

# UNITED STATES PATENT OFFICE

2,602,017

## MONOMETHYLOL DIMETHYL HYDANTOIN TO SHRINKPROOF CELLULOSE FABRICS

Leo Beer, Montreal, Quebec, Canada

No Drawing. Application December 1, 1949, Serial No. 130,609. In Canada November 22, 1949

2 Claims. (Cl. 8—116.3)

1

### INTRODUCTION

This invention relates to the chemical shrinkage control of textile fabrics.

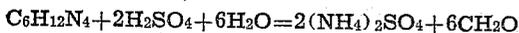
The process is applicable to cellulosic textiles. They may be made from natural cellulose or regenerated cellulose or mixtures of one or both of the said types with up to about 50% of a cellulose ester of an organic acid, for example, cellulose acetate.

### PRIOR ART

Many attempts have been made to develop and perfect processes which control the shrinkage of such fabrics. For this purpose, fabrics have been treated with mono- or dialdehydes such as formaldehyde or glyoxal in the presence of acids or in the presence of a salt which is acid reacting per se or becomes acid during processing, for example, during baking at elevated temperature. This results in deterioration in tensile strengths and abrasion resistance which is especially serious in the case of cotton and is often accompanied by discoloration.

The aldehyde is applied either as a watery solution or as a compound which only splits off the bound aldehyde by treating with acid or in the presence of a salt which is acid or becomes acid at elevated temperature. Compounds like hexamethylenetetramine, for instance, require the stoichiometric quantity of acid for their complete decomposition. If the quantity of acid for this purpose is not sufficient, the excess of hexamethylenetetramine acts as a buffer and counteracts the reaction between the aldehyde and the cellulosic material, and as a result, the intended effect is unsatisfactory.

Despite this, hexamethylenetetramine has been recommended as a protective agent. In British Patent 460,201 (1936) the inventors recommend adding a certain quantity of hexamethylenetetramine to the impregnating baths to protect the cellulosic material against the destructive action of the free acids. The reaction takes place as follows:



Other acids can be used.

The applicant in U. S. Patent 2,441,859 recommends the decomposition of the hexamethylenetetramine with volatile organic acids by steaming the fabrics, previously impregnated with a watery solution of hexamethylenetetramine and dried, in a steam chamber, in the presence of an excess of acetic or formic acid.

2

If watery solutions of aldehydes in the presence of an acid, for catalyzing the reaction are applied, certain disagreeable disadvantages are well-known. Working with formaldehyde solutions, is, besides other unfavourable consequences, a very unpleasant operation at all times. Therefore, more recently, the application of glyoxal has been recommended. According to U. S. Patent 2,436,076, glyoxal is used, preferably in the presence of oxalic acid with subsequent drying and baking the goods at elevated temperature. But, whereas rayon fabrics are made shrink-proof to a satisfactory degree and the shrinkage tendency significantly curbed in the case of cotton fabrics, the former display a loss in the range of 20% in tensile strength and the latter in the range of 50%.

In following the procedure of the applicant's co-pending U. S. patent applications 722,955, filed January 18, 1947, now U. S. Patent No. 2,484,545, and 750,159, filed May 23, 1947, now U. S. Patent No. 2,541,457, the loss in tensile strength and abrasion resistance will be avoided. But, here too, frequently a certain degree of discoloring after baking is unavoidable.

Therefore, it is always necessary after baking to soap the goods for a long time and, in most cases, to after-bleach them also. As a consequence therefore, to print or dye the fabrics normally prior to the anti-shrink procedure, only certain types of dye-stuffs can be used. In the present process, the treated fabric need only be neutralized and washed for a short time, for example, from about 5 to about 10 minutes at about 35° C. to 45° C.

### OBJECTS

It is the object of the present invention to eliminate the mentioned disadvantages and inconveniences by treating textile fabrics which are formed predominantly of natural cellulosic materials or regenerated cellulose, including mixtures containing up to about 50% of cellulose acetate fibres with dilute aqueous solutions of a specific type of aldehyde compound which gives off the bound aldehyde by treating either with acid solutions or in an alkaline medium, for stabilizing them against shrinkage but with no appreciable loss in tensile strength and having an increased resistance to abrasion without any tendency to discoloring by baking—curing.

