

## Methylolamides Containing Amino Acid Groups: Their Use as Wash-Wear Finishing Agents for Cotton

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### Synopsis

The acid-catalyzed etherification of cellulose with methylolamides containing a tertiary amino group is often inhibited by the presence of this basic group. In the production of wash-wear fabrics an incomplete reaction generally produces a low degree of wrinkle resistance and/or leaves the treated fabric susceptible to deterioration during use. In this work it is postulated that the insertion of a carboxylic acid group into such a crosslinking agent neutralizes the basic group by the formation of an inner salt (zwitterion). Such agents were prepared by methylolation of the products of a Michael addition of the sodium salt of selected amino acids to acrylamide. All the compounds synthesized are thought to be new. Those which were isolated and characterized include sodium *N*-2-carbamoylethylglycinate, sodium *N,N*-bis(2-carbamoylethyl)glycinate, *N,N*-bis(2-carbamoylethyl)glycine, sodium *N,N*-bis(2-carbamoylethyl) $\alpha$ -alaninate, and *N,N*-bis(2-carbamoylethyl)- $\alpha$ -alanine. Similar adducts from  $\beta$ -alanine, lysine, and aspartic acid were prepared; however, the adducts obtained were oils, and this complicated their isolation and characterization. For textile treatments isolation of the intermediates is unnecessary. The *N*-methylol crosslinking agents derived from these Michael adducts are highly reactive to cotton, as indicated by high add-ons at relatively mild conditions. The treated fabrics are highly wrinkle resistant and possess other desirable properties. The data obtained from the use of these agents indicate that further study is desirable, based on the concept developed in this work.

### INTRODUCTION

*N*-Methylolamides are widely used to produce wash-wear cotton fabrics which dry smoothly after washing and resist wrinkling when dry. Although they have been used to produce wash-wear finishes more than any other type of crosslinking agent, these desirable properties are generally accompanied by fabric damage. Smooth drying properties, wrinkle recovery, strength loss, and resistance to chlorine damage are all, in a practical sense, directly related to the amount of reaction of the particular crosslinking agent with cotton. Moreover, reaction conditions designed to achieve a high degree of wrinkle recovery and smooth-drying properties often required stronger catalytic conditions which, in turn, result in addi-

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Amino acids used include glycine (to form Ia),  $\beta$ -alanine (to form Ib),  $\alpha$ -alanine (to form Ic), lysine (to form Id), and aspartic acid (to form Ie). In general (Fig. 1), the sodium salt of the amino acid is formed, acrylamide is added (two molar equivalents of acrylamide for each amino group), and the solution, after standing overnight, is warmed to 60°C. for 2 hr. to form the amino acid-acrylamide adduct. Under the alkaline conditions used to promote this reaction, there was little or no hydrolysis of the amide group of either acrylamide or the desired products. Usually, the sodium salts of I are isolated either by precipitation from the reaction mixture or by evaporation. For textile treatment, isolation of the sodium salts is unnecessary. (The free acid, or inner salt, form of I may be isolated by addition of hydrochloric acid.) The reaction mixtures are buffered at a pH of about 8.0-10.0, and methylolated by addition of formaldehyde with the usual conditions of heating or standing at room temperature. Hydrochloric acid is then added to form I and sodium chloride. The solution is then diluted, and the curing catalyst is added.

#### Sodium *N*-2-Carbamoylethylglycinate

To 7.5 g. of glycine and 7.1 g. of acrylamide were added 8 g. of 50% sodium hydroxide and 60 ml. methanol. The mixture was stirred to dissolve the materials and was left standing at 20-25°C. for about three days. On chilling no crystals were obtained. The solution was partially evaporated on a steam cone and cooled to about -10°C. Solid material precipitated; after filtration and drying, it melted at 200-205°C. with decomposition starting at 190°C.

ANAL. Calcd. for  $C_5H_8N_2O_3Na$ :N, 16.7%. Found: N, 16.0%.

