance in utilizing the present invention but high frequency heating is preferred as each particle is heated outwardly to its surface and to the surface of the sheet or article giving a uniform heating effect emanating from within and becoming definitely effective throughout the layer of particles and, in many cases, resulting in greater tear and tension resistance (without loss in porosity) as compared with the results secured by other methods of heating.

The following two examples A and B are given by way of illustration of what is to be expected in respect to porosity and tear strength characteristics of porous plastics as heretofore known—i. e.—prior to the present invention:

Example A (one resin)

Ingredients:	Parts by weight
VYNY	66.46
Methox	29.20
VIN	2.20
Pigment	2.34

The VYNY is a copolymer comprising 97% to 99.5% by weight of vinyl chloride and 3% to 0.5% by weight of vinyl acetate and is produced by the Carbide and Carbon Chemicals Corp. of New York, N. Y.

Methox is di-methoxy ethyl phthalate—a plasticizer made by the Ohio-Apex, Inc., of Nitro, West Virginia.

The VIN is strontium octoate. It is a stabilizer product of Advanced Solvents and Chemical Corp. of New York, N. Y.

The above ingredients, intimately mixed and placed in the form of a fine powder as a layer .25 inch deep within a mold, is compressed to a thickness of .125 inch and sintered (using steam-heated platens) at a temperature of 132° C. After cooling and removal from the mold, the resultant sheet is porous (40 c.c./in.²/sec.) but its tear strength is only 28 (lbs./inch of thickness).

A duplication of the use of this example may not result in a product of the same porosity as it is difficult to make consecutive sheets identical. The figures as to porosity and tear strength are to be taken as merely illustrative in a general sense and as what may well be expected in a specific sense and this holds true in all the following examples.

Example B (one resin)

Ingredients:	Parts by weight
VYNY	900.
Methox	300.
Calcium stearate	4.5
Pigment	118.

The VYNY is a resin copolymer comprising 95% by weight of vinyl chloride and 5% by weight of vinyl ace-

tate and is produced by the Carbide and Carbon Chemicals Corporation of New York, N. Y.

The above ingredients are mixed, compressed and sintered as in Example A. The cooled resultant sheet has a porosity of 13 (c.c. of air in.²/sec.) and a tear strength of 12 (lbs./inch of thickness).

The present invention is illustrated by the following examples which demonstrate not a mere difference in degree of strength in the novel porous plastic but a multiplication thereof. The ingredients are intimately blended in conventional ways prior to the reduction of the blend into fine particles.

Example 1 (resin blend)

Ingredients:	Parts by weight
VYNY	125.
Hycar OR-15	94.
Methox	15.
Calcium stearate	2.5
VIN	3.75

The Hycar OR-15 is a copolymer comprising approximately 60% of butadiene and 40% of acrylonitrile and is produced by the B. F. Goodrich Chemical Company of Akron, Ohio.

A layer of particles, each composed of the ingredients as set forth above, is sintered under slight pressure and with high frequency heating into a micro-porous and integral sheet with a porosity of 40 (c. c. of air/in.²/sec.) and a tear strength of 120 (lbs./inch of thickness).

Example 2 (resin blend)

Ingredients:	Parts by weight
Polyblend 500X479	100.
Hycar OR-15	28.
Calcium stearate	2.0
Methox	3.0
Sulphur	2.0
Captax	1.7
Agerite Stalite	2.3
Altax	1.0

The Polyblend is a colloidal blend (not fluid) produced by the B. F. Goodrich Company and is composed of 70% polyvinyl chloride and 30% Hycar OR-15.

The Captax is mercaptobenzothiazole. It is a rubber accelerator produced by the R. T. Vanderbilt Co.

Agerite Stalite is heptylated diphenylamine, also a product of the R. T. Vanderbilt Co.

Altax is benzothiazyl disulfide—a rubber accelerator made by the R. T. Vanderbilt Co.

A milled mixture of the above ingredients is chilled and subdivided into small particles a layer of which is slightly compressed and sintered into a micro-porous sheet with the use of high-frequency heat. The porosity is found to be (40 c. c. of air/in.²/sec.) and the tear strength is 126 (lbs./inch of thickness).

Example 3 (resin blend)

Ingredients:	Parts by weight
QYNA	50.
Hycar OR-25	50.
Vanstay	1.8
Acrawax C	5.
Pigment	1.8

The QYNA is polyvinyl chloride and is a product of the Bakelite Division of the Union Carbide and Carbon Corp. of New York, N. Y.

The Hycar OR-25 is a copolymer comprising approximately 67% by weight of butadiene and 33% by weight of acrylonitrile and is produced by the B. F. Goodrich Chemical Company of Akron, Ohio.

The Vanstay is a stabilizer for the QYNA vinyl resin and a product of the R. T. Vanderbilt Co.

The Acrawax C is a hard, light tan synthetic wax of high luster and is a product of the Glyco Products Com-

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pany, Inc. of Brooklyn, N. Y. The Acrawax gives an improved surface appearance and helps to improve surface slip.

Particles of a milled mixture of the above are sintered, using high-frequency heat, into an integral sheet having a porosity of 40 (c. c. of air/in.²/sec.) and a tear strength of 114 (lbs./inch of thickness).

Example 4 (resin blend)

Particles, each of which is composed of the same ingredients as used in Example 3 above, are sintered into a sheet with a slightly increased pressure. The resultant sheet has a reduced porosity of 8.5 (c. c. of air/in.²/sec.) which, nevertheless, is far superior to leather and a tear strength of 264 lbs./inch which is surprisingly high for porous plastic material.

The novel materials, formed by the method of the present invention, are stable and, rather than easily tearing or crumbling when subject to tension or stitching stresses, demonstrate such improved characteristics that they may successfully be used in the making of insoles for footwear. For insole wear in particular an improved combination of porosity, flexibility and weight-sustaining power may be had without objectionable rubberiness.

Having fully described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

A flexible micro-porous sheet suitable for insoles and having sufficient firmness to sustain the weight of a wearer without compacting, and substantial tear resistance and

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strength in tension, said sheet comprising sintered together fine particles of polymeric material cohesively joined with interstices between the sintered particles forming continuous pores and the polymeric material in each of said particles comprising a vinyl chloride polymer resin from the group consisting of polyvinyl chloride and copolymers of vinyl chloride and vinyl acetate containing from 95% to 99.5% of vinyl chloride, plasticized with a rubbery copolymer of butadiene and acrylonitrile prepared from about 33% to about 40% acrylonitrile and from about 67% to about 60% of butadiene, the weight of said rubbery copolymer being from about 75% to 100% of the weight of said resin.

References Cited in the file of this patent

UNITED STATES PATENTS

2,297,248	Rudolph	Sept. 29, 1942
2,371,868	Berg et al.	Mar. 20, 1945
2,452,999	Daly et al.	Nov. 2, 1948
2,459,739	Groten et al.	Jan. 18, 1949
2,465,493	Strickhouser	Mar. 29, 1949
2,570,182	Daly et al.	Oct. 9, 1951

OTHER REFERENCES

Rubber Age,	April 1944,	page 67.
Emmett: Ind. & Eng. Chem.,	August 1944,	vol. 36,
No. 8,	pages 730-734.	
Young et al.: Ind. and Eng. Chem.,	November 1947,	
vol. 39, No. 11,	pages 1446 to 1448.	