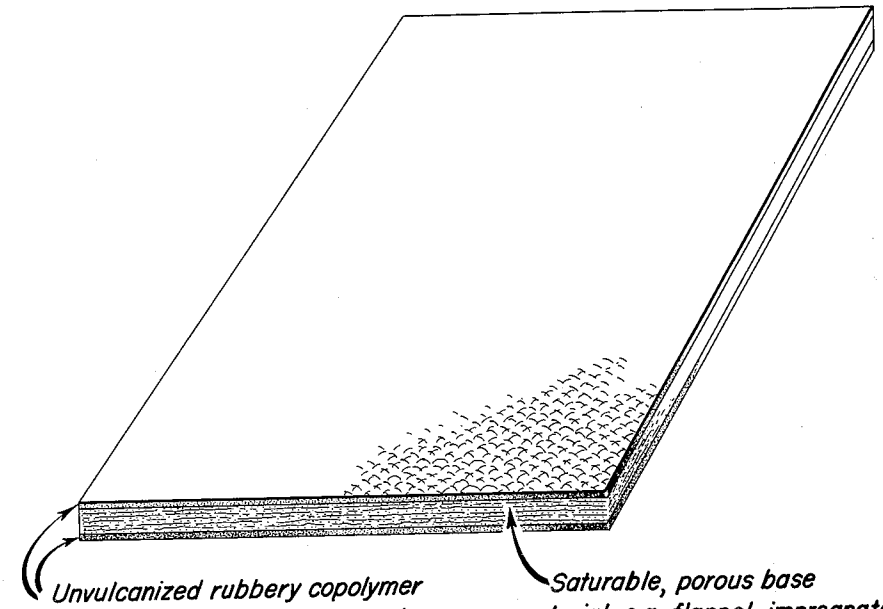
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SHEET MATERIAL FOR STIFFENING SHOE UPPERS

Original Filed Nov. 16, 1953



Unvulcanized rubbery copolymer of butadiene and acrylonitrile; resinous copolymer of styrene and butadiene; inert filling material.

Saturable, porous base material, e.g. flannel, impregnated with vulcanizable rubbers; vulcanizing agent; inert filling material.

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SHEET MATERIAL FOR STIFFENING SHOE UPPERS

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6 Claims. (Cl. 117—68)

This invention pertains to sheet material for stiffening shoe uppers and is directed particularly to subject matter divided from parent application Serial No. 392,302, filed November 16, 1953, now Patent No. 2,780,879, in the names of Raymond B. Harrison and Russell G. Edwards.

The general object of the basic invention to which it pertains is to improve the wearability and appearance of a shoe by providing it with a box toe or other upper stiffening element embodying fully cured rubber material having a high degree of permanent resilience, and yet at the same time avoiding all problems of conforming such elements to the shoe last and of varying or increasing shoe manufacturing operations, or costs, such as derive from the customary practice followed in incorporating fully cured or partially cured box toes or similar stiffening elements.

In the accomplishment of this general objective there has been developed a shoe stiffening sheet material impregnated with an uncured rubber and a curing agent, from which to cut and skive box toes, counters, and the like for incorporation in the upper of a shoe through the use of various rubber cements containing self-curing, migratory vulcanizing accelerators operative at room temperatures. Particularly advantageous in use and commercially available are the dithiocarbamate type room temperature accelerators.

Vulcanization or curing of the impregnant composition does not occur at room temperature until the dithiocarbamate or other accelerator migrates from the adhesive cement into the upper affixed or last-formed box toe, thus bringing together the sulphur or a curing agent and the accelerator essential for self-curing of the rubber. Various perfecting agents may be used with the sulphur to enhance the powerful action of the dithiocarbamate on the rate of reaction between rubber and sulphur. The impregnant composition is thus changed physically from a plastic condition to a resilient mass creating a lively rebound in the toe structure.

It is the specific object of the instant invention to provide shoe stiffener sheet material of the character indicated with an auxiliary saturant or coating that will add a different uncured rubber component to the sheet material for preventing "blocking" or welding of the sheet material to itself particularly while being "dinked" or cut.

These and other features of the invention will be particularized and more fully understood from the following detailed descriptions of preferred embodiments, when taken in connection with the accompanying drawing in which the single figure is an end perspective view of a preferred embodiment of such sheet material.

The shoe stiffener sheet material from which a toe stiffener blank or a counter stiffener blank is formed may be made of any suitable base material such as carded

felt, napped or unnapped woven textiles, paper and the like although only the use of a preferred flannel yard goods will be described in detail. Entirely suitable finished sheet materials in a desired range can be produced from four basic flannels having yard-to-pound relationships of 4.18, 3.00, 2.35 and 1.60.