#### Sodium *N,N*-Bis(2-carbamoylethyl)glycinate

Glycine (15 g.) was added slowly to 40 g. of 20% sodium hydroxide, with stirring and cooling to keep the temperature of the solution below 20°C. To this solution was added slowly, with stirring, 28.4 g. of acrylamide. After standing overnight at 20-25°C., the solution was heated for 2 hr. at 60°C. During this heating period, solids precipitated. These solids and those subsequently isolated by cooling were extracted with ethanol and dried in a vacuum oven. The dry product melted at 231-235°C. with decomposition.

ANAL. Calcd. for  $C_8H_{14}N_4O_4Na_2$ :N, 17.6%. Found: N, 17.6%.

#### *N,N*-Bis(2-carbamoylethyl)glycine

To 10 g. of the glycinate was added enough water to dissolve the salt almost completely. Concentrated hydrochloric acid was added dropwise until a pH of 6 was obtained. Solids which were formed during the acidification were filtered from the solution. A second precipitate was obtained by cooling the filtrate and filtering off the solids. The solids were washed

with ethanol and then dried in a vacuum oven. The *N,N*-bis(2-carbamoyl-ethyl)glycine melted at 209–210°C. with decomposition.

ANAL. Calcd. for  $C_8H_{16}N_2O_4$ : C, 44.23%; H, 6.96%; N, 19.35%. Found: C, 44.27%; H, 6.85%; N, 19.44%.

#### Sodium *N,N*-Bis(2-carbamoylethyl) $\alpha$ -alaninate

To 60 g. of 20% sodium hydroxide were added 30 g. of water and, with cooling, 27.3 g. of  $\alpha$ -alanine. The acrylamide (42.6 g.) was then added. The solution was allowed to stand at 20–25°C. for 18–24 hr. and was then heated for 2 hr. at 60°C. The solution was evaporated to dryness at 20–25°C., and then extracted with ethanol. The solids obtained melted with decomposition at 209–217°C.

ANAL. Calcd. for  $C_8H_{16}N_2O_4Na$ : N, 16.6%. Found: N, 16.4%.

#### *N,N*-Bis(2-carbamoylethyl) $\alpha$ -alanine

This was prepared by a procedure similar to that given for the analogous glycine derivative. The solids were crystallized from an ethanol–water mixture and then washed with ethanol. After being dried in a vacuum oven, the compound melted at 196–197°C. with slight decomposition.

ANAL. Calcd. for  $C_8H_{17}N_2O_4$ : C, 46.74%; H, 7.41%; N, 18.17%. Found: C, 46.67%; H, 7.51%; N, 17.96%.

#### Amino Acid–Acrylamide Adducts

Although not characterized, the following amino acid–acrylamide adducts, considered to be similar to those above, were prepared.

**$\beta$ -Alanine–Acrylamide Adduct, Presumably Sodium *N,N*-Bis(2-carbamoylethyl)- $\beta$ -alaninate.**  $\beta$ -Alanine (9.1 g.) was dissolved in 20 g. of 20% sodium hydroxide, while the temperature of the solution was kept below 20°C. To this solution were added 14.2 g. of acrylamide and 10 ml. of water. The solution was left standing overnight at 20–25°C., and was then heated for 3 hr. at 60°C. The solution was evaporated under vacuum at room temperature. The resulting viscous solution could be used without further purification.

**Lysine–Acrylamide Adduct, Presumably Sodium *N,N,N',N'*-Tetrakis(2-carbamoylethyl)lysinate.** Lysine monohydrochloride (50 g.) was added to 20% sodium hydroxide at 20°C. (no exotherm). To this solution were added 77.8 g. of acrylamide, and the reaction flask was cooled to keep the temperature below 40°C. The remainder of the procedure is similar to that described for the preparation of the  $\beta$ -alanine agent.

**Aspartic Acid (Aminosuccinic Acid)–Acrylamide Adduct, Presumably Disodium *N,N*-Bis(2-Carbamoylethyl)aminosuccinate.** Aspartic acid (26.6 g.) was added slowly with stirring and cooling to 80 g. of 20% sodium hydroxide (slight exotherm). After addition of 28.4 g. of acrylamide the solution was worked up similar to that described for the preparation of the  $\beta$ -alanine agent.

