

Patented Oct. 29, 1940

2,219,375

UNITED STATES PATENT OFFICE

2,219,375

PROCESS OF TREATING TEXTILES AND PRODUCT

Gustave Widmer, Basel, Switzerland, and Louis Klein, Frankford, Philadelphia, Pa., assignor to Röhm & Haas Company, Philadelphia, Pa.

No Drawing. Application August 31, 1934,
Serial No. 742,284

8 Claims. (Cl. 91-70)

This invention relates to securing improved effects on textiles by the use of non-resinous reaction products of carbamid and formaldehyde. Methods have been proposed in the past for treating textiles with reaction products of urea and formaldehyde. In U. S. Patent No. 1,355,834, John indicates that when urea and formaldehyde are allowed to react for a short time at a high temperature, a product results which is still water soluble and which is useful for impregnating textiles.

In U. S. Patent No. 1,871,087 dimethylol urea is used in combination with other substances to produce local effects on textiles. It serves essentially as a binder for pigments. In U. S. Patent No. 1,926,063, reaction products of urea and formaldehyde serve as a binder for a filler, and the production of filled fabric with improved water resistance is thus achieved. In U. S. Patent No. 1,693,926, reaction products of urea and formaldehyde are used in the treatment of wool, silk, and other animal fibers. The resin serves to inhibit the destructive action of alkaline agents added later in the process of treating the textiles. In U. S. Patent No. 1,734,516, which describes a particular method of crease-proofing textiles, urea formaldehyde resins are described among others. In order to obtain a satisfactory result, it is necessary to carry out the reaction between the urea and formaldehyde very carefully. The proper degree of resinification must be attained, or otherwise the treated fabric may be stiff and brittle instead of soft and flexible. Moreover, in addition to accurate control of production of the resin, it is essential that the entire process of heating and subsequent washing to remove excess resin between the fibers be carefully performed. All these operations require highly skilled labor in addition to a considerable amount of technical supervision.

Our invention differs from the known processes in which carbamide-formaldehyde products have been applied to textiles, in that it makes possible for the first time the production of improved finishes by a simple and inexpensive process. Depending on the actual conditions employed, varying effects are produced. In particular, it is possible to secure fullness, resistance to fraying, increased wet strength in rayons, and fabrics characterized by a reduced tendency to wrinkle. These results are secured by using non-resinous carbamide-formaldehyde reaction products in fairly concentrated solution for impregnation of the textile fabrics, and subsequently producing an insoluble product by the application of heat. Small amounts of catalysts may or may not be added to the solution used for impregnation. Other substances are sometimes added to stabilize the solution. In no sense, however, should it be construed that the carbamide-formaldehyde

product acts as a binder for other materials such as starch, pigment, talc, etc. On the contrary, the effect secured results from the precipitation of the carbamide-formaldehyde product itself in an insoluble form.

Our process is particularly applicable to the production of textile fabrics, characterized by a reduced tendency to wrinkle or crease. Until now, the commercial process of preparing fabrics, characterized by reduced tendency to wrinkle has comprised impregnating fabrics with a dilute acidified solution of a condensation product of urea and formaldehyde, subsequently drying them, and hardening the condensation product by heating the impregnated fabric at a relatively high temperature (about 330° F.). Following this, an essential part of the process was the soaping and rinsing to remove excess resin between the fibers. The fabric was then dried, and finished in the usual way. The difficulty of producing a uniform and satisfactory urea-formaldehyde condensation product has served as one of the chief barriers in the commercial development of this process.

