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3,049,446

PROCESS FOR THE MANUFACTURE OF UREA, GLYOXAL AND FORMALDEHYDE REACTION PRODUCT USEFUL FOR IMPROVING CELLULOSIC TEXTILE MATERIALS

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This invention relates to novel processes for the manufacture of compositions of matter and the resulting compositions of matter. The invention is also directed to processes for improving cellulosic textiles by impregnation with said composition and textiles resulting from said processes.

We have discovered a process for the manufacture of a chemical composition by the interaction of urea, glyoxal, and formaldehyde in one step and under acidic conditions which process was hitherto unknown. The pH which is maintained during the reaction is somewhat narrowly critical; at pH's below approximately 4, it is difficult to avoid the formation of acetylene diurea and/or derivatives thereof and for the reactants to condense and polymerize into higher molecular weight substances which are inferior to the monomeric compounds of our invention, for the uses as described below; at pH's of above 6, there is an excessive amount of discoloration of the product, and reduced yield of the new compound.

The actual structure of the chemical compound obtained by this invention is not known with certainty; however, it is known that the product of the present invention is different from those obtained by earlier workers in this field.

If we follow the teachings of United States Patent 2,574,114 (e.g. Example 1), which operates at pH's below 4, we obtain predominantly glyoxal diurea which is relatively insoluble in water and as such, is essentially ineffective to produce shrinkage control, crease resistance and smooth drying properties when applied to cellulosic goods. Moreover, the product of our invention is further differentiated as follows: If Example 1 of United States Patent 2,574,114 is carried out to completion, the reaction product obtained by reacting formaldehyde with glyoxal diurea in an alkaline solution, does produce notable improvements in the shrinkage, crease and smooth drying properties of cellulosic goods treated with same. However, it is essential to note that the resulting treated cloth retains considerable chlorine if it is bleached with a chlorine containing bleach, and the fabric turns brown and loses 50 to 80% of its strength if it is pressed with a hot iron after bleaching. As opposed to this, fabric treated with the product of our invention resists the degradative effects of chlorine-containing bleaches, and remains white and loses little or no strength after being pressed with a hot iron.

According to the teachings of Reibnitz in United States Patent 2,764,573, glyoxal monoureins form only under alkaline conditions. Therefore, it appears certain that the product of our invention is not a glyoxal monourein or derivative of same, because we practice our invention only in a acidic medium of pH 4 to 6, and preferably at pH of 5.2 to 5.8. It is also interesting to note that if we follow the teachings of Reibnitz and form the glyoxal monourein in an alkaline medium, the resulting reaction system becomes highly discolored. If this is further reacted with formaldehyde directly, the solution of the resulting methylol derivative is dark brown in color and it discolors cloth to which it is applied. Only by first isolating the glyoxal monourein and then reacting it with formaldehyde can a compound be obtained according to the teachings of Reibnitz which is of sufficiently low

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color that it can be applied to cloth without discoloring same. As compared to this, the product of our invention is of excellent light color and it is obtained directly in a single, simple reaction.

We have, furthermore, discovered that our chemical composition is useful to improve the dimensional stability and to impart crease recovery properties to cellulosic textiles. Another novel feature of this invention is that the light fastness of colored textiles, when impregnated with our chemical composition, remains essentially unimpaired. The absence of harmful effects on the light-fastness of dyestuffs when using the composition of our invention, is uniformly apparent with many classes of dyestuffs, such as direct dyes, diazotized and developed dyes, and the newer reactant type dyes which contain a reactive group such as cyanuric chloride (as described in the American Dyestuff Reporter, 47, No. 2, pp. 33-38 (1958) and 47, No. 11, pp. 377-383 (1958) or vinyl sulfon as described in the American Dyestuff Reporter 47, No. 24, pp. 895-899 (1958)) and which combine chemically with cellulose and become an integral part of the fiber to yield a dyed fabric possessing excellent brilliance and good fastness to light.

This absence of deleterious effect on light fastness is a surprising discovery since it is known that the light fastness of dyed textiles is usually diminished greatly by treatments intended to provide dimensional stabilization and crease resistance when using materials presently available, especially with the treatments classified as "chlorine resistant."

While it is an important object of this invention to produce shrink resistant, "wash-and-wear" effects on colored cellulosic textiles obtained by various methods of dyeing and printing, and with unimpaired light fastness, the invention is likewise applicable to white or predominantly white fabrics. In the case of white goods, our invention is also of great value for the reason that no objectionable yellowing of the white fabric occurs in contrast to certain treatments presently used. Furthermore, there is, in the practice of this invention, no problem incurred by the generation of objectionable odors, and the treated cloth is highly resistant to the degradative effects of chlorine bleaching and hot pressing.

