It is an object of this invention to produce a novel compound for the treatment of cellulosic textile materials. Another object is to produce a composition containing novel compounds suitable for the treatment of cellulosic textile materials.

Another object is to produce novel compounds which when employed in the treatment of cellulosic textile materials obtain a high order of resistance to creasing, to discoloration such as yellowing, and to strength loss due to chlorine retention and scorch.

Another object is a process of applying said novel compounds or compositions to a cellulosic substrate.

Another object is to produce a cellulosic substrate characterized by a high order of resistance to creasing, to discoloration, and to strength loss due to chlorine retention and scorch.

Other objects become apparent from the above and following disclosure.

The objects of this invention are obtained by synthesizing and applying the novel aminoplast compound of this invention, in a suitable solvent, to a cellulosic substrate in an amount sufficient to be effective, and thereafter curing the substrate preferably in the presence of any conventional acid-curing catalyst.

The novel aminoplast compounds of this invention are represented by the formula:

\[
\begin{align*}
R' & \text{N} - \text{O} - \text{N} - \text{CH}_2 - \text{O} - \text{R}^2 \\
R' & \text{C} - \text{O} - \text{R}^3 \\
O & \text{O} \\
O & \text{O} \\
R^2 & \text{R}' \\
R^3 & \text{R}'
\end{align*}
\]

where \( R^1 \) contains at least two carbon atoms and is selected from the group consisting of lower alkyl, allyl, aryl, aralkyl, cycloalkyl, and the substituted forms of each of the preceding members, the substituted forms typically including at least one substituent of the group consisting of halogen, hydroxy, and cyano, providing an alpha carbon atom of \( R^1 \) is not substituted by hydroxy, and in which \( R^2, R^3, R^4 \) and \( R^5 \) are each selected from the group consisting of hydrogen, lower alkyl, allyl, aryl, aralkyl, cycloalkyl, and the substituted forms of each of the preceding members, the substituents typically including at least one substituent of the group consisting of halogen, hydroxy, and cyano.

A novel cellulosic material is obtained by applying to a cellulosic substrate a solution of a compound selected from the group consisting of (1) the above-described novel aminoplast compound, and (2) an N-methyl-N'-substituted imidazolidinone of the formula:

\[
\begin{align*}
\text{CH}_2 - \text{N} - \text{O} - \text{N} - \text{CH}_2 - \text{O} - \text{R}^2 \\
R' & \text{O} - \text{C} - \text{R}^3 \\
O & \text{O} \\
O & \text{O} \\
R^2 & \text{R}' \\
R^3 & \text{R}'
\end{align*}
\]

in which \( R^7, R^8, R^9 \), and \( R^{10} \) are each selected from the group consisting of the members of \( R^2 \) as defined above. The preferred composition includes at least one of the above-described novel compounds of this invention.

The novel cellulosic material of this invention is characterized by a high order of resistance to creasing, to discoloration such as yellowing, and to strength loss due to chlorine retention and scorch. The crease resistance (i.e., wrinkle recovery properties) are about equivalent to compound such as 1-methyl-4,5-dihydroxy-2-imidazolidinone and 1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone, respectively; however, the novel cellulosic substrate of this invention resulting from the above treatment is superior in other characteristics such as the low formaldehyde lib-
eration during curing, low strength loss due to chlorine retention and scorch, and good non-yellowing properties. Additionally, the novel compound of this invention is characterized by the desirable property of being suitable for use with magnesium chloride as the curing catalyst whereby the employment of other conventional catalysts such as zinc nitrate may be avoided, thereby avoiding interference with brightener activity on white goods (cellulose).

Although the preferred solvent is water, any compatible conventional solvent may be employed, including for example, alcohols such as isopropyl alcohol, etc.

By the term “cellulosic substrate” it is meant fibres, filaments, yarns, fabrics, whether woven or non-woven, knitted, felted or otherwise formed, containing at least about 50% of cellulose fibres such as cotton, rayon, linen, hemp, jute or the like. The cellulose fibres may be present in combination with other natural or synthetic fibres, such as wool, silk, acetate, nylon, polyester fibres, acrylic fibres and the like. Preferably, the textile material is formed of woven cotton fabric.