It is well known to those skilled in the art that considerable difficulty is encountered in the manufacture of urea formaldehyde condensation products, particularly those in which the condensation is arrested before completion. This is due mainly to the sensitivity of these products to slight changes in temperature and to the effect of small amounts of acids, bases and salts. If the acidity or basicity and salt content of the solutions are not very accurately adjusted, precipitation of the condensation product occurs and this renders the material unsuitable for the production of crease-proof fabrics. Furthermore, this process is generally carried out in finishing plants which are, as a rule, not in a position to give adequate technical supervision to the production of the resin and thus it is easy to understand why considerable variability in the finish due to the non-uniformity of the resin, was encountered. Moreover, solutions of such resins prepared for crease-proofing, have been rather unsuitable and it is not unusual to find a considerable amount of the resin precipitated shortly after the solution is prepared. This condition is particularly noticeable after the solutions have been acidified and the precipitation often occurs within a few minutes after the addition of the acid. This of course, renders the material unsuitable for use in crease-proofing fabrics. Solutions suitable for use under factory conditions may be stabilized by the addition of such compounds as urea, thiourea, dicyandiamide, sodium sulphate, etc., according to our copending application No. 664,554, filed April 5, 1933, of which the present invention is a continuation-in-part.

It is an object of this invention to provide a

reaction product of carbamid and formaldehyde which is capable of yielding a fabric more resistant to wrinkling or creasing than those heretofore obtained.

5 A further object of this invention is to provide a material which can be hardened more rapidly than the ordinary urea-formaldehyde products thus making it possible not only to shorten the time required, but also to permit the process to be carried out at a lower temperature. In this way the finished product is stronger than those in which the hardening of the urea-formaldehyde product is carried out at high temperatures because at these high temperatures the individual fibers of the fabric are adversely affected.

10 In order to obtain the best crease-proofing effect, it is necessary for the urea-formaldehyde material to penetrate the individual fiber as much as possible. If a substantial amount of the material should be left on the surface of the fabric, the entire fabric is stiffened and made brittle, whereas if the material penetrates the fabric and all of it remains there, this effect is not present and the finished fabric is crease-proof.

15 Urea-formaldehyde condensation products are colloidal in nature and consequently the individual particles or micelles are so large that they cannot penetrate the individual fibers.

20 We have now found that if instead of using an intermediate condensation product of urea and formaldehyde, which is resinous in nature, we use a reaction product of non-resinous nature, the material will penetrate the individual fibers of the fabric and on subsequent drying and hardening, a considerably improved crease-proofing effect is obtained. For this purpose we use the initial reaction product of urea and formaldehyde, before any condensation whatever has taken place. In other words, starting with urea and formaldehyde, our impregnating solution contains only dimethylol urea or monomethylol urea, or both, and these compounds are present in the molecular state and are not condensed to the resinous or colloidal material.

25 Many advantages result from the use of this material for crease-proofing fabric, particularly with respect to the handling of the material by the workman. This material can be made in solid form and all that is necessary before use is to dissolve it in the proper amount of water. If desired a catalyst may also be added, but this is not necessary. Solutions thus prepared are far more suitable and less sensitive to added materials than are the solutions of the intermediate condensation products. It is therefore not necessary to make up fresh solutions continuously when operating on a large scale, but a large stock of the suitable solution can be made up at one time. Moreover, it is not necessary to exercise extreme care in keeping these solutions as is the case when solutions of the intermediate resinous condensation products are used.

30 We have also found that by properly adjusting the composition of the solution of the carbamid formaldehyde reaction product, that it is possible to eliminate the use of an acid catalyst and this also assists in imparting better keeping qualities to the solutions. For instance, if a mixture of eight parts of dimethylol urea, one part of thiourea and two parts of anhydrous sodium sulphate is made up into a 20% solution in water and used to impregnate fabric, the material absorbed by the fabric may be fully cured in two minutes at a temperature of 330°-340° F., without the use of any catalyst. This temperature

is rather high for the treatment of fabrics and a better product could be obtained if the curing temperature could be reduced to 275° F. or less. We have found that the use of a special catalyst makes this possible and this is also important because of the fact that in most textile finishing plants, no apparatus is available which could heat the fabric as high as 330° F. By using this special catalyst, however, it is possible to obtain a very satisfactory product within two to four minutes, at temperatures of 230 to 250° F., and good results may be obtained even at temperatures as low as 215 to 220° F.

