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3,029,164

PRODUCTION OF CREASE RESISTANCE IN CELLULOSIC FABRICS WITH THE AID OF 1,3-DIMETHYLOL-4,5-BIS(ALKOXY)-2-IMIDAZOLIDINONES

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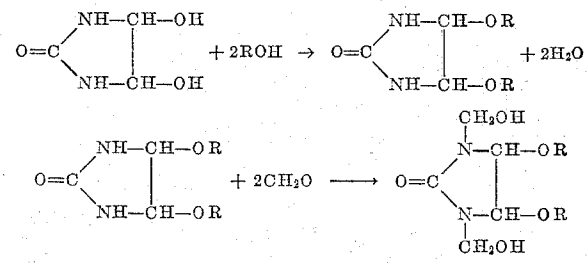
This invention relates to the appliction of 4,5-bis(alkoxy)-2-imidazolidinones and their methylol derivatives, to a textile fabric.

The new 4,5-bis(alkoxy)-2-imidazolidinones, which are of great use as the raw materials of various synthetic resins such as resins for finishing a textile fabric, resins for treating paper, and fixing agents for pigment resin colour printing paste and as intermediates for the synthesis of various organic compounds, obtained by reacting 4,5-dihydroxy-2-imidazolidinone with aliphatic lower alcohol containing from 1 to 5 carbon atoms, in an acidic medium, are disclosed and claimed in copending application, Serial No. 13,451, filed by some of the present co-applicants.

The new and valuable condensation products are obtained by reacting 4,5-bis(alkoxy)-2-imidazolidinone with formaldehyde or substances which split off formaldehyde, in an acidic or neutral region, as disclosed and claimed in copending application, Serial No. 101,678, of some of the present co-applicants. The methylol derivatives of 4,5-bis(alkoxy)-2-imidazolidinone obtained by the said method show superior usefulness in treating textile fabric, paper and the like or in fixing of pigment resin colour printing paste. Up to the present time, it has been known that 4,5-dihydroxy-2-imidazolidinone is reacted with formaldehyde to give the methylol derivatives thereof which impart crease-resistant and water-repellent effects on textiles, as evidently described in the specifications of U.S. Patents No. 2,764,573 and No. 2,731,364. The present inventors, however, have now found that the methylol derivatives of 4,5-bis(alkoxy)-2-imidazolidinone have much superior characteristics to those of the methylol derivatives of 4,5-dihydroxy-2-imidazolidinone. When textile fabrics are treated with the said methylol derivatives of 4,5-bis(alkoxy)-2-imidazolidinone, the goods thus treated have almost the same degree of efficiencies in the respect of crease proof and resistance to shrinkage as that of the methylol derivatives of 4,5-dihydroxy-2-imidazolidinone. Moreover, while in the latter case the practical usages of the methylol derivatives are spoiled in some degree because of the extremely hard hand of the treated goods, the textile fabrics treated with the methylol derivatives according to this invention have the characteristics of possessing the soft hand in the same degree as that of untreated textile. Furthermore, the textile fabrics treated with the latter resinous products have, on the one hand, indeed more superior characteristics in the respects of crease proof and resistance to shrinkage than is the case with the conventional resins such as dimethylol ethylene urea, but on the other hand, the treated goods have such defects that their tensile strengths are considerably lower than is the case with the conventional resins. Because of this fact, the practical usages of the methylol compounds of 4,5-dihydroxy-2-imidazolidinone have been limited. On the contrary, the textiles treated with the compounds according to this invention not only have such characteristics that the crease proof and resistance to shrinkage thereof are of almost the same degree with that of the case with the methylol derivatives of 4,5-dihydroxy-2-imidazolidinone, but also have such characteristics that negligible loss in tensile strength of the treated fabrics is observed. Consequently, the new condensation products of this invention are very valuable in an industrial application.