The preferred compound of this invention is N-methylol-N'-beta-hydroxyethyl-imidazolidinone of the above formula.

Compounds of the above representative formula for the broad invention, may be formed by various conventional methods. For example, compounds where R1, R2, and R3 are each hydrogen substituents, can be made by reacting an N-substituted urea with an alpha, beta-dicarbonyl compound of the formula R3—(CO)(CO)—R2 and formaldehyde. By taking this reaction product and further reacting it with a lower aliphatic alcohol in the presence of an acid, a compound of the above basic formula of this invention may be formed in which R1, R3, and R4 are each lower alkyl substituents.

Suitable N-substituted ureas which typically may be used include 1-methylurea, 1-ethylurea, 1-n-propylurea, 1-isopropylurea, 1-n-butylurea, 1-tertiary butylurea, 1-allylurea, 1-phenylurea, etc. The alkyl and phenyl groups may be substituted by inert substituents such as alkyl, hydroxyl (not in the alpha-positions), halogen, cyano, etc., as exemplified by 1-(2-hydroxyethyl)urea, 1-phenylurea, 1-(p-chlorophenyl)urea, 1-(1-cyanoisopropyl)urea, etc.

The alpha, beta-dicarbonyl compounds which typically may be used include, for example, glyoxal, methylglyoxal, ethylglyoxal, propargylglyoxal, isobutylglyoxal, dimethylglyoxal, methylthethylglyoxal, ethylproparglyoxal, etc. of these, glyoxal is preferred.

Formaldehyde in any of its forms can be used, but formalin is preferred.

Reaction of the N-substituted urea can be made first with the alpha, beta-dicarbonyl compound and then with formaldehyde, or the reverse procedure can be used. Also, the reaction can be carried out in a single step with both the alpha, beta-dicarbonyl compound formaldehyde present. Approximately stoichiometric amounts of the three reactants are normally used. From neutral to alkaline reaction conditions are suitably employed. Suitable alkalies include sodium hydroxide, potassium hydroxide, etc. An aqueous medium is normally used, but an inert water-miscible solvent may also be present. Temperatures between 0° and 100° C., preferably between 15° and 70° C., may be employed.

Lower aliphatic alcohols which may be used in the alkylation step include, for example, methanol, ethanol, the propanols, the butanols, etc.

Suitable acids for use in the alkylation step include, for example, the inorganic acids such as hydrochloric, sulfuric, and phosphoric acids, and the organic acids, such as formic and oxalic acids.

In the alkylation step, at least a stoichiometric amount of alcohol must be used. A substantial excess is normally desirable. Sufficient acid is employed to provide a pH below 4. Reaction temperatures between 0° and 50° C., preferably between 15° and 30° C., are used.

These exemplary creaseproofing resins may be employed singly or in combination with each other and with other creaseproofing resins known to those skilled in the art, in accordance with the present invention.

The novel resinous composition of this invention containing the imidazolidinone may be applied to cellulosic textile materials by any of the conventional techniques such as immersion, padding, spraying and the like followed where necessary by squeezing, hydroextrusion or similar procedures, in order to affix the desired amount of solids on the fabric.

The method of application should be such that from about 1 to about 25% and in some instances higher amounts of the product of this invention based on the weight of the fabric are deposited thereon. Within certain limits, the amount of agent applied depends upon the particular type of fabric being treated. Thus, when treating fabric consisting of fibrous cellulosic materials, the concentration of the order of about 1% to 25%, and preferably from 3 to 10% solids, based on the dry weight of the fabric, normally should be employed.

The catalyst or accelerator employed is an acidic type catalyst and may be a free acid, acid salt, alkanolamine salt, metal salt and the like of the type well known to those in the textile finishing art. The concentration of catalyst employed may range from about 0.1 to about 25% or higher, based on the weight of the novel aminoplast solids, depending upon the particular catalyst type employed. Thus, for example, from between about 0.1% and about 10% of a free acid such as phosphoric, tartaric, oxalic or the like may be employed, while in the case of ammonium chloride amounts of from between 0.5 and about 10% are used. In the case of amine salts including alkanolamine salts such as diethanolamine, from about 1 to about 10% are most useful, while with respect to salts such as magnesium chloride amounts of from between about 5 and 25% have been successfully employed. In addition to magnesium chloride, optionally zinc nitrate, aluminum chloride and other conventional metal salts may alternatively be employed alone or in combination in amounts corresponding to between about 5 and 25% based on the weight of aminoplast solids.