Cotton or rayon fabrics are frequently treated with a water-soluble resin, and then subjected to a mechanical treatment, such as schreinerizing, embossing, or glazing, followed by curing of the resin to provide wash-and-wear effects. The compositions of this invention can be used in such applications and are well suited for this type of work.

The compositions of our invention are advantageously prepared by first forming an aqueous mixture of formaldehyde, glyoxal and urea and in the mole ratio of 2 to 2.5:1:1, then adjusting the pH of the mixture to at least about 4.0 but not more than about 6.0. Reaction can take place without the application of external heat or heat can be applied to accelerate the reaction. The mixture during reaction is maintained at a temperature within the range of about 25° C. to about 95° C. for a general period of time ranging from 30 minutes to 72 hours. For best results in ease of reaction and optimum properties of the resulting composition, the pH of the reaction mixture is preferably maintained at 5.2 to 5.8 and its temperature is maintained within the range of 60° C. to 95° C. under which conditions a reaction time of 30 minutes to 5 hours is normally sufficient. The product, thus obtained, is employed directly in the treatment of textiles or it can be further altered, e.g., to change its water content or to add other materials to provide special effects.

In treating cellulosic textiles with the compositions of our invention, the cellulosic textile is impregnated with an aqueous or alcoholic solution advantageously contain-

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ing 2 to 20 weight percent solids (i.e., the reaction product of formaldehyde, glyoxal and urea) and an acid catalyst as hereinafter more fully described. The impregnated textile is then passed through squeeze rolls or other device to remove excess solution and provide the desired amount of pick up. Next, the impregnated textile is dried, followed by curing, or, if desired, the drying and curing can be performed at the same time. In any event, the impregnated textile is subjected to curing conditions so that the formaldehyde-urea-glyoxal-reaction product carried thereon is converted to an insoluble material. Curing is advantageously carried out at a temperature in the range of about 200° F., preferably about 280° F., to about 400° F. and usually requires about 30 seconds to 600 seconds.

The following examples illustrate our invention, but it is to be understood that the invention is not to be limited to these examples. All proportions and parts are by weight. Wet pick-up percentages and percentages of components employed in dyeing operations are all based on the weight of fabric being treated.

Example 1

39.5 parts of 40% aqueous glyoxal solution are mixed with 44.2 parts of formula (37% formaldehyde) and the mixture is adjusted to a pH of 5.5 with approximately 2.5 parts of 50% aqueous sodium hydroxide. 16.3 parts of urea are stirred in, and the solution is heated to 80° C. by the external application of heat and by the heat generated by the exothermic reaction which takes place. The solution is maintained at 80° C. for one to two hours and then cooled. The resulting product is a clear, colorless to light, straw-yellow liquid. Instead of the formalin used above, an equivalent amount of paraformaldehyde or other formaldehyde yielding substances can be used with equality satisfactory results. In place of the sodium hydroxide, other alkalis can be used. Instead of maintaining the reaction mixture at 80° C., lower temperatures can be used, but this will extend the time required to complete the reaction; similarly, the reaction can be conducted at higher temperatures and this will speed up the reaction.

Example 2

160 parts of material from Example 1 are dissolved in 1000 parts of water and 10 parts of zinc nitrate are added. A white cotton broadcloth is impregnated with this solution, dried and cured four minutes at 320° F. After this treatment, the cloth is odor-free, non-yellowed and dimensionally stable. The crease recovery angles are over 100% improved as compared to the untreated fabric. Moreover, the fabric does not yellow nor lose appreciable strength after bleaching with a chlorine containing bleach and pressing with a hot iron. Similar results are obtained if the zinc nitrate used above is replaced with maleic acid or zirconium oxychloride.

Example 2 is repeated, but instead of treating a white cloth, the treatment is applied to cotton which has previously been dyed with Procion Brilliant Blue H7GS. After this treatment, the cloth is free of objectionable odor and is dimensionally stable during laundering. The crease recovery angles are approximately twice those of the untreated fabric, and the finished fabric is chlorine resistant. The light fastness of the dye is unaffected even after 40 hours' exposure in the Fade-Ometer and an improvement in the cold water bleeding properties of the dye is noted. As compared to this, a similarly dyed fabric was treated with a solution containing N,N-dimethylol cyclic ethylene urea at the same concentration, and with all other details of the treatment being the same. The fabric treated with the N,N-dimethylol cyclic ethylene urea showed noticeable fading even after 20 hours' exposure in Fade-Ometer.