As hereinabove described, the 4,5-bis(alkoxy)-2-imidazolidinones are obtained by reacting 4,5-dihydroxy-2-imidazolidinone with an aliphatic alcohol containing from 1 to 5 carbon atoms, in acidic media, and the methylol derivatives of said 4,5-bis(alkoxy)-2-imidazolidinones are obtained by reacting the latter with formaldehyde or substances which split off formaldehyde, in an acidic or neutral region. The reactions may be represented by the following scheme.



wherein R is an alkyl radical containing 1–5 carbon atoms.

Following is the description of the method for manufacturing 4,5-bis(alkoxy)-2-imidazolidinone:

The alkyl-etherification reaction of 4,5-dihydroxy-2-imidazolidinone with an aliphatic lower alcohol can be carried out smoothly in an acidic region to give 4,5-bis-(alkoxy)-2-imidazolidinone in good yield. The aliphatic lower alcohol works as not only the reaction component, but also the reaction medium. The amounts of aliphatic lower alcohol in practicing the reaction are in excess of rather than the theoretical amounts. Practically, from 3 to 10 mols of aliphatic lower alcohol may be adequately employed per mol of 4,5-dihydroxy-2-imidazolidinone. There is, however, absolutely no adverse effect when more increased amounts of the alcohol are employed than the above limitation. The method in which the aliphatic lower alcohol per se serves as the reaction medium, has another advantage such that, when the reaction is over, the filtrate obtained by the separation of 4,5-bis(alkoxy)-2-imidazolidinone can be recovered and re-used as the raw material of the next batch. However, in order to carry out this reaction, other reaction media such as, for example, ethers, may be successfully employed.

The dehydration condensation of 4,5-dihydroxy-2-imidazolidinone with aliphatic lower alcohol can be carried out smoothly in an acidic region and particularly the reaction can be carried out almost quantitatively in a pH of less than 3. The said pH value is measured by glass electrode pH meter. As the acidifying agent, such inorganic acids as hydrochloric, sulfuric and phosphoric acid and such organic acids as formic and oxalic acid may be advantageously employed.

Concerning the reaction temperature of the said alkyl-etherification, it may be adequately chosen from the temperature range of 0° C. to the boiling point of the said reaction mixture, but in order that the said reaction may proceed smoothly, a temperature range of from 60° to 65° C. is preferable. The reaction time is correlated with the reaction temperature. In case the reaction temperature is from 60° to 65° C., the reaction is completed in about 30 minutes to 1 hour.

When the 4,5-dihydroxy-2-imidazolidinone is admixed with the aliphatic lower alcohol, the mixture thus obtained shows the heterogeneous state. But when the mixture is further admixed with an acidifying agent and

the combined mixture is heated to a temperature of 60° to 65° C. with stirring for a while, the homogeneous state is gradually observed and finally a perfect transparent solution can be obtained. In this step of the reaction, the 4,5-bis(alkoxy)-2-imidazolidinone is being formed as the alcoholic solution thereof.

In the aforedescribed method, the reaction conditions do not particularly vary depending upon the employed aliphatic lower alcohol, but the lower the number of carbon atoms of the aliphatic alcohol, the more rapidly the reaction is carried out to give the homogeneous and transparent reaction mixture.

When the reaction is over, the reaction mixture is cooled and allowed to stand to precipitate the white crystals of 4,5-bis(alkoxy)-2-imidazolidinone. The filtrate may be used repeatedly as the raw material of the next batch reaction. But if the filtrate is subjected to further concentration, the second crystals of the product can be obtained. The combined amounts of the first and the second crystals are normally equivalent to the yield of 90% based on the theoretical amounts.