### Methylolations and Fabric Treatments

Methylolations and fabric treatments were carried out in a conventional manner. Details of this procedure are given below for one agent. Sodium *N,N*-bis(2-carbamoylethyl) glycinate was dissolved in about four times its weight of water, and sufficient 36.9% formaldehyde solution was added to adjust the ratio of amido NH<sub>2</sub> groups to formaldehyde to 1:1.5. This solution (pH = 8–10) was heated for 30 min. at 60°C. or allowed to stand at 20–25°C. for 18–20 hr. The solution was then cooled, if necessary, to 20–25°C., and the pH adjusted to 4.0–6.5 with hydrochloric acid. A catalyst was added, and the solution diluted such that it contained a calculated 10% of sodium *N,N*-bis(2-carbamoylethyl) glycinate. A sample of 80 × 80 cotton print fabric was dipped in the treating solution to give about 80% increase in weight of the fabric. The wet fabric was then dried at original dimensions for 7 min. at 60°C. and cured for 3 min. at 160°C. unless noted otherwise. The treated fabric was then washed in warm water with a nonionic detergent and tumble dried.

### Testing Methods

Testing methods used were: wrinkle-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, American Association of Textile Chemists and Colorists tentative test method 92-1962 ("scorch test"); tearing strength, Elmendorf method, ASTM test D 1424-59.

The moisture regain of some of the treated fabrics was determined in the following manner: The sample was first heated to 100°C. for 15 min., then placed in a conditioning atmosphere at 70°F. and 65% R. H. for 72 hr., weighed, dried in oven at 100°C. for 4 hr., and reweighed.

% Moisture regain = 100 (Conditioned weight—dry weight)/dry weight

## RESULTS AND DISCUSSION

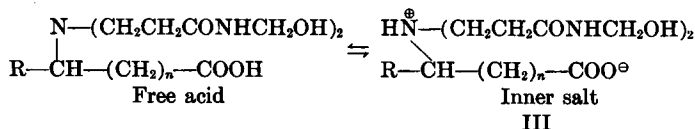
Previously reported *N*-methylol-2-carbamoylethylamines have been applied as amine hydrochlorides.<sup>1</sup> Of these, tris(*N*-methylol-2-carbamoylethyl) amine (II), produces a particularly durable wash-wear finish on



II

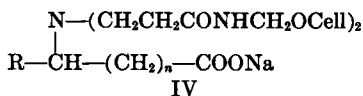
cotton fabric. However, under normal curing conditions, additional strength loss of the fabric is difficult to avoid in processing, especially in the presence of relatively high concentrations of acid-producing substances, such as amine hydrochlorides. Without very close control at the specified pH of 4.0–4.5 in the pad bath, excessive tendering of the fabric occurs during drying and curing. Since even more acidic curing conditions are required to assure an acceptable level of resistance of the treated fabrics to chlorine damage, the use of such treating agents and processes is limited.

In contrast, I, which contains both amino and carboxylic acid groups, can be applied to cellulose under relatively mild conditions, since the tertiary amino group is at least partially neutralized by the formation



R and  $n$  as in Figure 1

of an inner salt (zwitterion) (III). After curing and during subsequent washing and bleaching of the treated fabric, the alkali salt (IV) of the



R and  $n$  as in Figure 1

carboxylic acid group is formed. In this manner, the treated fabric is further protected from chlorine damage.

To demonstrate that I can be cured under mild conditions, pad baths containing the glycine agent (for simplicity, each finishing agent is designated as the amino acid agent from which it is prepared), were adjusted to various pH's from 4.2 to 6.3, the magnesium chloride catalyst added, and the solutions used to treat  $80 \times 80$  cotton print cloth under conventional conditions. From Table I it is seen that the pH of the pad bath has little or no effect on the add-on, crease recovery, or breaking strength of the treated fabrics. Essentially the same results were obtained in a similar study with the lysine agent, the pH being varied in the range 4.0-6.0. Add-on with the lysine agent is higher—10% in some cases.

