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RUBBER PRODUCTS

William S. Gocher, Fairfield, and Alfred J. Jennings, Bridgeport, Conn., and Carl M. Langkammerer, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the art of fabric preparation. More particularly it relates to filled rubber products. Still more particularly it relates to an improved leather filler for rubber compounds for use in coating fabrics and to the preparation and use of said filler.

It is well known in the art to employ certain types of finely divided leather as a filler in rubber products such as rubber heels, rubber-coated fabrics, and the like. However, the only types of leather adaptable to this use, other than whole finished tanned hides whose use is prohibited on account of cost, are scraps of finished tanned leather had during the manufacture of finished leather goods such as boots and shoes, leather luggage, and the like. Not only is the supply of such leather scraps limited but the scraps are deficient in certain essential respects. While said scraps when finely divided and employed as fillers in rubber-like materials produce certain desired properties such as increased bulk, reduced gloss, and improved porosity, they are inherently nonuniform in quality. It is impossible to avoid variations from batch to batch of said scraps. In the manufacture of colored rubber-coated fabrics this causes a great deal of extra work and expense because it is necessary to adjust the formula for each batch to match a color standard. In those cases in which the color cannot be matched the run has to be discarded. This of course operates to make control over the quality of the finished product difficult, if not impossible. In the manufacture of two-toned rubber-coated fabrics, made by applying a lacquer to the valleys of embossed material, spotting (believed due to the bleeding of dyes present in the leather scrap filler in the rubber coating) is ordinarily encountered, thus often rendering the product unsaleable. It is also very difficult to obtain light colored finished scrap leather to make ground leather for use in light colored rubber compounds. Furthermore, ground scraps of finished chrome-tanned leather are dispersed in rubber compositions only with the greatest difficulty. In addition, finishes had on fabrics by application thereto of rubber compositions containing ground chrome-tanned finished leather scraps have poor edge-cracking resistance, i. e., poor resistance to cracking under tension when exposed to the elements, thus deleteriously limiting their utility.

In the manufacture of leather, skins and hides are subjected to a shaving process immediately after tanning to reduce them on the flesh side to a uniform thickness. The shavings removed in this operation have been found unsuitable for use in rubber. As a matter of fact they are a waste product of the tanning industry, usually disposed of by being utilized in the manufacture of fertilizer.

We have discovered a process whereby the aforementioned shavings of chrome-tanned leather may be utilized profitably and whereby improved filled rubber products may be produced. Accordingly, this invention has as an object the profitable utilization of chrome-tanned leather shavings. A further object is the conversion of waste chrome-tanned leather shavings into a valuable rubber filler. A still further object is the production of a rubber filler of predetermined and uniform properties, such as color and the like. A still further object is the production of unspotted two-toned rubber-coated fabrics. A still further object is the provision of a leather filler adapted for the production of light colored rubber products. A still further object is the production of a leather filler which disperses readily in rubber compositions. It is also among the particular objects of my invention: to provide an improved method of treating chrome-tanned leather shavings; to provide a novel and improved chrome-tanned leather filler in rubber-like compositions, particularly for use in the coating of cellulosic fabrics; and the production of rubber-coated fabrics having hitherto unrealized durability and resistance to cracking when exposed to the elements. Additional objects will become apparent from an examination of the following description and claims.

These and other objects and advantages are accomplished by the herein described invention which broadly comprises fat-liquoring chrome-tanned leather shavings to an acetone-extractable content in the range of from about 8% to about 15%, drying the treated leather, dry milling the dried leather to an average fiber length in the range of from about 0.1 mm. to about 1 mm., and incorporating the resultant leather filler in a rubber-like material.

In a more restricted sense this invention comprises agitating a mixture of water and undried chrome-tanned leather shavings with an emulsion of a fat-liquoring agent in amount sufficient to increase the acetone-extractable content of the shavings to a value in the range of from about 8% to about 15%, dewatering and drying the treated shavings, dry milling the dried shavings to an average fiber length in the range of from about 0.1 mm. to about 1 mm., and incorporating the resultant leather filler in a rubber-like material.