The synthesis of 4,5-bis(alkoxy)-2-imidazolidinone by reacting 4,5-dihydroxy-2-imidazolidinone with aliphatic lower alcohol is carried out, as mentioned hereinabove, by a batch system, but this procedure may be also carried out by a continuous system. That is, in the latter case, the 4,5-dihydroxy-2-imidazolidinone and the aliphatic lower alcohol are introduced continuously into the same reaction vessel at the supplying ratio of 1 mol to from 3 to 10 mols, the contents of the said reaction vessel are heated with sufficient stirring and controlled to be held at the definite acidity by using pH meter, after a certain period of time the reaction mixture is taken out continuously through such means as over-flowing system and the mixture thus discharged is cooled to obtain the object crystals of 4,5-bis(alkoxy)-2-imidazolidinone. The filtrate thus obtained may be continuously sent with the fresh raw material into the said reaction vessel and may be used again. According to the continuous manufacturing method, it is quite possible to obtain the object product more efficiently than with the batch system. The reaction time in the continuous process is determined in correlation with the employed reaction temperature, but as an adequate condition in practice, for example, it is preferable to determine the holding time as from 20 to 40 minutes in case the reaction temperature is from 60° to 65° C.

The 4,5-bis(alkoxy)-2-imidazolidinones used in the method of this invention are all new compounds, which have not yet been described in the literature, and their water solubilities depend upon the number of carbon atoms in the alkoxy radicals. That is, as the number of the carbon atoms of the alkoxy radical increase, the water solubilities decrease gradually. For example, while 4,5-bis(methoxy)-2-imidazolidinone is easily soluble in water, 4,5-bis(butoxy)-2-imidazolidinone is hardly soluble in water.

The following examples further illustrate this phase of the present disclosure:

EXAMPLE 1

118.1 grams (1.0 mol) of 4,5-dihydroxy-2-imidazolidinone were added to 160.2 grams (5.0 mols) of methanol, and to the mixture was added 0.4 gram of concentrated hydrochloric acid to adjust the pH to such point that glass electrode pH meter indicated about 0.2. The reaction mixture was charged into a 300 milliliters capacity four necked flask connecting with a reflux condenser, and heated in a water bath. When the temperature of the reaction mixture was held at the range of from 60° to 65° C. with stirring, the heterogeneous mixture gradually turned to a homogeneous state within 5 minutes and finally a slightly yellow clear solution was obtained. The heating and stirring were further continued for 20 minutes and thereafter the reaction solution was allowed to cool, neutralized with a 40% aqeous sodium hydroxide solution, and the excess amounts of methanol distilled off at an inner temperature of about 30° C. under reduced pressure. Thus, the reaction solution was concentrated to about ⅔ of the original weight. During the course of the said concentration, the products were gradually precipitated as needle crystals. Upon cooling with ice-water, the products were completely crystallized out, and thereafter the precipitates were filtered and dried in vacuo. Thus, 110.0 grams of 4,5-bis(methoxy)-2-imidazolidinone were obtained as white needles, the yield amounting to 75.5% of the theoretical. Elementary analysis showed: Calculated for $C_5H_{10}O_3N_2$, C=41.09%, H=6.90%, N=19.17%.

Found, C=40.90%, H=6.73%, N=19.42%. This product had a melting point of 116° to 118° C.

EXAMPLE 2

118.1 grams (1.0 mol) of 4,5-dihydroxy-2-imidazolidinone were added to 230.4 grams (5.0 mols) of ethanol, and to this mixture 0.5 gram of concentrated hydrochloric acid was added in order to adjust the pH of the mixture to such point that glass electrode pH meter indicated about 1.0. The reaction mixture was charged into a 500 milliliters capacity four necked flask connecting with a reflux condenser, and heated in a water bath. When the inner temperature of the reaction mixture was held at the range of from 60° to 65° C. with stirring, the heterogeneous reaction mixture gradually turned to a homogeneous state within 5 minutes and finally a slightly yellow, clear solution was obtained. The heating and stirring were further continued for 25 minutes and thereafter the reaction solution was allowed to cool, neutralized with a 40% aqueous sodium hydroxide solution, and the excess amounts of ethanol distilled off at an inner temperature of about 35° C. under reduced pressure. Thus, the reaction solution was concentrated to about ¾ of the original weight. During the course of the said condensation, the products were gradually precipitated as needle crystals. Upon cooling with ice-water, the products were completely crystallized out, and thereafter were filtered and dried in vacuo. Thus, 78.0 grams of 4,5-bis(ethoxy)-2-imidazolidinone were obtained as white needles, and the yield amounted to 45.0% of the theoretical. Elementary analysis showed: Calculated for $C_6H_2O_3N_2$, C=48.26%, H=8.10%, N=16.08%. Found C=48.30%, H=7.23%, N=15.60%. The melting point of this product was 159° to 160° C.