Table II contains data relative to the fabric properties after treatment with the five agents of type I under similar curing conditions. The most

TABLE I  
Effect of pH of Reagent on Properties of Fabric Treated with the Glycine Agent<sup>a</sup>

pH of solution <sup>b</sup>	Add-on, %	Conditioned crease recovery angle (warp), degrees	Breaking strength (warp), lb.
6.3	6.3	132	32.9
5.5	6.2	141	31.1
4.6	6.2	133	33.5
4.2	6.8	145	30.0
Untreated fabric		83	45.4

<sup>a</sup> Catalysts was 4%  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Fabrics were dried for 6 min. at  $70^\circ\text{C}$ . and cured for 3 min. at  $160^\circ\text{C}$ .

<sup>b</sup> Concentration of agent in the pad bath is 10% sodium *N,N*-bis(2-carbamoylethyl)-glycinate. Percentage for the methylol derivative is higher depending upon extent of reaction with formaldehyde.

TABLE II  
Properties of Treated Fabrics<sup>a</sup>

Agent: amino acid precursor <sup>b</sup>	Conditioned crease recovery angle (warp), degrees	Breaking strength (warp), lb.	Tearing strength (warp), g.
Ia: glycine	135	35.4	667
Ib: $\beta$ -alanine	128	31.2	693
Ic: $\alpha$ -alanine	135	29.4	440 <sup>c</sup>
Id: lysine	140	31.2	520
Ie: aspartic acid	121	35.0	490 <sup>c</sup>
Untreated fabric	83	45.4	1,083

<sup>a</sup> pH = 5-6 before catalyst addition. Catalyst was 4% MgCl<sub>2</sub>·6H<sub>2</sub>O. Fabrics were dried 6 min. at 70°C. and cured for 3 min. at 160°C.

<sup>b</sup> Agent concentration as in Table I—10% of the sodium salt of the particular amino acid-acrylamide adduct.

<sup>c</sup> Tearing strength (warp) of untreated fabric was 960 g.

suitable catalyst for the agent is magnesium chloride. Zinc nitrate hexahydrate (0.7%), and an alkanolamine hydrochloride (1.0%) are not as effective at the indicated concentrations. The strength losses reported in Tables I and II are, in general, usual for the degree of wrinkle resistance conferred by other nitrogenous finishing agents.

The moisture regains of the fabrics are only slightly altered by the treatment. Fabrics treated with the glycine agent have a moisture regain of 6.2%; with  $\beta$ -alanine, 7.2%. Regain of the untreated fabric is 6.7%.

Durability to acid hydrolysis<sup>4</sup> of fabric finished with the glycine agent was determined by treating the fabrics for 30 min. at 80°C. with a solution containing 1.5% phosphoric acid and 5% urea. The nitrogen content was reduced only 28%, and the conditioned crease recovery angle (warp) was decreased to 127° from 142°. These conditions are much more severe than a fabric would ordinarily encounter in service. Another sample of this fabric was treated with 1% sodium hydroxide for 30 min. at 80°C. with no loss of conditioned crease recovery angle.

These data indicate that durable crosslinks between cellulose chains can be obtained with I under relatively mild curing conditions, compared to those used with agent II. However, the susceptibility of the treated fabrics to chlorine damage also must be considered.

For the scorch test, which is used as the criterion for chlorine damage, the fabrics are chlorinated in alkaline sodium hypochlorite solution. The sodium salt (IV) and the *N*-chloro derivative of the crosslink are formed, the total reaction being dependent on the accessibility of the crosslinked fabric. In Table III are listed various treatments, the curing conditions, and the fabric strength retained in the scorch test. Fabrics finished with the  $\beta$ -alanine and aspartic acid agents resisted chlorine damage to the greatest extent. Fabric finished with the  $\beta$ -alanine agent retained essentially all of its breaking strength, even though the finish was applied under a mild cure. Fabric finished with the glycine agent also retained its breaking

TABLE III  
Scorch Test Results on Treated Fabrics\*

Agent: amino acid precursor <sup>b</sup>	pH of agent	Curing conditions		Strength retained in scorch test, % <sup>c</sup>
		Temp., °C.	Time, min.	
Ia: glycine	4.6-6.3	160	3	63-73
Ia: glycine	4.2	160	3	78
Ia: glycine	4.2	170	3	90
Ib: $\beta$ -alanine	5.0	160	3	95
Ic: $\alpha$ -alanine	6.0	160	3	71
Id: lysine	4.0-6.0	160	3	62-69
Ie: aspartic acid	4.0-6.0	160	3	78-84
Untreated fabric	—	—	—	90

\* Catalyst was 4%  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Fabrics dried for 6 min. at 70°C.