### APPLICANT'S DEVELOPMENT

The applicant has now found that this object can be accomplished and highly effective shrinkage stabilization achieved by subjecting textile

fabric of any of the classes described above to the action of an aldehyde donor compound which is soluble in water and is capable of splitting off aldehyde under both alkaline and acid conditions. Such a compound is capable of forming with the fibers under acid conditions linkages which are stable to hydrolysis and characterized by a reduced swelling capacity when soaked in water. The preferred aldehyde donor is monomethylol dimethyl hydantoin.

In the monomethylol dimethyl hydantoin compound there is one mol of formaldehyde for every mol of dimethyl hydantoin. However, it usually requires high temperature under strong acid condition to release much of the formaldehyde. On the other hand, the monomethylol dimethyl hydantoin gives off all the bound formaldehyde under milder conditions. Therefore, it is the preferred formaldehyde donor. It contains 18.98% combined formaldehyde which is available for chemical use. It is very soluble in water and splits off the formaldehyde as well under alkaline conditions as in acid media. The liberated formaldehyde in statu nascendi is reacting with the cellulose at elevated temperature.

Using the above-mentioned substances, under alkaline conditions, the reaction product formed between the formaldehyde and the cellulose is not very stable, whereas under acid conditions probably polyoxymethylene-ether linkages are formed which are stable to hydrolysis and are characterized by a reduced swelling capacity when soaked in water and therefore reduce the shrinkage tendency of the so treated cellulosic material. If the treatment is carried out under controlled conditions the fabrics show no appreciable loss in tensile strength. An improved resistance to abrasion will result and there is not even the slightest tendency for discoloring. Dimethyl hydantoin probably remains as a by-product in the treated fabric after baking which can be easily removed by a short washing operation. Therefore, fabrics treated by this new method show no tendency toward chlorine retention.

It is a more specific object of the present invention to secure stabilization of the aforesaid types of textile fabrics against shrinkage but without significantly impairing their tensile strength and improving their abrasion resistance wherein the fibers are wetted with dilute watery solution of monomethylol dimethyl hydantoin, dried and subsequently baked at 100° C. or higher until the desired shrinkage control has been secured, i. e. a substantial reaction between the cellulose and the liberated formaldehyde has taken place.

Other objects and features of the invention will be apparent from the following description.

Broadly speaking, the invention includes employing nearly neutral aqueous solutions of monomethylol dimethyl hydantoin in the presence of a non-volatile organic acid catalyst capable of giving these solutions a pH from about 2 to about 2.5. Suitable acids are for example, oxalic acid, lactic acid, citric acid, tartaric acid and other non-volatile organic acids or mixtures thereof strong enough to catalyze the reaction between the aldehyde and the textile material. The acid must be such as to give a pH within the range from about 2 to about 2.5 which is a preferred range of the invention. The formaldehyde cellulose reaction must take place within the fibres of the natural or regenerated cellulose.

According to the invention, any form of the

textile materials of the type described are thoroughly impregnated with a watery solution of the aldehyde donor and the acid catalyst preferably in the presence of a small amount of sodium sulphate and which solutions may or may not also contain a small amount of a wetting agent or a small amount of basic aluminum acetate.

The surplus of the impregnating liquor is mechanically removed for instance by squeezing or other means allowing a pick-up of a predetermined percentage such as 100% liquid retention on the basis of the dry weight of the goods. They are then tensionless dried and finally cured or baked for about 2 to 5 minutes.

A drying range of 80 to 100° C. and a baking temperature within 120° C. to 150° C. is usually preferred. However, the exact formulation of the solution as to components and strength as well as the conditions of drying and baking may vary depending upon the construction, composition and form of the textile material. After curing, the fabrics are neutralized with an alkali, for example, soda ash, eventually soaped, rinsed, hydro-extracted and dried without tension before putting into industrial channels of trade or before making the physical measurements referred to in the comparative tests below.