EXAMPLE 3

59.0 grams (0.5 mol) of 4,5-dihydroxy-2-imidazolidinone were added to 185.3 grams (2.5 mols) of n-butanol and to this 0.5 gram of concentrated hydrochloric acid was added in order to adjust the pH of the mixture to such point that glass electrode pH meter indicated about 2.0. The mixed raw materials were charged into a 300 milliliters capacity four necked flask connecting with a reflux condenser, and heated in a water bath. When the inner temperature of the said reactor was held at the range of from 60° to 65° C. with stirring, the heterogeneous reaction mixture gradually turned to a homogeneous state within 5 minutes and finally a red-orange, clear solution was obtained. The heating and stirring were further continued for 20 minutes, and thereafter the reaction solution was allowed to cool, neutralized with a 40% aqueous sodium hydroxide solution, and the excess amounts of n-butanol distilled off at an inner temperature of about 40° C. under reduced pressure. Thus, the reaction solution was concentrated to about one-half of the original weight. The precipitated crystals were filtered, washed and dried to give 78.0 grams of 4,5-bis(butoxy)-2-imidazolidinone. The yield amounted to 68.0% of the theoretical. Elementary analysis showed: Calculated for $C_8H_{16}O_3N_2$, C=57.36%, H=9.63%, N=12.16%, and found C=

57.24%, H=9.44%, N=11.94%. The product had a melting point of from 103° to 104° C.

EXAMPLE 4

To a glass reactor (inner volume, 300 milliliters) connected with an over-flow tube a mixture of 116 grams of 4,5 - bis(methoxy) - 2 - imidazolidinone obtained by the method described in Example 1 and 128 grams of methanol was added and the reactor was heated until the inner temperature reached from 60° to 65° C. A glass electrode pH meter was arranged in the said reaction solution so as to be able to measure the pH thereof continuously. Then the dispersion mixture of raw materials comprising the following (A) and (B),

(A) 4,5 - dihydroxy - 2 - imidazolidinone ---------- 146
(B) methanol+filtrate obtained after the object product was separated--- 160 (by weight)

was added dropwise from the top of the reaction vessel at the rate of 15 milliliters per minute with stirring. On the other hand, the reaction mixture was always adjusted to a pH range of 1±0.5 by using hydrochloric acid. Thus, the reaction was carried out under constant conditions. The over-flowed solution was continuously cooled to precipitate out the white needle crystals, and the filtrate thus obtained was added to the said dispersion solution of raw materials for cyclic use. By handling the said operations continuously, the crystals of 4,5-bis(methoxy)-2-imidazolidinone could be obtained in the proportion of 5.8 grams per minute. The yield was almost quantitative and the product thus obtained had the same quality as that of Example 1. The melting point was 116° to 118° C. This continuous procedure was advantageously applied to the industrial production of the present compound.

In the next place, the hydroxymethylation of 4,5-bis-(alkoxy)-2-imidazolidinone is hereinunder described.

The reaction of 4,5-bis(alkoxy)-2-imidazolidinone with formaldehyde or substances which split off formaldehyde can be carried out usually by employing water as a reaction medium, but use can also be made of alcohols including methanol and ethanol, as well as conventional organic solvents for the purpose of the present reaction medium. However, from economical point of view, water is the most preferable reaction medium, and in usual case, the reaction of 4,5-bis(alkoxy)-2-imidazolidinone with formalin is considered to be the most practicable one.