A preferred embodiment of this invention comprises neutralizing an aqueous suspension of undried chrome-tanned leather shavings to a pH in the range of from about 5 to about 7.5 by addition of an alkali, adding to the neutralized suspension a fat-liquoring emulsion comprising 1 part by weight of fig soap, about 4 parts of sulfonated neat's foot oil, and about 5.5 parts of salted egg yolk (calculated as salted whole eggs), said emulsion being added in amount sufficient to increase the acetone-extractable content of the shavings to a value in the range of from about 8% to about 15%, circulating the resultant suspension in a paper beater, sheeting out and drying the treated suspension on a paper making machine, milling the resultant product in a rotary cutter to an average fiber length in the range of from about 0.1 mm. to about 1 mm., incorporating the resultant finely divided leather in a rubber stock, and applying the leather filled rubber stock to a fabric by calendering or other means known to the art.

By the term acetone-extractable content as employed herein and in the appended claims is meant the acetone-extractable content of the chrome-tanned leather shavings, as determined by the method described in Am. Soc. Testing Materials Standards Tentative Method D—297—41—T, pages 471–473, 1941 Supplement to Am. Soc. Testing Materials Standards, Part III, Non-metallic materials—General, for determining "Acetone Extract;" in rubber products, except that the extraction period employed in determining acetone-extractable content is 8 hours instead of the 16 hours set out in said method at page 473, column 1, lines 16 and 17.

The following examples are given for illustrative purposes and are not intended to place any restrictions or limitations on the herein described invention.

Example I

Two hundred and forty kilograms of damp leather shavings (45% solids) removed from chrome-tanned kid skins were placed in a large vat with 400 kilograms of water and 0.4 kilogram of borax was added. This was stirred occasionally by means of a long pole for 2 hours and the liquid then allowed to drain off. The shavings were again placed in the vat with 400 kilograms of warm water and an emulsion of 12 kilograms of sulfonated cod oil, and a small amount of hot water was added, and the mixture was stirred manually for 12 hours. The greater portion of the water was removed from the shavings on a large earthenware filter and the shavings were dried in a tray drier at room temperature for 3 days. The resulting shavings were reduced to an average fiber length of 0.3 mm. by passage through a swing hammer mill equipped with a bar type rotor revolving at a speed of 9600 R. P. M. and passing the ground material through a 0.027" herringbone screen. This material had an acetone-extractable content of 8%. It was tested as a reenforcing filler in the calender coat of a rubberized fabric.

In the manufacture of the rubberized fabric, useful particularly as a heavy-duty upholstery material, an anchor coat of rubber cement was applied to a cotton sateen. To this was calendered a filled rubber stock comprising a properly formulated mixture of pale crepe rubber, pigments, inorganic fillers, sulfur, accelerators, antioxidants and the leather filler described above. After the calender coat was applied the coated fabric was vulcanized, given a finishing treatment with a solution of sulfur chloride and bromine and finally neutralized in an atmosphere of ammonia. The final product was submitted to a standard exposure test in which a strip of the material was held under tension over a rod and exposed. Cracks had not appeared in the curved portions of the test specimen after 31 days exposure in Florida whereas a corresponding product differing from the above only in that the treatment with sulfonated cod oil was omitted in processing the shavings, cracked at the end of 17 days exposure. Another advantage of the filler which was treated with sulfonated cod oil was that it dispersed more rapidly and more completely in the rubber stock than did the untreated one. A still further important advantage of the treated filler was that the rubber product prepared using it was less susceptible to over-treatment with the solution of sulfur chloride and bromine. The hardening treatment could be controlled more readily in the case of the rubber coating containing the treated filler.

