Jan. 23, 1951 D. G. SLOVIN 2,539,334

GASEOUS DE-PINKING METHOD

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Fig. 1

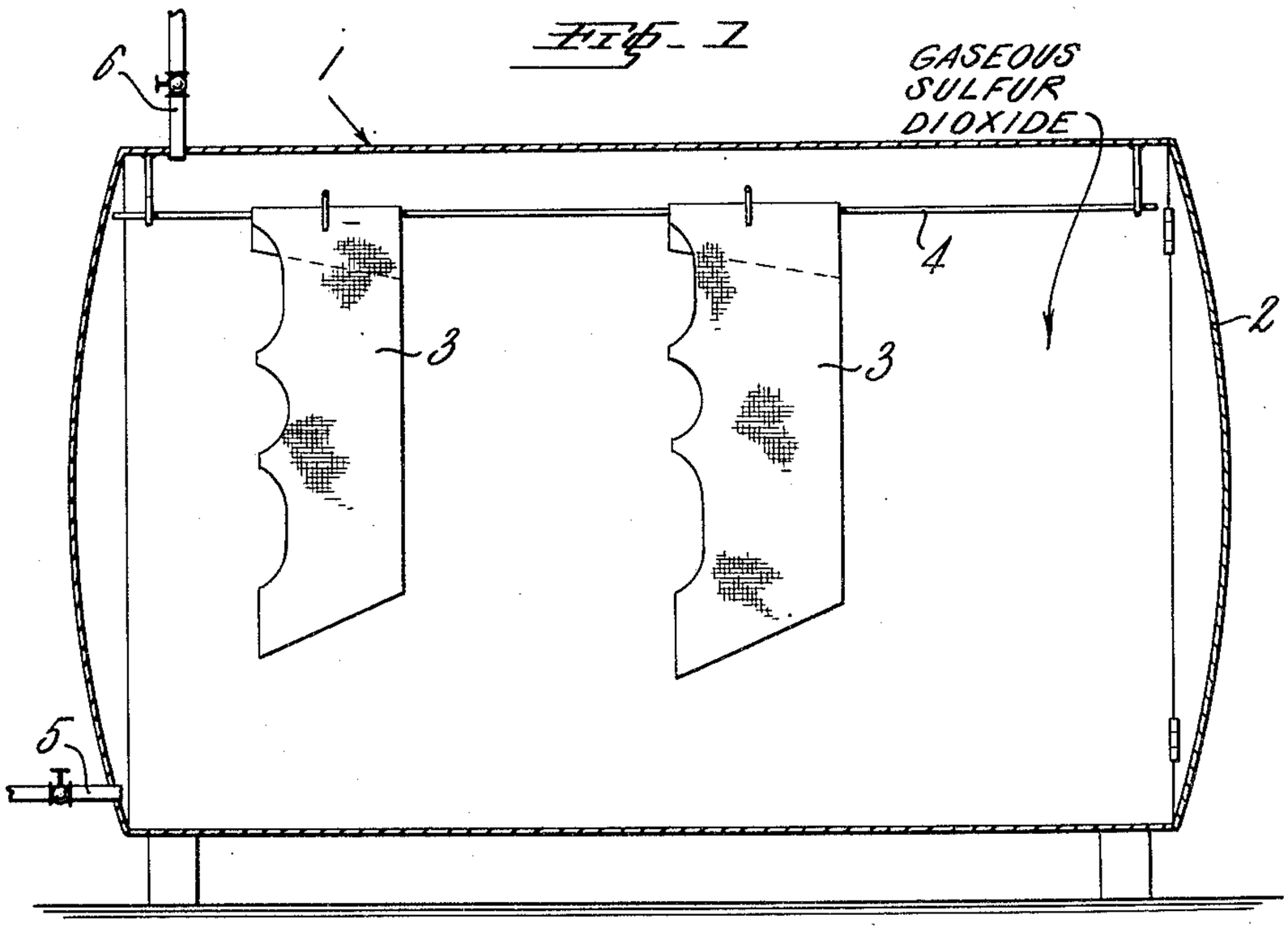
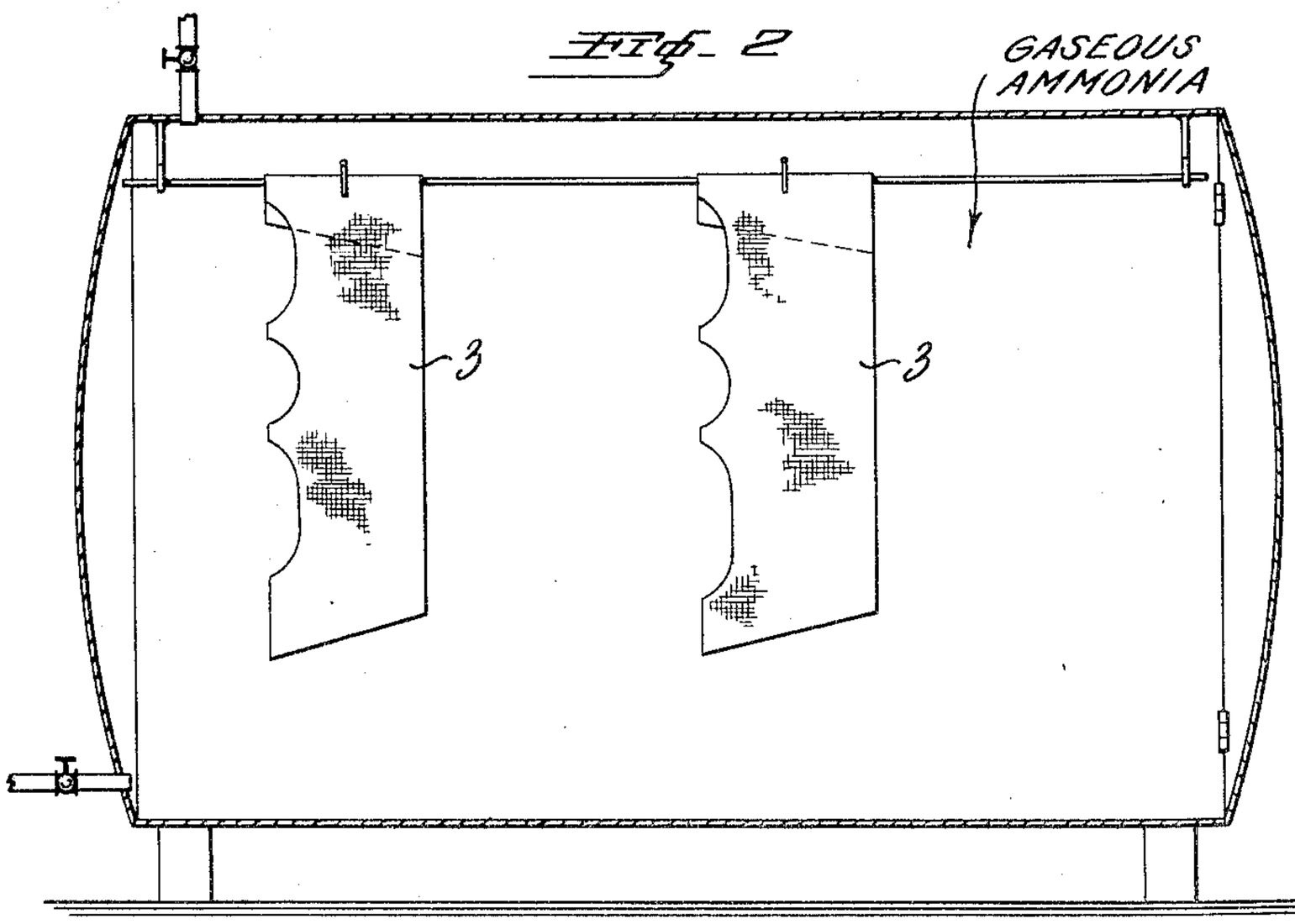