Before treatment of the fabric all traces of starch, gums, glue or natural resins and other sizing agents should be removed in order to permit the aqueous treating solution to penetrate the fabrics and enter the heart of the fibres.

Where shrinkage control of fabrics is desired, the dimensions at which the fabrics are finally dried must be predetermined by a preliminary wash test. If desired, the "hand" or body of the goods treated can be modified in the direction of either softness or a stiffer finish at will by the introduction to the impregnating baths of suitable agents such as cation softeners for the former effect or such vegetable or animal colloids as starches, gums, glues, gelatines, modified starches, or solutions or dispersions of polyvinyl alcohol, etc. for the latter effect. The process is usually carried out in the absence of any phenolic or amidic compounds capable of forming resinous bodies with aldehyde under the conditions.

When fabrics are treated by this new method in the absence of phenolic or amidic compounds, they do not show any tendency toward chlorine retention. Fabrics treated by the present invention are characterized by permanent stability against shrinkage and even successive washings at the boil do not affect the results.

In the aqueous wetting solution the suggested range of concentration of the monomethylol dimethyl hydantoin is 1% to 7.5% inclusive (preferably 1 to 5% inclusive) based upon the weight of the treating solution. The amount of the stabilizing compound or compounds employed is such as to furnish from about .2% to about 1.5% (preferably about 2% to about 1.0%) of active available formaldehyde based on the weight of the aqueous solution.

Fabrics of viscose or cuprammonium yarns so processed are further improved as borne out by the fact that they show less tendency to fuzz during washing as compared to an untreated material similarly washed.

This invention will be more clearly understood by reference to the following examples. It is to be understood, however, that these examples are merely illustrative of the process and that the invention is not limited thereto, but rather is de-

fined in the appended claims. In the examples, the term "check" has the meaning of untreated or original material.

EXAMPLE 1

C. Cotton

R. Spun Rayon

A cotton sheeting material and a spun rayon fabric were treated respectively for the purpose of obtaining shrink-proof effect with aqueous solutions of the following compositions. The check was not treated.

|                          |     |     |     |     |     |     |
|--------------------------|-----|-----|-----|-----|-----|-----|
| Monomethylol Dimethyl, g | 25  | 25  | 25  | 25  | 25  | 25  |
| Hydantoin, g             |     |     |     |     |     |     |
| Oxalic Acid              | 4   | 4   | 4   | 4   | 4   | 4   |
| Anhydrous Sodium, g      | 1   | 2   | 3   | 4   | 5   | 6   |
| Sulphate                 |     |     |     |     |     |     |
| Igepal CTA Extra, g      | 1   | 1   | 1   | 1   | 1   | 1   |
| Water to make            | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |

The fabric was subjected to treatment to remove any traces of starch, gums, glue, natural resins or other sizing agents present and dried. It was then passed through an aqueous impregnating solution of the above composition. The solution had a pH of about 2.2. After the fabric was passed through the solution and was well wetted out (this required about 5 seconds immersion) it was squeezed to remove solution in excess of 100% pick-up based on the dry weight of the fabric. It was then dried without tension on a pin-tenter frame in air at about 83° C. to the dimensions that the fabric possessed before impregnating. The dried, tented fabric was then cured in circulating air at about 135° C. for about 5 minutes in the case of the cotton and at about 149° C. for about 3 minutes in the case of rayon.

The fabric after curing was removed from the tenter frame and soaped, rinsed, hydro-extracted, and dried without tension. To measure their shrinkage in washing, samples were laundered together with the check sample by the accelerated 1 hour wash test described in U. S. A. Federal specification CCC-T-191A Cotton Wash Test.

Other samples were subjected to tensile strengths and abrasion resistance measurements.

The following shrinkages were observed based upon the measurements.