Example II

Grit and dust were removed from damp chrome-tanned calf skin shavings containing approximately 50% solids. Two thousand pounds of the screened damp shavings were placed in a Hollander type paper beater with sufficient water to permit good circulation and then cut sufficiently to permit handling through the paper machinery pumps and lines without plugging. As soon as this cutting was completed the knives were raised to clear the bed plate and the cutter run only to maintain agitation in the beater tank. The acidity was then adjusted to a pH of 7.0 to 7.5 by adding sodium carbonate solution. An emulsion was prepared by agitating 400 pounds of warm water, 33.2 pounds of fig soap, 132.4 pounds of sulfonated neat's-foot oil and 177.4 pounds of salted whole eggs. This emulsion was added to the contents of the beater and agitation continued for 2 hours, thereby increasing the acetone-extractable content of the shavings to 8–15%. The pulp was then diluted with water to the proper consistency to obtain a strong web on a Fourdrinier paper machine screen. It was then sheeted out on the Fourdrinier machine and the resulting sheet dried on can driers. The resultant sheet was then reduced to an average fiber length of 0.2–0.8 mm. in a rotary cutter. The flock was collected from the cutter by means of a pneumatic system. In production there has been no perceptible variation in batches prepared in this manner, and the rubber products manufactured with them have been much more uniform in color and quality, and markedly superior in durability and resistance to cracking when exposed to the elements than corresponding products made from the best commercial prior art ground leather fillers.

While the invention has been described with particular application to the treatment of chrome-tanned calf and kid skin shavings, the treatment of other types of chrome-tanned leather shavings is contemplated. Said shavings may be had from all types of chrome-tanned hides and skins, including those of cattle, sheep, goats, horses, swine, and the like. It is only essential that the shavings employed in our process be chrome-tanned leather shavings, by which term is meant the shavings produced when chrome-tanned animal skins and hides are subjected to a shaving operation after tanning, but before

subjection to subsequent finishing operations. Said shavings may be dried prior to treatment by our process, but for best results they should be maintained in a damp condition prior to treatment according to this invention.

In the practice of the present invention it is desirable, on account of the superior results thereby obtained, to neutralize the chrome-tanned leather shavings, preferably to a pH in the range of from about 5 to about 7.5, before fat-liquoring them. This may be done conveniently by adding an alkaline reacting material, preferably an inorganic alkaline reacting compound or admixture of such compounds, to an aqueous suspension of said shavings. Alkaline compounds contemplated for use in the invention include alkali metal and alkaline earth metal compounds, including ammonium compounds, which react with an inorganic acid, e. g., an aqueous solution of hydrogen chloride, to form water. Examples of such compounds include the oxides, hydroxides and carbonates of ammonium, sodium, potassium, calcium, strontium and barium. However, our preferred neutralizing agents, because of the superior results had through their use, are members of the class of inorganic alkaline reacting alkali metal compounds, which term includes ammonium compounds, or any combination of said alkali metal compounds. In this connection, it is to be understood that by the term alkaline reacting we mean forming with water a solution having a pH in excess of 7. Sodium carbonate, borax, sodium hydroxide, potassium hydroxide, ammonium hydroxide and potassium carbonate are examples of said preferred neutralizing agents.

The chrome-tanned leather shavings, preferably damp chrome-tanned leather shavings, may be fat-liquored in any suitable manner. It has been found satisfactory to simply stir the shavings manually with the fat-liquoring agent in a large vat. Paddle vats and similar types of agitating equipment are also suitable, as is also a paper pulp beater, such as a Hollander. The shavings are agitated in the presence of the fat-liquoring agent, and since this tends to shred and defiber them in a preliminary way, it makes the subsequent dry milling easier. Any of the fat-liquoring agents which are normally used in finishing leather may be employed in our process. Examples of such fat-liquoring agents are neat's-foot oil, cod liver oil, palm kernel oil, coconut oil and wool fat, soft thick soaps, castile soap, or hard tallow soaps, sulfonated castor oil, sulfonated neat's-foot oil, sulfonated cod liver oil, and sulfated alcohols of commerce. These materials are best employed as emulsions. A particularly suitable emulsifying agent is salted whole egg• yolk. Our preferred fat-liquoring agent, in view of the superior results obtained through its use, is an aqueous emulsion comprising fig soap, egg yolk, and sulfonated neat's-foot oil, preferably an emulsion containing 1 part by weight of fig soap, about 5.5 parts (calculated as whole eggs) of egg yolk, and about 4 parts of sulfonated neat's-foot oil in about 12 parts of water.