Fig. 2



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GASEOUS DEPINKING METHOD

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8 Claims. (Cl. 8—102)

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This invention relates to a method for removing from vulcanized rubber articles, particularly articles made of or containing elastic yarns having a core of vulcanized rubber and a wound covering of textile yarn, the pink discoloration which results from the presence of symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant in the vulcanized rubber. Still more particularly the invention relates to a method of removing such pink discoloration from oven textile materials comprising such elastic yarn, particularly when such woven textile material is in the form of cut pieces intended to be formed into a garment or the like, without wetting such materials with a liquid.

Symmetrical di-beta-naphthyl-para-phenylene diamine is one of the best all-around anti-oxidants for vulcanized rubber thus far developed. However, it exhibits the objectionable characteristic that it turns pink when it is subjected to certain conditions, particularly when subjected to light and oxidizing conditions. Under ordinary storage conditions pinking does not occur. However pinking appears to be catalyzed by light, and certain oxidizing media such as nitric oxide fumes and ozone; and where these conditions prevail, pinking often becomes very rapid. Pinking readily occurs also during bleaching operations, such as with chlorine and hydrogen peroxide, especially the former. This pink discoloration changes the color or shade desired for the article and is highly objectionable.

The problem of pinking as a result of the use of this anti-oxidant in rubber compositions and articles containing the same is especially serious in the case of light-colored vulcanized rubber compounds, such as those having a light pastel color or those which are white in color. The reason is that the development of the pink by decomposition or other change of the anti-oxidant changes the shade from that which is desired.

The problem of pinking is especially serious in the case of articles or materials made from or containing elastic yarn comprising a core of vulcanized rubber containing the above anti-oxidant and a wound covering of textile yarn. This problem is particularly serious where white or light-colored textile yarns are used as the covering for the elastic core or in association with the elastic yarn to make the fabric of which the article or material is formed or woven. The pink discoloration which occurs as a result of the above anti-oxidant in the vulcanized rubber core of the elastic yarn usually shows through the associated white or light-colored textile

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yarns and fibers, often in an irregular or non-uniform manner, and this is highly objectionable.

Elastic yarn of the type just referred to is described in detail in the Adamson Patent 1,822,847. This elastic yarn typically has a core of elastic vulcanized rubber under tension with a covering of a plurality of helical, preferably both right and left, windings which hold the core elongated, the yarn having a predetermined capacity to stretch.

The elastic vulcanized rubber core of the elastic yarn may be made in any suitable manner. The method of making this core is well-known to the art and constitutes no part of the present invention. It is preferred to utilize rubber of a grainless character such as that obtained by coagulation, drying and vulcanization of suitably compounded rubber latex especially the latex from *Hevea brasiliensis*. It is preferred to use rubber thread of circular cross-section as the core. The latex may be compounded, prior to coagulation, with suitable types and amounts of rubber compounding ingredients such as sulfur or other vulcanizing agents, vulcanization accelerators, activators such as zinc oxide, and an effective amount of symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant. The amount of the latter may vary widely but should be sufficient to be effective to prevent or greatly retard the oxidation of the rubber. The amount will usually range from 0.25 to 2.0% by weight based on the rubber present. The statements just made with reference to the compounding of the rubber core of elastic yarn apply equally to the compounding of rubber in any other form to which the present invention is applied.

The present invention is based on the discovery that the pink discoloration which develops in vulcanized rubber-containing articles, such as woven textile fabrics comprising the above-described elastic yarn, as a result of the presence of symmetrical di-beta-naphthyl-para-phenylene diamine in the rubber, can be completely removed therefrom by subjecting the pinked materials to the action of gaseous sulfur dioxide. I do not at this time know what reactions the anti-oxidant in question undergoes in pinking or in de-pinking in accordance with my invention. It may be that the sulfur dioxide gas combines with the traces of moisture always normally present in the goods being treated to form sulfurous acid, a weak acid with a mild reducing action, which effects the de-pinking. Alternatively, the sulfur dioxide may combine with the

anti-oxidant or its decomposition products in some manner to destroy the pink discoloration.

It appears that the action of the gaseous sulfur dioxide is not one of bleaching, since the action of such bleaching agents as chlorine and hydrogen peroxide is to cause pinking rather than to remove it.

Whatever the explanation be, the exposure of the pinked material to gaseous sulfur dioxide effects removal of the pink discoloration and the material which has been de-pinked in this manner is more resistant to subsequent pinking than was the original material before the first pinking, such as the normal woven fabric containing the elastic yarn having a core of vulcanized rubber containing the anti-oxidant in question. However, should the de-pinked material subsequently develop pinking, such subsequent pinking can be easily removed by means of the present invention.

In practicing my invention, the pinked material is subjected to the action of gaseous sufur dioxide in any suitable way, preferably by placing the material in an atmosphere of sulfur dioxide gas. The treatment is effected while the material is maintained in its normally dry condition, i. e., without wetting the material which might cause shrinkage, distortion or other difficulties. Typically, the procedure of the present invention is carried out by suspending the pinked material on racks, pins, etc., in a closed container containing gaseous sulfur dioxide, either in concentrated form or diluted with a suitable diluent, usually air.