In a preferred embodiment of the invention, an aqueous bath containing 7.5% of 1-methyl-3-methylol-4,5-dihydroxy-2-imidazolidinone and 0.9% of magnesium chloride is applied to 80 x 80 cotton percale by a padding procedure. The 0.9% of magnesium chloride in the bath is equivalent to 12.6% based on the weight of the imidazolidinone in the bath. An 80% wet pickup by the fabric is normally obtained, thereby depositing about 6% of the imidazolidinone on the fabric. The fabric is dried at a temperature of about 225° F. for one minute and is then heated at about 350° F. for about 1.5 minutes.

Following the application of the agent and curing catalyst to the textile fabric, the material is subject to drying and curing operations in order to affect wrinkle resistance and shrinkage control thereon. The drying and curing operation may be carried out in a single step or in separate steps. The temperatures at which the drying and curing operations are effected vary widely and are influenced to some extent by the type of catalyst employed. Normally, the range of temperature extends from about 180° F. to about 450° F. or even higher. Generally speaking, the time of the drying and curing steps is inversely proportional to the temperatures employed and of course is influenced by whether or not separate or combined drying and curing steps are employed. Generally, when drying and curing is carried out in a combined operation a time of from about one minute to about 10 minutes may be employed at temperatures from 450 to 250° F., respectively. When the fabric has been dried preliminarily to curing, curing times of the order of 5 minutes to about ¼ hour at a temperature of from
between 250 and 450° F., respectively, have been successfully employed.

The following examples are for purposes solely of illustrating the invention described herein, and do not limit the scope of this invention except insofar as the appended claims are limited. Unless otherwise stated the following examples are expressed in terms of parts and percentages by weight.

EXAMPLE I

1-methyl-3-methylol-4,5-dihydroxy-2-imidazolidinone

The pH of a solution of 70 parts (1.2 mole) of glyoxal in 104 parts of water is adjusted to 6.7 by the addition of sodium bicarbonate. To the solution there is added in the period of one hour 74 parts (2.0 mole) of 1-methylurea while maintaining a temperature of 45–50° C. After a 3-hour reaction period at 45–50° C., the pH of the solution is adjusted to slightly above 9 with sodium hydroxide, and 68.2 parts (1.0 mole) of 44% Formalin is added. Reaction is maintained at a temperature of 35–50° C. and at a pH of above 9 until the unreacted formaldehyde is 2.0% or below of the total composition. The resulting solution is adjusted to a solids content of 50% of the total composition by adding water and to a pH of about 5.2 by adding hydrochloric acid.

EXAMPLE II

1-(beta-hydroxyethyl)-3-methylol-4,5-dihydroxy-2-imidazolidinone

The procedure of Example I is followed, substituting 104 parts of 1-(beta-hydroxyethyl)urea for the 1-methylurea. The resulting solution is adjusted to a solids content of about 50% and a pH of 5.0.

EXAMPLE III

1-isopropyl-3-methylol-4,5-dihydroxy-2-imidazolidinone

To a solution of 5.0 parts (0.05 mole) of 1-isopropylurea in 10 parts of water there is added 4.0 parts (0.05 mole) of 37% Formalin and sufficient sodium hydroxide to provide a pH of 9–10. After about 1.5 hours, the precipitate is separated by filtration and washed with water. The product is 1-isopropyl-3-methylolurea.

To 10 parts of water and 4.0 parts of 68% aqueous glyoxal (0.1 mole), pH 8–9 by addition of sodium hydroxide, there is added the above 1-isopropyl-3-methylolurea. About 160 parts of ethanol are added and the reaction mixture is heated for about 15 hours. The resulting solution is evaporated at room temperature. A 50% aqueous solution of product is thus prepared.

EXAMPLE IV

1-n-butyl-3-methylol-4,5-dihydroxy-2-imidazolidinone

The procedure of Example III is followed, using 11.6 parts (0.1 mole) of 1-n-butylurea and 8.1 parts (0.1 mole) of 37% formalin.