The catalysts which are particularly effective for this purpose are salts of moderately strong acids and weak volatile bases. We have found that diammonium phosphate is particularly effective as a catalyst for this purpose. The action of this type of salt is probably due to the fact that on heating, the volatile basic group is vaporized, or if the base is ammonia or an amine, it combines with the free formaldehyde, thus leaving a moderately strong acid in a solution which accelerates the conversion of the resin to the final insoluble state and makes possible the complete insolubilizing of the resin at a lower temperature. Salts of strong acids are objectionable because the presence of even traces of strong acid in the fabric would be detrimental at the temperatures necessary for curing, and would destroy the fabric. If salts of weak acids are used, such for instance, as ammonium acetate, the catalytic effect is very weak. If a strong acid were to be used alone, the solution would probably gelatinize very rapidly and thus become unfit for the purposes of the present invention, because when the solution gelatinizes, a colloidal material is formed and this would not penetrate the individual fibers of the fabric.

In carrying out our process, we prefer to use a solution containing approximately 10-30% of the initial addition product of the carbamid and formaldehyde such as for example, dimethylol urea containing a catalyst. The fabric is impregnated with this solution and then squeezed between rollers. The amount of the material taken up by the fabric is dependent on the nature of the fabric, the concentration of the solution employed, and the result desired, and is usually approximately equal to the original dry weight of the fabric. The impregnated fabric is then dried and heated to the desired temperature for two to four minutes in order to harden the methylol urea and render it insoluble. Following this operation, the fabric may be washed with soap and water so as to remove any particles of resin which may be adhering to the outside of the fibers, and dried.

In the following examples and claims, the term formaldehyde is used in its widest sense, including its polymers.

The following examples are given by way of illustration and are not to be considered a limitation of the scope of the invention. Many deviations will suggest themselves to anyone versed in the art and all such are included in the spirit of the invention, which is limited only by the appended claims. In these examples parts are by weight.

Example 1.—25 parts of a mixture of equal parts of urea and dimethylol urea are dissolved in 75 parts of water and 1/2 part of glacial acetic acid or 1/4 part of tartaric acid is added. Cotton or rayon cloth is impregnated with this solution and squeezed through rollers so that the amount

of solution taken up is approximately equal to the original weight of the fabric. The cloth is then dried at a low temperature and cured by treating it with a hot iron for 2 to 4 minutes at 330° F.

It is then washed with soap and water, rinsed and dried. The resulting fabric has a good feel and an improved resistance to wrinkling. This resistance to wrinkling is not affected to any appreciable extent by subsequent laundering.

Example 2.—15 parts of dimethylol urea is dissolved in 85 parts of hot water and after cooling $\frac{1}{2}$ part of glacial acetic acid is added. Cotton voile is impregnated with this solution and treated as in Example 1. The resulting fabric is crease-proofed and has the same resistance to subsequent laundering as a fabric obtained according to Example 1. Instead of the dimethylol urea, monomethylol urea may be used.

Example 3.—A sample of rayon or cotton fabric is impregnated with a 25% solution of dimethylol thiourea and squeezed between rollers so that the fabric has taken up about 100% of its dry weight of solution. The fabric is then dried and cured by heating for 2 to 4 minutes at 330° F. The resulting fabric is very resistant to wrinkling.

Example 4.—A mixture containing 4 parts of dimethylol urea and 1 part of thiourea is made up to a 20% solution in water. A sample of cloth treated with this solution by the procedure given in Example 3, yields similar results.

Example 5.—A mixture of 8 parts of dimethylol urea, one part of thiourea and two parts of anhydrous sodium sulphate is made up to a 25% solution in water. A sample of cloth impregnated with this solution and treated according to the procedure given in Example 3, has very good wrinkle resisting properties.