The sulfur dioxide gas may be obtained from any suitable source. A very convenient way of forming the sulfur dioxide atmosphere is to place on the bottom of the closed container a pan holding a water solution of sodium hydrosulfite. The solution may be of any convenient concentration, typically 10%. The solution is unstable and releases sulfur dioxide fumes. The whole may be allowed to stand at room temperature until the pinking has disappeared which may be a matter of a few minutes or a few hours, depending upon the severity of the pinking and the ease of penetration of the sulfur dioxide gas through the material. For example if the pieces of material are stacked, considerable time has to be allowed for penetration. Over-treatment with sulfur dioxide does no harm whatsoever. An overnight treatment is often convenient. With regard to the amount of sodium hydrosulfite required, an amount equal to about 5% by weight based on the weight of the goods is generally sufficient but more or less can be used as needed. The use of warm water in making up the sodium hydrosulfite solution speeds up the evolution of sulfur dioxide gas and will generally shorten the time of treatment required.

Alternatively, instead of placing an aqueous solution of sodium hydrosulfite in the bottom of the container used for the treatment, sulfur dioxide from any other source, as for example from a cylinder or generated from any simple chemical reaction, such as by the action of concentrated sulfuric acid upon sodium bisulfite solution, may be used. Where sulfur dioxide gas from a cylinder is employed, the procedure may be the same as that just described except that instead of using a pan of the sodium hydrosulfite solution, arrangements are made for feeding the gas slowly to the container used for carrying out the treatment; an outlet from the treatment container to the outside atmosphere is preferable to

prevent building up of dangerous pressures in the treatment vessel.

It is difficult to specify exactly the amount of sulfur dioxide actually employed in the treatment. However the use of amounts of the order of from 1 to 2% by weight based on the weight of the fabric or other material being treated is generally ample.

When the de-pinking action is complete, I prefer to subject the de-pinked material or goods to the action of gaseous ammonia (NH_3) until any acidic material present therein has been neutralized. This may be done in the same container as that in which the de-pinking was accomplished by removing the source of the sulfur dioxide and substituting a source of ammonia, for example a pan of aqua ammonia. It will be understood that the treatment with sulfur dioxide will usually leave some excess sulfur dioxide, which is mildly acidic, on and in the de-pinked material and that the ammonia will neutralize this acidity. Ammonia from any source may be used for this purpose. For example, I may employ ammonia from a cylinder, feeding the gaseous ammonia into the neutralizing chamber in a manner similar to that suggested above for sulfur dioxide. The treatment with ammonia gas should be of sufficient duration to completely neutralize any acidic material present in the de-pinked goods. A relatively short exposure of from 5 to 10 minutes will often suffice. Again the length of the treatment will depend upon the rapidity of penetration of the gas into the goods.

The treatment with ammonia may take place in the same chamber as that in which the de-pinking was effected or in another chamber.

While my invention is often practiced in a batchwise manner, it will be understood by those skilled in the art that, if desired, it may be carried out continuously, for example by continuously passing the goods or material to be de-pinked through an atmosphere of gaseous sulfur dioxide and thereafter continuously passing them through an atmosphere of gaseous ammonia.

It will be apparent from the foregoing that the material, while undergoing treatment in accordance with my invention, is in its normally dry condition, i. e., any water content is so small that it is not visible to the eye or detectable to the touch as water. Usually the water content of the goods treated varies between 1 and 7% by weight depending on the type of material and the humidity prevailing.

My invention is particularly advantageous in those cases where the goods or other material turn pink after finishing and where no wet finishing is normally required, since the expense of re-wetting the goods and re-drying them is eliminated by the present invention. Furthermore, most users of the goods are not equipped to remove the pink by a wet bath treatment and would have to have it done by outside finishers. In addition there are many cases where it is not permissible to wet the goods because of the danger of shrinkage or distortion, danger of discoloration, etc. My new method takes care of such situations and permits anyone to carry out the de-pinking process. The invention is especially applicable where the goods, such as fabrics containing the elastic yarn mentioned above, turn pink after they have been cut into patterns preparatory to sewing into a garment or other article; in such cases a wet treatment generally is out of the question since the cut sections display an objectionable tendency to shrink or become

distorted in shape. The gaseous treatment of my invention, involving no wetting whatever of the goods, is ideally adapted to de-pinking of such cut pieces.