In actual practice ideal results have been obtained by the use of two saturations and a final spread coating on one or both sides of the saturated base material. Double saturating appears desirable because it has been found difficult to obtain the ounce load required with a single saturation. Further, a second saturation permits the use of a different compound, which, though subject to full curing by the room temperature accelerators contained in the cement, acts to decrease the tendency of the finished stiffener sheet to block to other adjacent sheets, as would occur in packaging and also in cut box toe and counter blanks when die cut in multiple thicknesses on a beam dinker or clicking machine. Final insurance against blocking is obtained by spread coating a film of the material comprising the second saturating compound on one side of the finished sheet goods. It is possible, however, to obtain adequate impregnation of the saturable base material with only a single saturation of either saturating compound.

An exemplary formula for the first saturating compound is as follows:

First saturant

	Parts by Weight	Trade Names
Crude Rubber (smoked sheet)	100	
Vulcanized Vegetable Oil	10	Amberex-S.
Stearic Acid	1	
Sulphur	3.5	
Zinc Oxide	5	
Calcium carbonate	90	Atomite.
Titanium Dioxide	15	
Antioxidant	1	Antox.
	225.5	
Petroleum Naptha	200	
Denatured Alcohol	6	

In the above formula, which is a preferred one, the vulcanized vegetable oil may range from 10 to 20 parts, the sulphur from 2 to 3.5 parts, the zinc oxide from 5 to 10 parts, and the inert calcium carbonate particles from 30 to 150 parts. GR–S synthetic rubber (butadiene-styrene copolymer) may be used in place of the crude rubber providing the sulphur is increased to 4.5 to 5 parts.

It will be noted that the above compound includes, in addition to sulphur and other vulcanizing agents, a predominant amount of crude rubber and a very substantial portion of calcium carbonate which acts as a filler. Other rubber latices may be employed in the unvulcanized form.

This first saturating compound may be made by premasticating the crude rubber on a rubber mill and thereafter adding the other solid ingredients until all are uniformly milled together. Using the petroleum naphtha as a solvent for the rubber, and denatured alcohol as a viscosity reducer, the milled material is finally churned to a viscosity suitable for saturation.

The second saturating compound which is used also as a final spreading compound differs in that the predominant elastomeric component is an unvulcanized synthetic rubber which is a rubbery copolymer of butadiene

and acrylonitrile. This compound, an exemplary formula of which is as follows, also contains a substantial portion of a resinous copolymer of styrene and butadiene:

Second saturant and spreading compound

	Parts by Weight	Trade Names
Synthetic Butadiene (Acrylonitrile Elastomer).	100	Paracril B J.
Zinc Oxide	10	
Sulphur	3.5	
Styrene-Butadiene Copolymer (Resin)	35	Marbon 8000.
Calcium Carbonate	70	Atomite.
Stearic Acid	1	
High Melting Synthetic Wax	4	Acrawax C.
Titanium Dioxide	15	
Antioxidant	1	
	239.5	
Toluol	280	

In the preceding formula, which is a preferred one, the zinc oxide may range from 2 to 10 parts, the sulphur from 2.5 to 3.5 parts, the styrene-butadiene copolymer from 10 to 35 parts, the calcium carbonate from 20 to 70 parts, the stearic acid from 1 to 2 parts, and the wax from 4 to 6 parts.

In this instance the compound may be produced by premasticating the synthetic butadiene elastomer on a rubber mill, and then adding all other solid components until a uniformly milled condition is obtained. Employing toluol as a solvent, the milled material is churned to a suitable saturating or spreading viscosity.

It has been found that an entirely satisfactory shoe stiffening blank material is obtained by saturating and coating a 1.60 double-napped flannel with the above compounds in the following manner: The flannel is saturated with the saturant of the first compound, and thereafter it proceeds through a drier having a temperature of the order of 180° F. for a suitable period. The thus dried saturated material in rolled form is then fed to the second saturant, after which it also travels through a drier having a temperature of the order of 180° F. This roll of dried, double saturated base material is then fed through a knife spreader, which imparts a light coating to one surface only, using the same compound employed in the second saturating treatment. The spreading operation is continuous and the base material coated with the spreading compound proceeds through a drying zone having a temperature of the order of 190° F.

The room temperature, ultra-accelerators that will ultimately contact the surface of the finished box toes, counters, and like shoe stiffening elements will cure both the natural and synthetic rubbers of the two saturating compounds. The particular reason for using the crude rubber impregnant first is that more "bounce," as a characteristic of the finished box toe, develops from the finally cured crude than from the finally cured synthetic rubber. The uncured crude rubber, however, is slightly tacky and prone to weld or block to itself. By using it as a first impregnant and then covering it with the second impregnant comprising a synthetic rubber which, though curable, has much less tendency to weld in its uncured state, welding of either uncured sheet goods or uncured cut shoe stiffener blanks is successfully avoided. It is possible also to use only the second saturant compound by following the previously described procedure with the second saturant compound used for each impregnation. The resulting cured box would have moderately less "life" and "bounce" as compared to one embodying the crude rubber saturant. In this connection it will be recalled that the shoe stiffening, sheet material will in each instance remain uncured until it is incorporated into the shoe with accelerator-laden cement.

The term "rubber" as used broadly herein comprehends synthetic as well as natural rubber.