Example 6.—A mixture of 4 parts of dimethylol urea and one part of anhydrous sodium sulphate is made up into a 25% solution in water, to which is then added $\frac{1}{4}$ part tartaric acid. Cloth impregnated with this solution according to the procedure given in Example 3 may be cured in 4 to 8 minutes at 312° F. to yield a well crease-proofed material.

Example 7.—A mixture of 4 parts of dimethylol urea, one part of dicyandiamid and one part of sodium nitrate is made up into a 25% solution in water to which is added $\frac{1}{4}$ part of tartaric acid. This solution may be used for crease-proofing according to the method given in Example 3 and yields a very satisfactory product.

Example 8.—To 100 parts of the solution used in Example 5, $\frac{1}{2}$ part of diammonium phosphate is added, and the resulting solution used to impregnate cotton cloth. The cloth is then squeezed between rollers until the amount of solution absorbed is equal to about 75% of the dry weight of the fabric. It is then carefully dried at 190° F. and finally heated for 3 minutes to 240° F. After soaping, washing and finishing in the usual way, the fabric has an improved resistance to wrinkling which is not very readily removed by ordinary laundering.

Example 9.—A mixture of 4 parts of dimethylol urea and one part of sodium sulphate is made up to a 20% solution in water to which is then added one part of di-(mono-methylammonium) phosphate and the resulting solution is used to impregnate cotton voile. The impregnated fabric is treated as in Example 8 and after finishing has very good crease-resisting properties.

Other non-resinous addition products of form-

aldehyde and carbamid or its derivatives, such as dimethylol thiourea, monomethylol thiourea, etc., may be used in place of the dimethylol urea in the foregoing examples without departing from the spirit of the invention.

It is to be understood that, although the step of washing the fabric after curing the resin is often desirable, it is not a necessary nor essential part of the process.

We claim:

1. The process of creaseproofing textile fibers comprising impregnating the fibers with a 10-30% solution of an addition product of carbamide and formaldehyde free from condensation products thereof, and a catalyst which is an ammonium salt of a moderately strong acid until the fibers take up from 10-30% of their dry weight of said addition product, drying the impregnated fibers and insolubilizing the carbamide-formaldehyde product by heat.

2. The process of creaseproofing textile fibers comprising impregnating the fibers with a resin free 10-30% solution of an addition product of carbamide and formaldehyde to which has been added 0.5% of diammonium phosphate until the fibers take up from 10-30% of their dry weight of said addition product, drying the impregnated fibers and insolubilizing the carbamide-formaldehyde product by heat.

3. The process of creaseproofing textile fibers comprising impregnating the fibers with a resin free 10-30% solution of an addition product of carbamide and formaldehyde which also contains sodium sulfate in amount sufficient to stabilize said solution, and as a catalyst 0.5% of diammonium phosphate until the fibers take up from 10-30% of their dry weight of said addition product, drying the impregnated fibers and insolubilizing the carbamide-formaldehyde product by heat.

4. Process of improving the crease-resistance of textile fabrics which comprises impregnating the fabric with a solution of a reaction product of urea and formaldehyde consisting mainly of a methylol urea and containing a potentially acid ammonium salt and then heating the impregnated fabric to insolubilize the resin.

5. Process of improving the crease-resistance of textile materials which consists in impregnating the material with a solution of partially condensed resin components which is unstable in acid solution, and which solution contains a potentially acid ammonium salt, and heating the impregnated material to insolubilize the resin and produce a crease-resisting product.

6. Process of improving the crease-resistance of textile material which consists in impregnating the material with a partially condensed solution of urea and formaldehyde which is unstable in acid solution, which solution contains a potentially acid ammonium salt, and heating the impregnated material to insolubilize the resin and produce a crease-resisting product.

7. Process as in claim 5 in which an ammonium salt of a strong mineral acid is used.

8. A crease-resisting textile fabric containing a synthetic resin insolubilized by heating a partially condensed resinous product in situ in presence of acid liberated from an ammonium salt of a mineral acid.

GUSTAVE WIDMER.
LOUIS KLEIN.