The present invention has many other advantages which will be apparent to those skilled in the art. It provides a simple and effective way of removing the pink discoloration developed in rubber goods containing the above anti-oxidant. It can be carried out with simple inexpensive equipment. It obviates use of complicated liquid treatment and drying equipment. The materials being treated need not be wet which as indicated above would often distort the goods and moreover would rquire subsequent drying. While the procedure of my invention is generally used on elastic yarns and fabrics containing the same, it may be applied to any rubber-containing material which shows a pink discoloration due to the presence of the anti-oxidant mentioned above.

In the accompanying drawing, which is substantially self-explanatory in the light of the foregoing description, Fig. 1 shows a tank-like chamber 1 having a door 2 and within which there is an atmosphere of gaseous sulfur dioxide, generated in any suitable manner. The cut pieces of goods 3 are suspended on any suitable supporting means such as a bar 4, in this atmosphere. The sulfur dioxide atmosphere may be achieved by supplying sulfur dioxide gas from any suitable source through inlet 5. An outlet 6 may be provided as a bleed to prevent excessive pressure build-up of sulfur dioxide in chamber 1. In Fig. 2 the same pieces of goods 3 are shown as being subsequently treated in a gaseous atmosphere of ammonia. The construction of the Fig. 2 chamber may be the same as that shown in Fig. 1.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. A method of removing visible pink discoloration which has developed in a vulcanized rubber article as a result of the presence therein of symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant therefor which comprises subjecting said article, while maintaining it in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared.

2. A method of removing visible pink discoloration which has developed in a vulcanized rubber article as a result of the presence therein of symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant therefor which comprises subjecting said article, while maintaining it in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared, and then subjecting the resulting article, while maintaining it in the dry condition, to the action of gaseous ammonia until any acidic material present in said article has been neutralized.

3. A method of removing visible pink discoloration which has developed in an article comprising elastic yarn having a core of vulcanized rubber containing symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant and a wound covering of textile yarn, said discoloration resulting from the presence of said anti-oxidant, which comprises subjecting said article, while maintaining it in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared.

4. A method of removing visibile pink discoloration which has developed in an article comprising elastic yarn having a core of vulcanized rubber containing symmetrical di-beta-naphthyl-para-phenylene diamine as an an anti-oxidant and a wound covering of textile yarn, said discoloration resulting from the presence of said anti-oxidant, which comprises subjecting said article, while maintaining it in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared, and then subjecting the resulting article, while maintaining it in the dry condition, to the action of gaseous ammonia until any acidic material present in said article has been neutralized.

5. A method of removing visibile pink discoloration which has developed in woven textile fabric comprising elastic yarn having a core of vulcanized rubber containing symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant and a wound covering of textile yarn, said discoloration resulting from the presence of said anti-oxidant, which comprises subjecting said fabric, while maintaining it in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared.

6. A method of removing visible pink discoloration which has developed in woven textile fabric comprising elastic yarn having a core of vulcanized rubber containing symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant and a wound covering of textile yarn, said discoloration resulting from the presence of said anti-oxidant, which comprises subjecting said fabric, while maintaining it in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared, and then subjecting the resulting fabric, while maintaining it in the dry condition, to the action of gaseous ammonia until any acidic material present in said fabric has been neutralized.

7. A method of removing visible pink discoloration which has developed in cut pieces of woven textile fabric comprising elastic yarn having a core of vulcanized rubber containing symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant and a wound covering of textile yarn, said discoloration resulting from the presence of said anti-oxidant, which pieces cannot be given a liquid treatment without objectionable change in shape, which comprises subjecting said cut pieces, while maintaining them in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared.

8. A method of removing visible pink discoloration which has developed in cut pieces of woven textile fabric comprising elastic yarn having a core of vulcanized rubber containing symmetrical di-beta-naphthyl-para-phenylene diamine as an anti-oxidant and a wound covering of textile yarn, said discoloration resulting from the presence of said anti-oxidant, which pieces cannot be given a liquid treatment without objectionable change in shape, which comprises subjecting said cut pieces, while maintaining them in the dry condition, to the action of gaseous sulfur dioxide until the pink discoloration has disappeared, and then subjecting the resulting pieces, while maintaining them in the dry condition, to the action of gaseous ammonia until any acidic material present therein has been neutralized.

DAVID G. SLOVIN.

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