As the molar ratio of 4,5-bis(alkoxy)-2-imidazolidinone to formaldehyde is concerned, it is usual to employ 1 mol of the former to 2 mols of the latter, that is, the amounts of these materials are selected to be sufficient to give the dimethylol derivative.

The hydroxymethylation of 4,5-bis(alkoxy)-2-imidazolidinone with formaldehyde can be carried out smoothly in the neutral or alkaline condition and particularly the reaction can be carried out extremely rapidly in a pH of more than 8. As the products obtained by the method according to this invention are water soluble, the reaction mixture turns gradually into a transparent solution as the hydroxymethylation proceeds, and finally water-white, clear solution is obtained.

In order to carry out the said reaction, the alkalizing agent may be properly selected from the group consisting of alkali-metal hydroxides such as sodium and potassium hydroxide, alkaline-earth-metal hydroxides such as calcium and barium hydroxide and organic amines such as lower alkyl amines and lower alkylol amines.

This is not to say that the reaction can not at all be performed in an acidic region, the reaction proceeds considerably slowly than in neutral or alkaline region. The acidic condition is of little value for industrial scale production.

As the hydroxymethylation of 4,5-bis(alkoxy)-2-imidazolidinone in the neutral or alkaline region can be carried out considerably rapidly, the reaction can be promoted at the temperature range of from 0° to 100° C. without any difficulties. In practice it is preferable to employ the temperature range of from 30° to 60° C. to accomplish the said reaction. While the reaction time of the hydroxymethylation varies with such conditions as pH of the reaction mixture and the reaction temperature to be employed, the standard reaction condition is such that the time period of from about 30 minutes to 1 hour is adequate for the pH of 10 and reaction temperature of 35° C.

For observing the reaction of 4,5-bis(alkoxy)-2-imidazolidinone with formaldehyde, the free formaldehyde content in the reaction mixture is measured by the conventional analytical method in the field of aminoplast chemistry. Furthermore, as the combined formaldehyde exists in the form of methylol group, it is possible to find out the end point of the reaction by measuring the amounts of methylol group by iodometric titration. As the result of these analytical methods, the products obtained by the described method have been ascertained to be the methylol derivatives of 4,5-bis(alkoxy)-2-imidazolidinone.

The above mentioned descriptions are all concerned with the hydroxymethylation of 4,5-bis(alkoxy)-2-imidazolidinone with formaldehyde or substances which split off formaldehyde. However, when the reaction mixture obtained by the reaction of 4,5-dihydroxy-2-imidazolidinone with an aliphatic alcohol containing from 1 to 5 carbon atoms in an acid region are employed as the starting material instead of the 4,5-bis(alkoxy)-2-imidazolidinone, the hydroxymethylation therewith may be attained under the same conditions as that of the above described case.

Following is the description of the method for treating textile fabrics with the methylol derivatives of 4,5-bis (alkoxy)-2-imidazolidinone according to this invention.

Up to the present, in order to treat textiles including cellulosic materials to render the fabrics crease-resistant, such materials as methylolureas and methylol melamines have been used. Most recently, the so-called "cellulose-reactant" type resin such as dimethylol cyclic ethylene urea, dimethyloltriazone, dimethylol uron and tetramethylol acetylenediurea have been developed for the same purpose. However, these groups of resins have one or more undesirable tendencies in the properties; thus when fabrics are treated with these resins, bleached with a chlorine-containing bleaching agent and ironed, the treated fabrics have a tendency of yellowing or to be impaired in their tear strength, and when dyed fabrics are treated with these resins the treated dyeings have a tendency to be impaired seriously in their fastness to light.

When textile fabrics are treated with the methylol derivatives of 4,5-dihydroxy-2-imidazolidinone, the treated fabrics have, on the one hand, indeed, superior characteristics in the respect of crease-proof, resistance to shrinkage, the said chlorine resistance and fastness to light, but on the other hand, they have such defects, too, as the hard hand and extremely decreased tear strength. For that reason, the practical usages of the methylol derivatives of 4,5-dihydroxy-2-imidazolidinone have been limited.