The advantages attained through the use of the shoe stiffening sheet material of this invention are without increase in the cost of shoemaking operations, and are accompanied by such an enhanced superiority of shoe product, that any increase in impregnated sheet material and cement costs is more than compensated by satisfaction to the users of such shoes.

It will be understood that variations, changes, and adaptations can be made in the invention set forth without departing from the principles thereof and the scope of the appended claims.

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

1. As an article of manufacture and sale, a non-blocking shoe upper stiffening sheet material that is pliable and extensible and comprises saturable base material impregnated with vulcanizable rubber in an unvulcanized condition and vulcanizing agent in amount sufficient for eventual curing of the vulcanizable rubber but no vulcanizing accelerator, and a surface coating on at least one side comprising 100 parts of an unvulcanized rubbery copolymer of butadiene and acrylonitrile, from 10 to 35 parts of a resinous copolymer of styrene and butadiene, about 2.5 to about 3.5 parts of sulphur, and about 20 to 70 parts of inert filling material, but no vulcanizing accelerator, said parts being by weight, said article of manufacture being adapted to be adhesively incorporated into the upper of a shoe by an adhesive cement that contains a migratory vulcanizing accelerator.

2. As an article of manufacture and sale, a non-blocking shoe upper stiffening sheet material that is limp and extensible and comprises porous base material impregnated with vulcanizable rubber in an unvulcanized condition and vulcanizing agent in amount sufficient for eventual curing of the vulcanizable rubber, but no vulcanizing accelerator, and has a surface coating on at least one side comprising 100 parts of an unvulcanized rubbery copolymer of butadiene and acrylonitrile, from 10 to 35 parts of a resinous copolymer of styrene and butadiene, about 2.5 to about 3.5 parts of sulphur, and about 20 to 70 parts of inert filling material, but no vulcanizing accelerator, said parts being by weight, said article of manufacture being adapted to be adhesively incorporated into the upper of a shoe by an adhesive cement that contains a migratory vulcanizing accelerator.

3. As an article of manufacture and sale, a non-blocking shoe upper stiffening sheet material that is limp and extensible and comprises porous base material impregnated with vulcanizable rubber in an unvulcanized condition, vulcanizing agent in amount sufficient for eventual curing of the vulcanizable rubber, but no vulcanizing accelerator, and a surface coating on each side comprising 100 parts of an unvulcanized rubbery copolymer of butadiene and acrylonitrile, from 10 to 35 parts of a resinous copolymer of styrene and butadiene, 2 to 10 parts of zinc oxide, 1 to 2 parts of stearic acid, about 4 to 6 parts of wax, about 2.5 to about 3.5 parts of sulphur, and about 20 to 70 parts of calcium carbonate, but no vulcanizing accelerator, said parts being by weight, said article of manufacture being adapted to be adhesively incorporated into the upper of a shoe by an adhesive cement that contains a migratory vulcanizing accelerator.

4. As an article of manufacture and sale, a non-blocking shoe upper stiffener material comprising a sheet of saturable base material impregnated with vulcanizable rubber, vulcanizing agent in amount sufficient to cure the vulcanizable rubber, and inert filling material, but no vulcanizing accelerator; and an anti-blocking surface coating containing 100 parts of an unvulcanized rubbery copolymer of butadiene and acrylonitrile, from 10 to 35 parts of a resinous copolymer of styrene and butadiene, from 2.5 to 3.5 parts of sulphur, and from 20 to 70 parts of inert filling material, but no vulcanizing accelerator, said parts being by weight, said article of manufacture being adapted to be adhesively incorporated into the

upper of a shoe by an adhesive cement that contains a migratory vulcanizing accelerator.

5. As an article of manufacture and sale, a non-blocking shoe upper stiffener material comprising a pliable sheet of saturable base material having an impregnant containing 100 parts of an unvulcanized rubbery copolymer of butadiene and acrylonitrile, from 10 to 35 parts of a resinous copolymer of styrene and butadiene, 2 to 10 parts of zinc oxide, 1 to 2 parts of stearic acid, 4 to 6 parts of wax, from 2.5 to 3.5 parts of sulphur, and from 20 to 70 parts of calcium carbonate, but no vulcanizing accelerator, said parts being by weight, said article of manufacture being adapted to be adhesively incorporated into the upper of a shoe by an adhesive cement that contains a migratory vulcanizing accelerator.

6. As an article of manufacture and sale, a non-blocking shoe upper stiffener material comprising a pliable sheet of saturable base material impregnated with vulcanizable rubber containing a vulcanizing agent in amount sufficient for subsequent curing of the vulcanizable rubber, but no vulcanizing accelerator, and having a coating on at least one surface essentially consisting of an unvulcanized rubbery copolymer of butadiene and acrylonitrile, resinous copolymer of styrene and butadiene; vulcanizing agent; and inert filling material, but no vulcanizing accelerator, said article of manufasture being adapted to be adhesively incorporated into the upper of a shoe by an adhesive cement that contains a migratory vulcanizing accelerator.

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