C. Cotton

[Warp Shrinkage in percentages]

| Sample Identification | Treated and Scoured | 1 Hour Wash Test | Loss from Original Length | Gain over compressive shrinkage |
|-----------------------|---------------------|------------------|---------------------------|---------------------------------|
| Check                 | -3.61               | -5               | -5                        |                                 |
| #1                    | -3.06               | -0.3             | -3.09                     | 1.91                            |
| #2                    | -3.1                | -0.56            | -3.66                     | 1.34                            |
| #3                    | -3.33               | -0.45            | -3.78                     | 1.22                            |
| #4                    | -3.4                | -0.5             | -3.9                      | 1.1                             |
| #5                    | -3.33               | -0.7             | -4.04                     | 0.97                            |
| #6                    | -3.33               | -0.83            | -4.13                     | 0.87                            |

R. SPUN RAYON

| Sample Identification | Treated and Scoured | 1 Hour Wash Test | Loss from Original Length | Gain over compressive shrinkage |
|-----------------------|---------------------|------------------|---------------------------|---------------------------------|
| Check                 | -9.17               | 12.7             | -12.7                     |                                 |
| #1                    | -4.2                | 0                | -4.2                      |                                 |
| #2                    | -4.72               | 0                | -4.72                     |                                 |
| #3                    | -4.17               | -0.56            | -4.73                     |                                 |
| #4                    | -6.8                | -1.2             | -8                        |                                 |
| #5                    | -6.5                | -1.7             | -8.2                      |                                 |
| #6                    | -4.5                | -4.17            | -8.67                     |                                 |

|       | Warp Tensile Strength (in lbs.) |         | Abrasion (Taber Cycles) |         |
|-------|---------------------------------|---------|-------------------------|---------|
|       | C Cotton                        | R Rayon | C Cotton                | R Rayon |
| Check | 53                              | 58      | 500-600                 | 280-320 |
| #1    | 38                              | 57      | 500-550                 | 430-500 |
| #2    | 44                              | 59      |                         | 480-500 |
| #3    | 44                              | 61      | 550-650                 | 450-480 |
| #4    | 45                              | 64      |                         | 450-480 |
| #5    | 45½                             | 64      |                         | 480-500 |
| #6    | 46                              | 64      | 650-700                 | 475-500 |

As it can be seen by the results obtained, the amount of Na<sub>2</sub>SO<sub>4</sub> added to the bath has not to be exaggerated, especially in the case of stabilizing rayon fabrics but good results in every respect are achieved if carried out under the right conditions.

EXAMPLE 2

C. Cotton

R. Spun rayon

A cotton sheeting material and a spun rayon fabric were treated respectively for the purpose of obtaining shrink-proof effects with aqueous solutions of the following compositions. The check was not treated.

|                                 |       |     |
|---------------------------------|-------|-----|
| Monomethylol dimethyl hydantoin | grams | 25  |
| Oxalic acid                     | do    | 5   |
| Na <sub>2</sub> SO <sub>4</sub> | do    | 3   |
| Igepal CTA extra                | do    | 0.5 |
| Water to make                   | litre | 1   |

The samples were immersed with the above solutions as described in Example #1 and after drying cured.

|            |              |         |
|------------|--------------|---------|
| Cotton     | 4 minutes at | 135° C. |
| Spun rayon | 3 minutes at | 149° C. |

and washed and dried as previously described.

C. Cotton

[Warp Shrinkage (in percentages.)]

| Sample Identification | Treated & Scoured | 1 Hour Wash Test | Loss from Original Length | Gain over Compressive shrinkage |
|-----------------------|-------------------|------------------|---------------------------|---------------------------------|
| Check                 | -3.5              | -5.5             | -5.5                      |                                 |
| #1                    | -3.1              | -0.8             | -3.9                      | 1.6                             |
| #2                    | -3.1              | -0.9             | -4                        | 1                               |

R. RAYON (SPUN)

| Sample Identification | Treated and Scoured | 1 Hour Wash Test | Loss from Original Length | Gain over Compressive shrinkage |
|-----------------------|---------------------|------------------|---------------------------|---------------------------------|
| Check                 | -8.06               | -12.5            | -12.5                     |                                 |
| #1                    | -4.7                | 0                | -4.7                      | 7.8                             |
| #2                    | -5                  | -0.2             | -5.2                      | 7.3                             |

|       | Warp Tensile Strength (in lbs) |         | Abrasion (Taber Cycles) |         |
|-------|--------------------------------|---------|-------------------------|---------|
|       | C Cotton                       | R Rayon | C Cotton                | R Rayon |
| Check | 54                             | 65      | 600-650                 | 200-250 |
| #1    | 48                             | 67      | 825-850                 | 600     |

In all cases, a very good stabilization effect is obtained. Moderate loss in tensile strength on cotton material. No loss in tensile strength in rayon material. In both cases considerable improved abrasion resistance.