On the contrary, the textile fabrics treated with the methylol derivatives of 4,5-bis(alkoxy)-2-imidazolidinone obtained by the method of this invention not only have such characteristics that the crease-proof, resistance to shrinkage and fastness to light thereof are of almost the same degree with that obtained with the methylol derivatives of 4,5-dihydroxy-2-imidazolidinone hereinabove described, but also have such superior characteristics that the treated fabrics have almost the same degree of soft hand as that of the original textile fabrics and no decrease in the tear strength is observed therein.

Moreover, the abilities of the treated fabrics can be

freely changed in various ways by selecting the chain length of the two alkyl groups in the methylol derivatives of 4,5-bis(alkoxy)-2-imidazolidinone to be employed. For example, the methylol derivatives of 4,5-bis(methoxy)-2-imidazolidinone give high wrinkle-resistant properties to the treated fabrics with but little loss of mechanical strength, and the methylol derivatives of 4,5-bis(n-butoxy)-2-imidazolidinone renders the fabrics crease-resistant with full hand. Furthermore, combined effects of respective components are realized in case of mixed formulation.

The methylol derivatives employed according to this invention are generally very stable in the lapse of time and even in the resin bath containing a curing catalyst the stabilities of the compounds are not influenced.

The curing catalysts utilized in the present invention may be selected from the conventional groups of acidic catalysts, for example, either inorganic salts such as zinc nitrate, magnesium chloride, ammonium phosphate and ammonium sulfate, or organic salts such as the mineral acid salts of 2-amino-2-methylpropanol-1 and ethanol amine. As for the treatment conditions, the curing temperature and time which are commonly employed in the treatment of textile fabrics are successfully utilized. For instance, to 10 parts of the resin solution of this invention (concentration of 50%) are added 2 parts of a zinc nitrate aqueous solution (concentration of 30%) and to this, sufficient quantities of water are added to make the total volume 100 parts. Into the said resin bath, cotton broadcloth fabrics (40's) are dipped and the fabrics are nipped to give a wet pick-up of from 65 to 68%. The impregnated fabrics are subjected to pre-drying at a temperature of 105° C. for 2 minutes, and then heated at a temperature of 140° C. for 5 minutes. Thereafter, the fabrics are subjected to soaping with 0.2% of soda ash and 0.2% of soap at a temperature of 45° C. Upon drying, the treated fabrics have permanent crease-resistance.

In order to make up the resin bath from the resinous products of this invention and the curing catalysts, other additives such as softening agents and water repellents may be employed if necessary. In the combined formulation comprising the resinous products of this invention and these conventional textile auxiliaries, combined effects of these agents are produced in textile fabrics.

The following examples further exemplify the last-described aspect of this application:

EXAMPLE 5

To 162 grams (2.0 mols) of 37% formalin, about 1 gram of a 40% sodium hydroxide aqueous solution was added to adjust the pH of the solution to 10 and the solution was poured into a 500 milliliters capacity three necked flask. To this, 146 grams (1.0 mol) of crystalline 4,5-bis(methoxy)-2-imidazolidinone were added and the mixture was stirred. The heating and stirring were continued for 1 hour at a temperature of 35° C., thereafter the solution was neutralized with concentrated hydrochloric acid and 94 grams of water added. Thus, 403 grams of a 50% 1,3-dimethylol-4,5-bis(methoxy)-2-imidazolidinone aqueous solution was obtained. The analysis by the ammonium chloride method showed that 1.4% of free formaldehyde was contained in the said products, and the analysis by iodometric titration showed 14.2% of methylol type formaldehyde was contained therein. (The theoretical amounts are 14.5%.) This composition was very useful as the resin for the treatment of cellulosic textile fabrics.