It is to be understood that the amount of fat-liquoring agent required will vary somewhat with the agent, the type and previous history of the leather shavings being treated, the concentration of the shavings suspension, the degree of agitation of said suspension, the length of time the shavings are in contact with the agent, and the properties desired in the finished product. It is critical, however, to the results which are obtained, that the amount of fat-liquoring agent employed be such that the acetone-extractable content of the dried shavings produced be not less than about 8% nor more than about 15% of the weight of said shavings. If the acetone-extractable content lies below about 8% the resulting ground leather product is difficult to disperse in a rubber stock so that an excessive amount of milling is required. Furthermore, a rubber material containing such filler provides a surface coating on textile fabrics and the like which is deficient in resistance to cracking under tension on outdoor exposure. On the other hand, if the acetone-extractable content of the dry leather product is in excess of about 15% it is substantially impossible, by dry milling means, to reduce said dried product to the requisite fiber length for incorporation in rubber or other rubber-like material. Furthermore, such a leather product, when ground and incorporated in rubber, detracts from the physical properties of the final product.

After the leather shavings are fat-liquored they are dewatered, as by filtering or centrifuging, and are then dried. The aqueous suspension may be filtered and dried in any convenient manner and it has been found very convenient to do so by sheeting on a paper making machine wire, e. g., Fourdrinier or cylinder, and to dry the resultant sheet on paper machine driers.

The present process comprises the step of dry milling the treated and dried leather shavings. It is to be understood that it is essential that said milling be conducted in such a manner that the average fiber length of the resultant product is in the range of from about 0.1 mm. to about 1 mm. Said dry milling may be accomplished in any convenient manner. It may, for example, be effected by a pulverizing process as by milling the dried treated leather shavings in pulverizing mills such as ring roll mills, edge runner mills, pebble mills, buhrstone mills, and the like. Ring roll mills are usually preferred for this type of milling and in practice are best equipped with an air separation system which depends on centrifugal force to separate out the oversize particles and return them to the mill for further pulverizing, while allowing those of proper size to pass on as finished product. Another suitable type of drymilling is by disintegrating which is accomplished in rotary hammer mills, squirrel cage disintegrators, and the like. Milling of the dried treated leather shavings by means of a rotary cutter is also quite effective. A preferred dry milling means comprises a combination of an attrition mill and a rotary cutter, the fiber length of the milled product being controlled by the choice of grinder and the size of screen.

Although this invention is described particularly with reference to filled natural rubber compositions, it is to be understood that the production of all types of rubbery or rubber-like materials filled with our novel leather filler is within the scope of said invention. By rubbery or rubber-like material is meant a substance which has physical properties resembling those of natural rubber; that is it can be stretched to an elongation of at least 300 percent, and when released will quickly and forcibly retract to substantially its original dimensions. Among said rubber-like materials are included rubber, and synthetic rubbers such as chloroprene polymers (including 1-chlorobutadiene-1,3 polymers), butadiene polymers (including butadiene-1,3

polymers, and copolymers such as polymers of butadiene-1,3 with styrene, acrylonitrile, or the like), organic polysulfides (including reaction products of aliphatic polyhalogen compounds with soluble metal sulfides or polysulfides), isobutene polymers, plasticized vinyl chloride polymers, and dimethyl butadiene polymers, and the like.

The leather filler of this invention may be incorporated in rubber-like materials in any convenient manner.