EXAMPLE V

1-phenyl-3-methylol-4,5-dihydroxy-2-imidazolidinone

A solution of (a) 7.6 parts of 1-phenyl-3-methylolurea (0.06 mole), and (b) 4.3 parts of 80% aqueous glyoxal in a small amount (minimal) ethanol with pH adjusted to 8 by addition of sodium hydroxide is heated for several hours. The solution is diluted with water to a solids content of 50%.

EXAMPLE VI

1-allyl-3-methylol-4,5-dihydroxy-2-imidazolidinone

A solution of 100 parts (1.0 mole) of 1-allylurea in 100 parts of water and 68 parts of 44% formalin (1.0 mole of formaldehyde) is heated at pH 8.3 and 60° C. for 30 minutes. There is added a solution of 58 parts (1.0 mole) of glyoxal in 73 parts of water at pH 8.5. The mixture is heated at 60° C. for 30 minutes, and the resulting solution is found to contain 47% solids.

EXAMPLE VII

1-tertiary-butyl-3-methylol-4,5-dihydroxy-2-imidazolidinone.

A mixture of 45 parts (0.55 mole) of 37% formalin, 58 parts (0.5 mole) of tertiary-butylurea and 30 parts of water is heated at pH 9.5 and 70° C. for 10 hours. To the resulting solution, there is added a slightly alkaline solution of 29 parts (0.5 mole) of glyoxal in 150 parts of water, and the combined solutions are heated at 60° C. for 5 hours. The resulting solution contains about 46.5% solids.

EXAMPLE VIII

Three aqueous pad-baths (A, B, C) are prepared, each bath containing 7.5% of one of the methylol 2-imidazolidinones listed below, 0.84% (11.2% based on the weight of the amino-plast solids) of zinc nitrate, 0.07% (0.93% based on the weight of the amino-plast solids) of acetic acid, and 0.1% of the non-ionic surface active agent obtained by condensing 1 mole of nonylphenol with an average of 9.5 moles of ethylene oxide. The above percentages are based on the weight of the bath.

Pad-bath A.—1-methyl-3-methylol-4,5-dihydroxy-2-imidazolidinone (product of Example I).
3,488,701

Pad-bath B.—1,3-dimethylol-4,5-dihydroxy-2-imidazolidinone.

Pad-bath C.—1 - methylol - 4,5 - dihydroxy-2-imidazolidinone.

The three pad-baths are applied to swatches of 80 x 80 bleached cotton percale by standard padding procedure using 80% wet pickup. The swatches, containing 6% O.W.F. of the reactants, are dried at 225° F. of one minute and are then heated at 350° F. for 1.5 minutes.

The following tests are carried out on the treated swatches of fabric and on a untreated swatch of fabric.

Wrinkle recovery.—AATCC Tentative Test Method 66-1959T.

Tensile strength.—ASTM Standard Method D-39 using a Scott tensile strength tester.


Liberated Formaldehyde.—A sample of the dried, but not cured, fabric is heated at the curing temperature, and the amount of liberated formaldehyde is measured by vapor phase chromatography.

The washes under "Damage by retained chlorine" are carried out at about 212° F. as described in AATCC Tentative Test Method 96-1960F, Procedure IV.

The test results are shown in Table I. Fabrics A, B, and C correspond to Pad-baths A, B, and C, respectively.

TABLE I

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrinkle recovery, total, degrees</td>
<td>281</td>
<td>289</td>
<td>298</td>
</tr>
<tr>
<td>Damaged by retained chlorine, original tensile strength warp, lb</td>
<td>31</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>Tensile strength, chlorine and search warp: Initial, lb</td>
<td>34</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>After 4 washes, lb</td>
<td>35</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>Liberated Formaldehyde, grams/500 g. of fabric</td>
<td>0.178</td>
<td>0.205</td>
<td></td>
</tr>
</tbody>
</table>

Table I illustrates the superiority of A as compared to B and C, as to damage from chlorine retention.