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Example 3

150 parts of the product of Example 1 are dissolved in 1000 parts of water, and 10 parts of maleic acid are added.

White cotton broadcloth is immersed in this solution, the excess liquid removed by passing through squeeze rolls to give a wet pick-up of approximately 65 weight percent. The impregnated fabric was dried 2 minutes at 250° F., then cured 2 minutes at 330° F. The resulting treated fabric was essentially free of objectionable odor and the whiteness of the fabric was unimpaired by the treatment. The fabric showed approximately 260 degrees crease recovery (total of warp plus filling), and after washing with soap and sodium hypochlorite bleach, and hanging, the fabric dried with a smooth appearance and suffered no discoloration or loss in strength even when pressed with a hot iron; thus, demonstrating the properties known as "wash-and-wear" and chlorine resistance.

Another experiment was performed using the same treatment as above, but instead of treating white cotton, a piece of viscose rayon which had been previously dyed with Procion Brilliant Red 5BS, was treated in the same manner. The resulting treated fabric showed reduced shrinkage, improved crease recovery and smooth drying properties. In addition, the dye present on the treated fabric showed only an insignificant amount of fading when the fabric was exposed for 40 hours in the Fade-Ometer. In place of the maleic acid used in the above treatments, other acid substances can be used as the catalyst; for example, zinc nitrate, zirconium oxychloride, etc.

As compared to the results cited above, another piece of the fabric dyed with Procion Brilliant Red 5BS was treated in the same way but with the exception that the product of Example 1 was replaced with an equal weight of 1,3-dimethylol-2-keto-5-ethyl-s-triazone. The triazone-treated fabric showed noticeable fading even after only 20 hours' exposure in the Fade-Ometer.

Example 4

An 80 x 80 cotton print cloth was dyed with Remazol Yellot RT according to the following. The fabric was padded at 100° F. with 75 weight percent wet pick-up in a pad bath containing 1.5 oz./gal. Remazol Yellow RT, 0.25 oz./gal. Synthrapol N (non-ionic ethylene oxide condensate) and 1.50 oz./gal. Glauber's salt. The fabric was dried at 180° F. and then padded through an aqueous solution containing 1.5 oz./gal. caustic flakes and 39.0 oz./gal. common salt. It was steamed 30 second, rinsed, soaped at 200° F. in 0.13 oz./gal. Synthrapol SP for 5 minutes, rinsed and dried. The dyed fabric was then discharge printed with a flower pattern. Part of the print pattern was discharged to white, and part of the print pattern was illuminated with color using Ahcovat Printing Pink FF Paste (Part I, New Color Index—Vat Red 1, and Part II, New Color Index—73360) and Ahcovat Printing Jade Green B Extra Double Paste (Part I, New Color Index—Vat Green 1, and Part II, New Color Index—59825). After printing, the fabric was steamed, oxidized and soaped off thoroughly in accordance with standard discharge printing practice. The printed fabric was then passed through a solution containing 15 parts of the product of Example 1, 1 part glycerol monostearate (added as a lubricant) and 1 part of zinc nitrate dissolved in 83 parts of water. The impregnated fabric was passed through squeeze rolls to remove excess liquid, and to provide a wet pick-up of approximately 60 weight percent. The fabric was then partially dried on a clip frame at 220° F. so as to leave 10% moisture in the fabric. Following this, the partially dried fabric was immediately passed through a schreiner calender, and finally the fabric was passed through a curing chamber where it remained for 2.5 minutes at 320° F. The resulting treated cloth had the deep-seated luster character of the schreiner effect, and this property persisted even after many launderings. In addition, the white