EXAMPLE 6

To 162 grams (2.0 mols) of 37% formalin, about 1 gram of a 40% sodium hydroxide aqueous solution was added to adjust the pH of the solution to 10 and the solution was poured into a 500 milliliters capacity three necked flask. To this, 174 grams (1.0 mol) of crystalline 4,5-bis(ethoxy)-2-imidazolidinone were added and the mixture was stirred. The heating and stirring were continued for 1 hour at a temperature of 35° C., thereafter the solution was neutralized with concentrated hydrochloric acid and 121 grams of water added. Thus, 458 grams of a 50% 1,3-dimethylol-4,5-bis(ethoxy)-2-imidazolidinone aqueous solution were obtained. According to the same analytical methods as in Example 5, the quantities of free formaldehyde were 1.3% and methylol type formabldehyde were 12.0% (theory, 12.8%). This composition was employable for the same purpose as that of Example 5.

EXAMPLE 7

To 162 grams (2.0 mols) of 37% formalin, about 1 gram of a 40% sodium hydroxide aqueous solution was added to adjust the pH of the solution to 10, and the solution was poured into a liter capacity four necked flask. To this, 230 grams (1.0 mol) of powdered 4,5-bis(n-butoxy)-2-imidazolidinone were added and the mixture was stirred. The heating and stirring were continued for 1.5 hours at 50° C., and when the mixture turned transparent the reaction was stopped. Thereafter, the solution was neutralized with concentrated hydrochloric acid and 175 grams of water added. Thus, 568 grams of a 50% 1,3-dimethylol-4,5-bis(n-butoxy)-2-imidazolidinone aqueous solution were obtained. According to the same analytical methods as in Example 5, the amounts of free formaldehyde were 1.0% and methylol type formaldehyde were 10.1% (theory 10.3%). This composition was employable as the treatment agent for paper.

EXAMPLE 8

To a mixture of 64 grams (2.0 mols) of methanol and 100 grams of water, about 2 grams of concentrated hydrochloric acid were added to adjust the pH of the solution to 1.5 and the mixture was poured into a 500 milliliters capacity three necked flask. To this mixture, 118 grams (1.0 mol) of 4,5-dihydroxy-2-imidazolidinone in crystalline form were added and the mixture was stirred. The heating and stirring were continued for 30 minutes at a temperature of 35° C., and the transparent solution thus obtained was adjusted to a pH of 10 by adding about 4 grams of a 40% sodium hydroxide aqueous solution. After adding 71 grams (2.0 mols) of 85% paraform aldehyde, the mixed solution was heated for 1.5 hours at a temperature of 35° C. with stirring. Thereafter, the solution was neutralized with concentrated hydrochloric acid, treated with a small amount of active carbon and filtered. Upon adding to the filtrate 20 grams of water, 350 grams of a 50% 1,3-dimethylol-4,5-bis(methoxy)-2-imidazolidinone aqueous solution were obtained. This composition was employable, like that of Example 5, as the resin for the treatment of cellulosic textile fabrics.

EXAMPLE 9

The 50% resin solution obtained by the method of Example 5 was divided into three portions of 7.5, 10 and 15 grams. To these liquids, 1.5, 2.0 and 3.0 grams of 30% zinc nitrate aqueous solutions were added respectively and each portion was diluted with water to a total volume of 100 cc. Thus, three resin baths, A, B and C, were provided. Into the said resin baths, cotton broadcloth fabrics (40's) were dipped and the fabrics were nipped to give a wet pick up of 65%. Then the impregnated fabrics were subjected to the pre-drying at a temperature of 105° C. for 2 minutes, then heated at a temperature of 140° C. for 5 minutes. Thereafter, the fabrics were subjected to soaping with 0.2% of soap and 0.2% of soda ash. Such treated fabrics showed an increased chlorine resistance and superior crease resistant properties in each sample.