EXAMPLE IX

Two aqueous pad-baths (A, B) are prepared, each bath containing 7.5% of one of the methylol-2-imidazolidinones listed below, 0.9% (12.0% based on the weight of the aminoplast solids) of magnesium chloride and 0.1% of the non-ionic surface active agent obtained by condensing 1 mol of nonylphenol with an average of 9.5 moles of ethylene oxide. The above percentages are based on the weight of the bath.

Pad-bath A.—1-methyl - 3 - methylol-4,5-dihydroxy-2-imidazolidinone (product of Example I).

Pad-bath B.—1-methylol-4,5-dihydroxy - 2 - imidazolidinone.

The two pad-baths are applied to swatches of 80 x 80 bleached cotton percale by standard padding procedure using 80% wet pickup. The swatches, containing 60% O.W.F. of the reactants, are dried at 225° F. for 1 minute and the fabrics are then heated at 350° F. for 1.5 minutes.

The results of tests carried out as described in Example VIII are shown in Table II. Fabrics A and B correspond to Pad-baths A and B, respectively.

Table II illustrates the superiority of A as compared to B, as to damage from chlorine retention.

EXAMPLE X

Two par-baths (A, B) are prepared, each bath containing 7.5% of one of the methylol-2-imidazolidinones listed below, 0.84% (11.2% based on the weight of the aminoplast solids) of zinc nitrate, 0.07% (0.93% based on the weight of the aminoplast solids) of acetic acid, and 0.1% of the non-ionic surface active agent obtained by condensing 1 mol of nonylphenol with an average of 9.5 moles of ethylene oxide. The above percentage are based on the weight of the bath.

Pad-bath A.—1-(2-hydroxyethyl) - 3 - methylol-4,5-dihydroxy-2-imidazolidinone (product of Example II).

Table III illustrates the superiority of A as compared to B, as to damage from chlorine retention.

TABLE III

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Untreated (control)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrinkle recovery, total, degrees</td>
<td>293</td>
</tr>
<tr>
<td>Damage by retained chlorine</td>
<td>41</td>
</tr>
<tr>
<td>Original tensile strength warp, lb</td>
<td>30</td>
</tr>
<tr>
<td>Tensile strength, chlorine and search warp: Initial, lb</td>
<td>37</td>
</tr>
<tr>
<td>After 5 washes, lb</td>
<td>37</td>
</tr>
<tr>
<td>Yellowness Index</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The test results are shown in Table III. Fabrics A and B correspond to Pad-baths A and B, respectively.

Table III illustrates the superiority of A as compared to B, as to damage from chlorine retention, and discoloration.
EXAMPLE XI
An aqueous pad-bath is prepared containing 7.5% of 1-(2-hydroxyethyl) - 3 - methylol-4,5-dihydroxy-2-imidazolidione (product of Example II), 0.9% (12.0% based on the aminoplast solids) of magnesium chloride and 0.1% of the non-ionic surface active agent obtained by condensing 1 mole of nonylphenol with an average of 9.5 moles of ethylene oxide. The above percentages are based on the weight of the bath.

The pad-bath is applied to a swatch of 80 x 80 bleached cotton percale by standard padding procedure using 80% wet pickup. The swatches, containing 6% O.W.F. of the reactants, are dried at 225° F. for 1 minute and then heated at 350° F. for 1.5 minutes.

Measurements for wrinkle recovery and damage caused by retained chlorine are measured by the procedure of Example VIII. The yellowness index is calculated by the procedure described in Example X.

The test results are shown in Table IV.

<table>
<thead>
<tr>
<th>Tab IV</th>
<th>Fabric</th>
<th>Treated</th>
<th>Untreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Wrinkle Recovery, total, lb</td>
<td>272</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>II. Damage by retained chlorine</td>
<td>34</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>A. Original tensile strength-warp, lb</td>
<td>36</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>B. Tensile strength, chlorine and search warp</td>
<td>38</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>1. Initial, lb</td>
<td>2.5</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>III. Yellowness Index</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table IV results, as compared to Table III results, illustrate the improved results obtained by the use of magnesium chloride instead of a catalyst such as zinc nitrate. Particularly note "less" yellowing with magnesium chloride, this being opposite of the conventional effect of magnesium chloride.