portion of the print was unaffected by the resin treatment, and the quality of the white was unimpaired by bleaching with a chlorine containing bleach followed by pressing. Also, the fabric showed good dimensional stability toward laundering, and the fabric had excellent crease recovery and smooth drying properties. When exposed to the Fade-Ometer, there was no more than an insignificant fading even after 40 hours' exposure. As compared to this, the same dyed and printed fabric was passed through a solution containing 15 parts of a 50% solution of bis-(methoxymethyl)urea. All other materials in the solution were the same as those described above, and the treating procedure was identical to that described above. When the resulting treated fabric was checked for light fastness, it was found that it had essentially the same light fastness properties as those obtained with the treatment using the product of our invention. However, as the bis-(methoxymethyl)urea treatment was subjected to multiple launderings, the luster due to the Schreiner pattern diminished greatly and practically disappeared after 5 launderings. Similarly, the initial high crease recovery of the treated fabric was rapidly lost on multiple launderings, and although the smooth drying property was satisfactory after the first laundering, the fabric showed very poor smooth drying properties after 5 or 10 launderings. Furthermore, when the bis-(methoxymethyl)urea treatment was laundered in the presence of chlorine containing bleach, and the laundered fabric was pressed with a hot iron, the fabric became badly discolored, the white portions of the print turned brown, and the tensile strength of the fabric was reduced about 80 to 90%.

Example 5

Viscose rayon is dyed with a direct dye (Fastusol Blue LRRU-Color Prototype PR 615—Part I, New Color Index Dir. Blue 80) by using a 20:1 bath: fabric ratio. The goods were thoroughly wet out using 0.5% of Igepon T-51 (anionic, surfactant fatty methyl tauride). The dye was predissolved in boiling water and then added to the bath at 100° F. The temperature was raised to 160° F. and then 20% common salt was added. The temperature was raised to a boil and boiling continued for 45 minutes. The bath was allowed to cool for 15 minutes, and then the cloth was rinsed cold until the rinse water was clear.

This dyed viscose fabric was treated in a solution containing 200 parts of the product of Example 1, 15 parts of zinc nitrate, 10 parts of polyvinyl alcohol and 75 parts of water. The surplus liquor was squeezed out of the cloth and the fabric was dried and cured 7 minutes at 310° F. when the resulting treated fabric was tested, it was found to be free of objectionable odor, it had good crease recovery properties, and when the fabric was laundered, it dried smoothly, and eliminated the need for pressing. When a sample of the treated fabric was placed in the Fade-Ometer, there was no fading after 20 hours' exposure. On the other hand, when a piece of the same dyed fabric was treated in the same way in a solution containing 200 parts of a 50% solution of N,N-dimethylol cyclic ethylene urea, with all other ingredients in the treatment being the same as indicated above, the resulting treated fabric showed a very substantial drop in light fastness when exposed in the Fade-Ometer.

Example 6

A light weight cotton poplin is dyed with a diazotized and developed color (Pontamine Diazo Bordeaux 2BL—Color Prototype PR 172, New Color Index Dir. Red 127, and using Beta Naphthol as the developer) by applying 1% of the dye in a bucket using a 40:1 bath: fabric ratio. After the fabric was thoroughly wet out, the predissolved dye was added at 120° F. and the bath brought to the boil. Common salt (1%) was added and the bath held at the boil for 15 minutes. The fabric was then rinsed with cold water and then diazotized at room temperature with 2% sodium nitrite plus 3% concentrated hydrochloric acid. After the fabric was rinsed with cold water, the

color was developed by adding 1% of the predissolved developer (using caustic soda to dissolve) and then running at room temperature for 20 minutes. The fabrics were then rinsed cold, soaped hot, and finally rinsed thoroughly.

When this dyed fabric was treated with the product of our invention as set forth in Example 2, the resulting treated fabric was found to have excellent crease recovery properties, was resistant to shrinkage during laundering, and showed good smooth drying properties after laundering. In addition, when exposed in the Fade-Ometer, there was only a slight break in light fastness after 20 hours exposure. Furthermore, when this treated fabric was laundered with soap and chlorine-containing bleach, followed by hot pressing, there was no discoloration of the cloth and the strength of the cloth remained unimpaired.

Another piece of the fabric dyed with the Pontamine Diazo Bordeaux 2BL is treated with a solution containing 200 parts of a 50% solution of tetramethylol glyoxal diurein instead of the product of Example 1, with all other ingredients of the treating solution, as well as details of the treatment, being the same as indicated above, the resulting treated cloth showed satisfactory crease recovery properties. However, when bleach is used during launderings, the finish tends to absorb the chlorine, and on subsequent pressing with a hot iron, the cloth turns dark brown and loses from 50 to 95% of its strength.

When applying the product of our invention to cloth, it is necessary to have present also an appropriate acid catalyst which includes acidic and acid-forming substances to accelerate the curing of the product and/or promoting the reaction of the product with the cellulose. Typical acid catalysts are metal salts (such as zinc nitrate, zirconium oxychloride, etc.), organic acids (such as maleic acid, oxalic acid, lactic acid, etc.), amine hydrochlorides (such as the hydrochloride of 2-amino-2-methyl-1 propanol, etc.) and other compounds which release an acidic material at high temperatures.

In addition to the product of our invention and the catalyst, other materials may be added to the treatment such as lubricants, softeners, firming agents, water repellants, mildew inhibitors, etc. The only precaution that need be taken in the use of such other additives is that they be selected with caution so as to be sure that such additives do not interfere with the proper functioning of the acid catalyst nor that such additives contribute to chlorine retention or to adversely affect the light fastness of dyes.

The Procion dyes employed herein are more fully described in British 781,930 of August 28, 1957; Journal of the Society of Dyers and Colourists, 73, pp. 237 to 247, 1957; American Dyestuff Reporter, 47, No. 2, pp. 33 to 38, 1958 and 47, No. 11, pp. 377 to 383, 1958. The Remazol dyes employed herein are more fully described in American Dyestuff Reporter, 47, No. 24, pp. 895, 899, 1958.

The product of our invention is particularly effective to produce the desired results when applied to cellulosic fabrics such as cotton, linen, viscose rayon, cupra-ammonium rayon and other forms of regenerated cellulose. However, very useful effects have been obtained, also, by the use of our product on blends of such cellulosic fibers with other non-cellulosic fibers such as nylon, Orlon, cellulose acetate, Dynel, etc., and the term "cellulosic goods" in the claims is intended to embrace not only cotton and regenerated cellulose but also blends of these fibers with other non-cellulosic fibers.

What is claimed is:

1. A process of preparing novel compositions of matter which comprises forming an aqueous solution of 1 mole of urea, 1 mole of glyoxal, and 2 to 2.5 mols of formaldehyde and thereafter reacting said urea, glyoxal and formaldehyde at a pH of 4.0 to 6.0 and at a temperature of 25° C. to 95° C. for a period of time ranging from 30 minutes to 72 hours.

2. The product obtained by the process as described in claim 1.

3. The process of treating cellulosic textiles with the product of claim 2 to obtain improved properties which comprises impregnating the goods with a solution from the class consisting of aqueous and alcoholic solutions containing between 2 and 20 weight percent of the said product and an acid catalyst and then drying and curing the impregnated textile at a temperature between 200° F. and 400° F. for a period of time in the range of 30 seconds to 600 seconds.

4. The process of treating cellulosic textiles with the product of claim 2 which comprises impregnating the goods with an aqueous solution containing between 2 and 20 weight percent of said product and an acid catalyst, partially drying said impregnated textile, passing the partially dried textile through a heated calender to alter the surface texture and appearance of said textile, and then curing the textile at a temperature between 280° F. to 400° F. to insolubilize the resin.

5. A process of preparing novel compositions of matter which comprises mixing 1 mole of urea, 1 mole of glyoxal, 2 moles of formaldehyde and water to form an aqueous solution and thereafter reacting said urea, glyoxal and formaldehyde at a pH of 5.2 to 5.8 and at a temperature of 60° C. to 95° C. for a period of time ranging from 30 minutes to 5 hours.

6. The product obtained by the process as described in claim 5.

7. The process of treating cellulosic textiles with the product of claim 6 to obtain improved properties, which comprises impregnating the textile with an aqueous solution containing between 2 and 20 weight percent of the said product and an acid catalyst, and then drying and

curing the impregnated textile at a temperature between 200° F. and 400° F. for a period of time from 30 seconds to 600 seconds.

8. The process of treating cellulosic textiles with the product of claim 6 which comprises impregnating the textile with an aqueous solution containing between 2 and 20 weight percent of said product and an acid catalyst, partially drying said impregnated textile, passing the partially dried textile through a heated calender to alter the surface texture and the appearance of said textile, and then curing the textile at a temperature between 280° F. and 400° F. to insolubilize the resin.

9. A process of preparing novel compositions of matter which comprises mixing one mole of urea, one mole of glyoxal, 2 to 2.5 moles of formaldehyde and a solvent to form a solution and thereafter reacting said urea, glyoxal and formaldehyde at a pH in the acid range and at a temperature of 25 to 95° C. for a period of time ranging from 30 minutes to 72 hours.

10. The product obtained by the process as described in claim 9.

11. Cellulosic textiles having an impregnation of the product claimed in claim 10 in hardened condition.

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