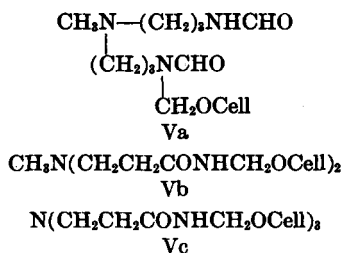
<sup>b</sup> Agent concentration as defined in Tables I and II.

<sup>c</sup> All treated fabrics discolored slightly in scorch test. Discoloration similar to that obtained with II or the standard triazone agents.

strength, but stronger curing conditions (higher acidity and higher cure temperatures) were necessary. Damage to fabric treated with the lysine and  $\alpha$ -alanine agents were generally moderate, though not generally acceptable.

As a class of finishing agents, I appears to offer little over II with respect to scorch test data, although the  $\beta$ -alanine agent does appear promising. It can be rationalized that this agent should be the most effective of the I agents from the standpoint of resistance to chlorine damage, since  $\beta$ -amino groups are more basic than similar  $\alpha$ -amino groups. However, other effects should be considered.

The potential acidity to be neutralized must be considered with reference to the available neutralization defined to be the ratio of basic amino groups to available amido NH groups. To illustrate this point, the theoretical structures of several cellulose ethers, containing only tertiary amino groups as "neutralizers," are shown (Va-Vc). The highest tertiary amine to



available NH group ratio, 1:1, is represented by Va (a bisformamide). Structures Vb and Vc represent the most efficient crosslinking (in a practical sense), and represent the lowest amine to available NH group ratio of 1:2 and 1:3, respectively. Conditions for producing the cellulose deriva-



tives Va-Vc raise the ratio of amine to available NH groups for Va, and lower the ratio for Vb and Vc. Thus, on the basis of available neutralization, scorch damage in the order Va < Vb < Vc would be predicted. The same order would be predicted if basicity of the tertiary amino group were considered. However, the actual order<sup>1,5</sup> is the opposite of the above. The actual order would be predictable if it were assumed that strength retention in the scorch test is related directly to the conditioned crease recovery (possibly a measure of accessibility). Therefore, it is concluded that a valid correlation between the relative basicity of amino groups and scorch damage from these data is not forthcoming.

For I the scorch damage-neutralization relationship is further complicated by the presence of an unknown quantity of a second neutralizing group—COONa. Presumably, some of the carboxyls will be lost by decarboxylation and ester formation with the *N*-methylol groups<sup>6</sup> during the drying and curing operation. Since I has little to offer over II with respect to the scorch test data, it appears that the carboxyl groups are useful during curing but are not completely available to assist during the scorch test procedures. It is of interest to note that the aspartic acid agent, which contains relatively more carboxyl groups than the other agents, produced the fabrics of lowest crease recovery yet produced one of the better finishes with regards to chlorine damage. These data indicate that the esterification reaction has, in this case, significantly reduced the cellulose crosslinking reaction, but that sufficient carboxyl groups remain to reduce strength losses in the scorch test.

The fabrics chlorinated for the scorch test procedure were found to have a relatively high content of available chlorine (0.5–1.0%). The lowest value was obtained from fabrics treated with the  $\beta$ -alanine agent; the highest value, with the  $\alpha$ -alanine agent.

In conclusion, new crosslinking agents of methylolamides containing amino acid groups, prepared by the Michael addition of the sodium salt of selected amino acids to acrylamide, have been shown to be highly reactive to cotton. Several of the acrylamide-amino acid adducts have been isolated and characterized. The new crosslinking agents produced cotton fabrics of high crease recovery under convenient and easily reproducible curing conditions. A new concept developed in this work has been shown to be workable through the successful utilization of five new crosslinking agents and, therefore, further work in this area should contribute additional improvements.