EXAMPLE XII
Three pad-baths (A, B, C) are prepared using water or dimethylformamide as the medium. Each pad-bath contains 7.6% of a 3-methylol-4,5-dihydroxy-2-imidazolidinone and 0.9% (12.0% based on the aminoplast solids) of magnesium chloride.

Pad-bath A.—1-isopropyl-3-methylol-4,5-dihydroxy-2-imidazolidinone (product of Example III) and water.

Pad-bath B.—1-allyl-3-methylol-4,5-dihydroxy-2-imidazolidinone (product of Example VI) and water.

Pad-bath C.—1-tertiary-butyl - 3 - methylol-4,5-dihydroxy-2-imidazolidinone (product of Example VII) and dimethylformamide.

The pad-baths are applied to swatches of 80 x 80 bleached cotton percale by standard padding procedure using 80% wet pickups. The swatches, containing 6% O.W.F. of the reactants, are dried at 225° F. for 2 minutes and the fabrics are then heated at 350° F. for 1.5 minutes.

The measurements for wrinkle recovery are carried out as described in Example VIII.

The test results are shown in Table V. Fabrics A, B, and C correspond to Pad-baths A, B, and C, respectively.

<table>
<thead>
<tr>
<th>Tab V</th>
<th>Fabric</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Untreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrinkle recovery, total, degrees</td>
<td>208</td>
<td>269</td>
<td>284</td>
<td>182-190</td>
<td></td>
</tr>
</tbody>
</table>

Table V illustrates the continued good wrinkle recovery obtained by employment of other miscellaneous novel compounds of this invention.

We claim:

1. A composition consisting essentially of an aqueous solution of at least 1% solids content of an aminoplast compound of the formula:

\[
R_1^1-N^1-C^1-N^2=O^2-R_2^2
\]

where each R₁ is hydroxy lower alkyl of at least two carbon atoms, provided that an alpha carbon of R₁ is not substituted by hydroxy, and in which R₃ and R₄ are each selected from the group consisting of hydrogen and lower alkyl, and R₅ and R₆ are hydrogen; and magnesium chloride in an amount sufficient to be effective as a curing agent.

2. A process of applying to a cellulosic substrate a composition according to claim 1, and thereafter curing said substrate, said composition being in an amount and said curing being at a temperature, respectively, sufficiently high to impart a high order of resistance to creasing, to discoloration, and to strength loss.

3. A cellulose substrate in combination with a composition according to claim 1, in a cured state, and said combination being characterized by a high order of resistance to creasing, to discoloration, and to strength loss.

4. A composition according to claim 1 in which said aminoplast compound is selected from the group consisting of (1) a compound according to claim 1, and (2) an N-methyl-N'-substituted-imidazolidinone of the formula:

\[
\text{CH}_3-N^1-O=O-N^2=O-R_3^3
\]

in which R₇, R₈, R₉, R₁₀ and R₁¹ are each selected from the members of R₂.

5. A process of applying to a cellulosic substrate a composition according to claim 4 and thereafter curing said substrate, said composition being applied in an amount and said curing being at an elevated temperature, respectively, sufficiently to impart a high order of resistance to creasing, to discoloration, and to strength loss.

6. A cellulose substrate in combination with a composition according to claim 4, in a cured state, and said combination being characterized by a high order of resistance to creasing, to yellowing, and to strength loss.
impart from about 3% to about 10% solids on the dry weight of the fabric, and in which said composition in said aqueous medium includes magnesium chloride at a concentration of from about 5% to about 25% based on the weight of said compound, said process including drying the treated substrate and thereafter curing, said drying and curing being at temperatures respectively sufficient to dry and to cure, said curing temperature ranging up to about 450° F. for at least about one-fourth of one minute.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,488,701  Dated January 6, 1970

Inventor(s) William Frank Herbes and John Peter Dundon

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 5, line 23, delete "2.0" and insert -- 1.0 --.

Col. 7, line 59, delete "60%" and insert -- 6% --.
Col. 9, line 46, delete "2-" at beginning of line.
Col. 10, Claim 4, in both formulas, delete "R^1" and insert -- R^7 --.

Signed and sealed this 6th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCALK
Commissioner of Patents