Our process possesses advantages not previously combined in a single process. Furthermore, the fillers obtained by our process possess advantages not previously combined in a rubber filler. Moreover, the ultimate products of our process possess advantages not previously combined in a rubber product. Not only do the fillers of this invention produce rubber products, particularly rubber coatings on fabrics, having desired increased bulk, reduced gloss, and improved porosity; they also impart to said rubber products long sought but hitherto unrealized characteristics and advantages, and effect this result through the employment of a material available in abundant quantities which has been a waste and substantially worthless by-product of the tanning industry, namely chrome-tanned leather shavings. Among the hitherto unrealized characteristics and advantages obtained in rubber-like materials through the employment of this invention are included markedly superior durability and resistance to cracking when exposed to the elements, e. g., sun and rain; predetermined and uniform properties such as color and the like; brighter color; a rubber-coated fabric which is adapted for the manufacture of an unspotted two-toned product by the application of a lacquer to the valleys of said fabric after it is embossed; and light color. Furthermore, our novel filler may be incorporated readily in rubber-like materials. Said filler is particularly and peculiarly adapted for incorporation in said rubber-like materials; when so employed it acts quite differently from the fillers of the prior art, including all known prior art leather fillers, producing a unique leather/rubber-like material composition having properties which are novel, useful and unforeseen.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

Having described the present invention, the following is claimed as new and useful:

1. In a process for making a rubber product, the steps of fat-liquoring chrome-tanned leather shavings to an acetone-extractable content in the range of from about 8% to about 15%, drying the treated shavings, and dry milling the dried shavings to an average fiber length in the range of from about 0.1 mm. to about 1 mm.

2. In a process for making a rubber product, the steps of mixing water and chrome-tanned leather shavings, adding an alkaline reacting material thereto in amount sufficient to provide a pH in the range of from about 5 to about 7.5, agitating the thus neutralized mixture with an amount of fat-liquoring agent sufficient to increase the acetone-extractable content of the shavings to a value in the range of from about 8% to about 15% based on the dried weight of the shavings, filtering and drying the thus treated shavings, and dry milling the dried shavings to an average fiber length in the range of from about 0.1 to about 1 mm.

3. In a process for making a rubber product, the steps of agitating a mixture of water and undried chrome-tanned leather shavings, adding an inorganic alkaline reacting material thereto in amount sufficient to provide a pH in the range of from about 5 to about 7.5, agitating the thus neutralized mixture with an emulsion of a fat-liquoring agent in amount sufficient to increase the acetone-extractable content of the shavings to a value in the range of from about 8% to about 15% based on the dried weight of the shavings, filtering and drying the thus treated shavings, and dry milling the dried shavings to an average fiber length in the range of from about 0.1 mm. to about 1 mm.

4. In a process for making a rubber product, the steps of beating a mixture of water and undried chrome-tanned leather shavings in a paper beater, adding an alkaline reacting compound of an alkali metal thereto in amount sufficient to provide a pH in the range of from about 5 to about 7.5, continuing circulating but not cutting of the thus neutralized mixture in the beater and adding thereto an aqueous emulsion of a fat-liquoring agent comprising fig soap, sulfonated neat's-foot oil, and egg yolk, said emulsion being added in amount sufficient to increase the acetone-extractable content of the shavings to a value in the range of from about 8% to about 15% based on the dried weight of the shavings, sheeting the thus treated shavings on a paper machine wire and drying the sheet on a paper machine dryer, and dry milling the dried sheet in a rotary cutter to an average fiber length in the range of from about 0.1 mm. to about 1 mm.

5. In a process for making a rubber product, the steps of fat-liquoring chrome-tanned leather shavings to an acetone-extractable content in the range of from about 8% to about 15%, drying the treated shavings, dry milling the dried shavings to an average fiber length in the range of from about 0.1 mm. to about 1 mm., and incorporating the resultant filler in rubber.

6. A rubber product comprising rubber and chrome-tanned leather shavings which have been fat-liquored to an acetone-extractable content in the range of from about 8% to about 15% based on the dry weight of said shavings and which have an average fiber length in the range of from about 0.1 mm. to about 1 mm.

7. As an improved rubber filler, chrome-tanned leather shavings which have been fat-liquored to an acetone-extractable content in the range of from about 8% to about 15% based on the dry weight of said shavings and which have an average fiber length in the range of from about 0.1 mm. to about 1 mm.

WILLIAM S. GOCHER.
ALFRED J. JENNINGS.
CARL M. LANGKAMMERER.