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### Résumé

L'éthérisation de la cellulose en milieu acide, par des méthylolamides contenant un groupe aminé tertiaire est souvent inhibée par la présence de ce groupe basique. Dans la fabrication de tissus lavables, une réaction incomplète donne un produit à basse résistance au frippage et/ou laisse le tissu traité en état de se détériorer à l'usage. Dans ce travail on postule que l'insertion d'un groupe carboxylique dans un agent de pontage de cette espèce neutralise le groupe basique par la formation d'un sel interne (zwitterion). Ces agents ont été préparés par méthylation des produits d'une addition de Michael du sel sodique de certains acides aminés à de l'acrylamide. Tous les composés synthétisés étaient nouveaux. Ceux qui ont été isolés et identifiés comprenaient le *N*-2-carbamoyléthylglycinate de sodium, le *N,N*-bis-(2-carbamoyléthyl)-glycinate de sodium, la *N,N*-bis(2-carbamoyléthyl)glycine, le *N,N*-bis(2-carbamoyléthyl)- $\alpha$ -alaninate de sodium, et la *N,N*-bis(2-carbamoyléthyl)- $\alpha$ -alanine. Des produits similaires d'addition à partir de la  $\beta$ -alanine, la lysine, et l'acide aspartique ont été préparés; pourtant les produits obtenus étaient des huiles ce qui rendait complexe leur isolement et leur identification. Pour le traitement des textiles point n'est besoin d'isoler les produits intermédiaires. Les agents de pontage *N*-méthyloliques dérivés de ces produits d'addition selon Michael, sont fort réactionnels vis-à-vis du coton; une addition importante dans des conditions relativement douces en est la preuve. Les tissus traités sont très résistants au frippage et possèdent d'autres propriétés désirées. Les résultats obtenus par l'usage de ces agents démontrent l'intérêt de poursuivre l'étude en se basant sur l'idée développée dans ce travail.

### Zusammenfassung

Die säurekatalysierte Verätherung von Zellulose durch Methylolamide mit einer tertiären Aminogruppe wird oft durch die Gegenwart dieser basischen Gruppe inhibiert. Bei der Erzeugung von "Wash-wear"-Gewebe führt eine unvollständige Reaktion im allgemeinen zu einem niedrigen Grad von Knitterfestigkeit und setzt die Gebrauchsbeständigkeit des behandelten Gewebes herab. In der vorliegenden Arbeit wird die Annahme gemacht, dass die Einführung einer Carboxylgruppe in ein solches Vernetzungsmittel die basische Gruppe durch Bildung eines inneren Salzes (Zwitterion) neutralisiert. Solche Stoffe wurden durch Methylierung des Produkts einer Michael-Addition des Natriumsalzes ausgewählter Aminosäure an Acrylamid dargestellt. Alle synthetisierten Verbindungen scheinen neu zu sein. Zu den isolierten und charakterisierten Verbindungen gehören Natrium-*N*-2-Carbamoyläthylglycinat, Natrium-*N,N*-bis(2-carbamoyläthyl)glycinat, *N,N*-Bis(2-carbamoyläthyl)glycin, Natrium-*N,N*-bis(2-carbamoyläthyl)- $\alpha$ -alaninat und *N,N*-Bis(2-carbamoyläthyl)- $\alpha$ -alanin. Ähnliche Addukte wurden aus  $\beta$ -Alanin, Lysin und Asparaginsäure dargestellt, die erhaltenen Addukte waren jedoch Öle, was ihre Isolierung und Charakterisierung erschwerte. Für die Textilbehandlung ist eine Isolierung der Zwischenstoffe nicht notwendig. Die von diesen Michael-Addukten abgeleiteten *N*-Methylolvernetzungsmittel sind, wie die hohe Additionsfähigkeit bei verhältnismässig milden Behandlungsbedingungen zeigt, gegen Baumwolle sehr reaktionsfähig. Die behandelten Gewebe besitzen eine hohe Knitterfestigkeit und andere erwünschte Eigenschaften. Die bei der Verwendung dieser Stoffe erhaltenen Ergebnisse zeigen, dass eine weitere Untersuchung auf der Grundlage des in der vorliegenden Mitteilung entwickelten Konzepts wünschenswert ist.

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