7

## EXAMPLE 3

A spun rayon fabric was treated for the purpose of obtaining a shrink-proof effect with aqueous solutions of the following composition. The check was not treated.

|   | 1   | 2   |
|---|-----|-----|
| Monomethylol Dimethyl Hydantoin.....grams.....        | 25  | 25  |
| Lactic Acid 50%.....do.....                           | 50  | 100 |
| Na <sub>2</sub> SO <sub>4</sub> Anhydrous.....do..... | 4   | 4   |
| Igepal CTA Extra.....do.....                          | 0.5 | 0.5 |
| Water to make.....litres.....                         | 1   | 1   |

The samples were immersed in the above solutions as described in Example 1 and cured after drying for 3 minutes at 149° C., washed and dried as previously described in Example 1.

[Warp Shrinkage (in percentages.)]

| Sample Identification | 1 hour washes <sup>1</sup> |      |      |      |                 |
|-----------------------|----------------------------|------|------|------|-----------------|
|                       | Scoured                    | 1st  | 2nd  | 3rd  | Total Shrinkage |
| Check.....            | -7.5                       | -1.4 | -2.5 | -5.2 | -12.7           |
| #1.....               | -4.5                       | -0.7 | -0.6 | -0.4 | -4.9            |
| #2.....               | -3.9                       | -0.3 | -0.3 | -0.2 | -4.1            |

<sup>1</sup> Measured from scoured dimensions.

|            | Warp Tensile strength in lbs. |
|------------|-------------------------------|
| Check..... | 60                            |
| #1.....    | 60                            |
| #2.....    | 59                            |

The achieved stabilization effect is very satisfactory, practically without any change in tensile strength and without any discoloring effect.

I claim:

1. In a process of shrinkage control of a textile fabric selected from the group consisting of natural cellulose, regenerated cellulose and their mixtures with up to about 50% of cellulose acetate, the steps of impregnating said fabric with an aqueous solution of monomethylol dimethyl

8

hydantoin, said aqueous solution containing from 1 to 7% by weight of monomethylol dimethyl hydantoin which, upon baking, decomposes to form from 0.2 to 1.5% of available active formaldehyde and containing a non-volatile organic acid in an amount such as to give to the solution a pH of from about 2 to about 2.5, squeezing the surplus liquid from the fabric, drying said fabric, baking the dried fabric at a temperature of from 120 to 150° C. for a time sufficient to effect reaction between liberated formaldehyde and the textile fabric, and neutralizing and washing said fabric to remove acid and reaction by-products thereby to provide a fabric which has substantially permanent stability against shrinkage in successive washings at the boil and which has substantially retained its color and tensile strength.

2. The process of claim 1, wherein the non-volatile organic acid is selected from the group consisting of oxalic acid, lactic acid, citric acid, and tartaric acid.

LEO BEER.

## REFERENCES CITED

The following references are of record in the file of this patent:

## UNITED STATES PATENTS

| Number    | Name            | Date          |
|-----------|-----------------|---------------|
| 2,108,520 | Wolf et al.     | Feb. 15, 1938 |
| 2,159,743 | Latham et al.   | May 23, 1939  |
| 2,441,859 | Weisberg et al. | May 18, 1948  |

## FOREIGN PATENTS

| Number  | Country       | Date           |
|---------|---------------|----------------|
| 547,846 | Great Britain | Sept. 15, 1942 |
| 880,185 | France        | Dec. 18, 1942  |

## OTHER REFERENCES

Chemical and Engineering News, November 3, 1947, page 3243, and February 9, 1948, p. 415.