By using the 50% resin solution of the dimethylol derivatives of 4,5-dihydroxy-2-imidazolidinone obtained by the method similar to that of Example 5 from 4,5-dihydroxy-2-imidazolidinone and formalin, additional resin

baths were prepared in accordance with the above described prescription. The cotton broadcloth fabrics (40's) were treated with these resin baths under the same treatment conditions as hereinabove described. The treated fabrics had as good crease-resistant properties as the goods treated with the dimethylol compounds according to this invention. However, in the respect of tear strength, the treated fabrics were far inferior to that of the present invention and what is more, while the latter had the soft hand like original fabrics, the former had the hard hand.

The results of the tests were shown in Table 1.

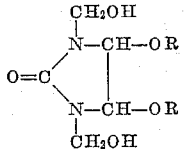
Table 1

	Crease-resistance (W+F, degrees)			Tear strength (after chlorine treatment) (g.) (W+F)		
	A	B	C	A	B	C
Resin of Example 5	231	251	276	1,270	1,245	1,057
Dimethylol derivative of 4,5-dihydroxy-2-imidazolidinone	230	256	268	1,080	1,000	910

The said crease proofing was determined in accordance with the Monsanto method and the tear strength was determined in accordance with the Elmendorf method. And as for boilable test, the treated fabrics were boiled with an aqueous solution of 1.0% soap and 0.75% soda ash for 1 hour, neutralized with 1.0% acetic acid solution, and finally subjected to washing and dried; this boiling treatment being applied twice. Thereafter, the chlorine damage and the yellowing Index were determined by using the chlorine resistance test method of AATCC 65–52. As for the control, the tear strength of untreated textile was 1,370 g.

What we claim is:

1. A method for producing permanent crease-resistance in cellulosic textile fabric which comprises impregnating the fabric with an aqueous solution containing 1,3-dimethylol-4,5-bis(alkoxy)-2-imidazolidinone of the general formula:



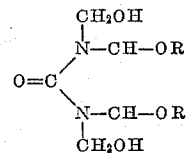
wherein R stands for alkyl containing from 1 to 5 carbon atoms, and an acidic catalyst, drying the impregnated fabric and heating the dried fabric to convert the impregnated fabric into a thermoset fabric product.

2. A method according to claim 1, wherein 1,3-dimethylol-4,5-bis(alkoxy)-2-imidazolidinone is 1,3-dimethylol-4,5-bis(methoxy)-2-imidazolidinone.

3. A method according to claim 1, wherein the 1,3-dimethylol-4,5-bis(alkoxy)-2-imidazolidinone is 1,3-dimethylol-4,5-bis(ethoxy)-2-imidazolidinone.

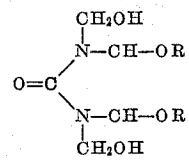
4. A method according to claim 1, wherein the 1,3-dimethylol-4,5-bis(alkoxy)-2-imidazolidinone is 1,3-dimethylol-4,5-bis(n-butoxy)-2-imidazolidinone.

5. Cellulosic textile fabrics having an impregnation of hardened 1,3 - dimethylol - 4,5 - bis(alkoxy)-2-imidazolidinone



wherein R stands for alkyl radicals containing from 1 to 5 carbon atoms.

6. Cotton fabrics having an impregnation of hardened 1,3 - dimethylol-4,5-bis(alkoxy)-2-imidazolidinone of the formula



wherein R stands for alkyl radicals containing from 1 to 5 carbon atoms.

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2,731,364	Reibnitz et al.	Jan. 17, 1956
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UNITED STATES PATENT OFFICE

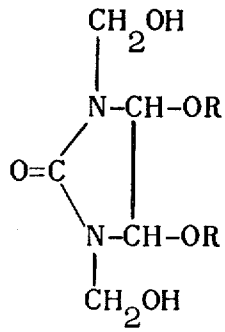
CERTIFICATE OF CORRECTION

Patent No. 3,029,164 April 10, 1962

Hideo Seki et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, lines 17 to 23, and lines 29 to 35, the formula in each of claims 5 and 6 should appear as shown below instead of as in the patent:



Signed and sealed this 28th day of August 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents