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GLYOXAL-AMIDE REACTION PRODUCTS

Sidney L. Vail, Clifford M. Moran, and Harry B. Moore, New Orleans, La., assignors to the United States of America as represented by the Secretary of Agriculture

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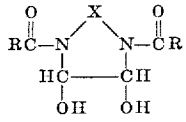
6 Claims. (Cl. 8—116.2)

(Granted under Title 35, U.S. Code (1952), sec. 266)

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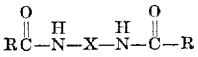
This application is a division of Serial No. 170,848, filed February 2, 1962.

This invention relates to the formation and use of compounds having the following general structure:



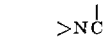
wherein X=>CR_2 or —CR_2CR_2— and where R is a member of the group consisting of H and an alkyl group of one to four carbon atoms. These compounds, which are similar in structure to the urea-glyoxal adducts, may be used in resin applications, textile finishing, pharmaceutical, and allied industries, or as intermediates in these fields. Moreover, these compounds may also be used as glyoxal generators; that is, under conditions of heat and/or acid, glyoxal (and the starting bisamide) can be generated from the parent compounds.

The compounds of this invention are formed by the reaction of the bisamide



with glyoxal. Since one mole of the bisamide reacts with one mole of glyoxal to form the desired compounds, it is preferable to react the starting materials on a near equimolar basis. In some cases an excess of the bisamide is useful to concentrate the solution and aids in the precipitation of the desired compounds. The reaction has been found to proceed at low temperatures (about 25° C. has been found satisfactory to initiate the reaction) and at varying pH's. Extreme acid or basic conditions should be avoided to exclude undesirable side reactions.

In general, it has been shown that N-methylol groups of amides, ureas, and similar compounds are reactive with a variety of materials. Difunctional compounds of this type are known to readily form useful polymers and serve as effective crosslinking agents. In a recent publication [American Dyestuff Reporter 50, 550 (1961)] it has been shown that the N-methylol groups need not only be free >N—CH_2OH groups to be reactive, but that



groups, when part of a ring system, are also quite reactive.

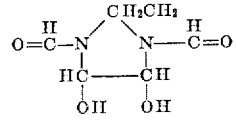
For example, such compounds of this invention are useful in the crosslinking of cellulosic fabrics or fibers. Furthermore, the absence of >NH groups in the molecule decreases the possibilities of chlorine retention and the subsequent disadvantages of yellowing or scorch damage to the fabric. These and other advantages, such as an unusually high resistance to acid hydrolysis, will be evident in the examples given.

The following examples are given by way of illustration and are not to be construed as limiting. Many variations or additions within these procedures can be made,

as will be readily apparent to those skilled in the art. In the examples, all parts and percentages are by weight unless noted otherwise. The fabrics were tested by standard methods: Crease recovery angle, Monsanto method, American Society for Testing Materials (ASTM) Test D, 1295–53T; breaking strength (ASTM) Test D, 39–49; damage caused by retained chlorine (scorch test), American Association of Textile Chemists and Colorists tentative test method 69–1952.

Example 1

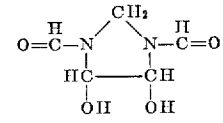
1,4-diformyl-2,3-dihydroxypiperazine



was prepared in the following manner: 11.6 grams ethylenebisformamide were added to 19.3 grams of a 30% solution of glyoxal which had been adjusted to a pH of 7. After solution of the bisamide, the pH was raised to 8–9 with aqueous sodium hydroxide. The product formed rapidly resulting in a pasty mass. Recrystallization from ethanol produced a white product. The 1,4-diformyl-2,3-dihydroxypiperazine was found to contain 41.37% carbon, 5.79% hydrogen and 15.98% nitrogen. The molecular weight of the compound isolated was found to be 176. (Theory 41.38% carbon, 5.79% hydrogen and 16.09% nitrogen, and molecular weight 174 for $C_6H_{10}N_2O_4$.)

Example 2

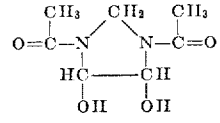
1,3-diformyl-4,5-dihydroxyimidazolidine



was prepared in the following manner: to 9.8 grams of neutralized 30% glyoxal solution were added 7.7 grams of methylenebisformamide and 10 grams of water. The pH was adjusted to 8–9, and the solids dissolved by shaking. After standing at room temperature for about four hours, the solution was stored at 5–10° C. Colorless crystals of 1,3-diformyl-4,5-dihydroxyimidazolidine were obtained by filtration. The compound contained 17.54% nitrogen. (Theory 17.50% nitrogen for $C_5H_8N_2O_4$.) On heating in ethanol the starting materials are recovered.

Example 3

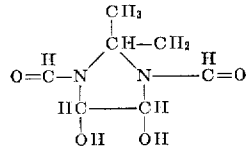
1,3-diacetyl-4,5-dihydroxyimidazolidine



was prepared in a manner similar to Example 2 using methylenebisacetamide as the starting bisamide. The product, recrystallized from 50% ethanol-50% acetone, melted at 176–177° C. and contained 14.79% nitrogen. (Theory: 14.89% nitrogen for $C_7H_{12}N_2O_4$.)

Example 4

1,4-diformyl-2,3-dihydroxy-5-methylpiperazine



was prepared from 3.9 grams of 30% glyoxal and 2.6 grams of propylenebisformamide (prepared from propylenediamine and ethyl formate). The alkalinity of the solution was adjusted as before; and after remaining at room temperature for about four hours, the solution was stored at −12° C. A white crystalline product, which melted at 163–164° C. with decomposition, was isolated by filtration and found to contain 14.72% nitrogen. (Theory: 14.89% nitrogen for $C_7H_{12}N_2O_4$.)

Example 5

1,4-diformyl-2,3-dihydroxypiperazine prepared as described in Example 1, was dissolved in water, and an acid substance or a substance producing acidity at elevated temperatures was added to serve as a catalyst. A textile fabric, cotton in this case, was immersed in the solution, and the excess liquid removed mechanically. The fabric was pinned to a frame, dried, and cured. All these steps can be conveniently carried out with conventional textile finishing equipment. Table I more fully describes the conditions used for this particular experiment.

TABLE I

Agent Concentration, percent	Catalyst	Catalyst Concentration, percent	Drying Conditions, °C./min.	Curing Conditions, °C./min.
10	Pyridine·HCl	2	60/7	160/3

The crease recovery angle of the treated fabric was increased by some 39% over the untreated fabric. Further, this treated fabric was found not to yellow on repeated bleachings in hypochlorite solution. Chlorine damage in the "scorch test" was negligible. On heating the treated fabric in a urea-phosphoric acid stripping solution (30 min. at 80° C.), under conditions which essentially completely remove common finishes such as urea-formaldehyde, the crease recovery angle and the nitrogen content of the "stripped" fabric were reduced by less than 6% of their original values.

Example 6

In addition to being employed as the sole agent in the treating solution, the agent described in Example 1 but with 4% formaldehyde added to the pad bath, and the fabric treated in the same fashion as in Example 5, produced a fabric with an even greater crease recovery angle.

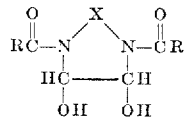
In this case the crease recovery angle was increased some 71% over the untreated fabric.

Example 7

1,3-diacetyl-4,5-dihydroxyimidazolidine and 1,4-diformyl-2,3-dihydroxypiperazine were added to a dilute solution of 2,4-dinitrophenylhydrazine, which was acidified with HCl. After about an hour, a precipitate, identified as the hydrazone of glyoxal, began to appear. Glyoxal generation appeared complete after 24 hours.

We claim:

1. A process which comprises impregnating a textile material with an aqueous solution containing about 10% by weight of a compound of the formula



wherein X is a member of the group consisting of —CR_2— and —CR_2CR_2— and wherein R is a member of the group consisting of H and an alkyl group having from one to four carbon atoms, and from about 0.5% to about 5% by weight of an acid catalyst and curing the impregnated material at a temperature of from 130° C. to 160° C.

2. The process of claim 1 wherein the compound is 1,4-diformyl-2,3-dihydroxypiperazine.

3. The process of claim 1 wherein the compound is 1,3-diformyl-4,5-dihydroxyimidazolidine.

4. The process of claim 1 wherein the compound is 1,3-diacetyl-4,5-dihydroxyimidazolidine.

5. The process of claim 1 wherein the compound is 1,4-diformyl-2,3-dihydroxy-5-methylpiperazine.

6. The process of claim 1 wherein the compound is 1,4-diformyl-2,3-dihydroxypiperazine and the aqueous solution contains, in addition to the said compound and an acid catalyst about 4% by weight of formaldehyde.

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