ABSTRACT

A process for decreasing the flammability of textiles comprising a cellulosic fiber component and preferably a nitrogen-free thermoplastic fiber component which comprises treating the cellulosic fiber component with a condensate or a physical admixture of an allylurea and a phosphine/formaldehyde condensate such as a tetrakis (hydroxymethyl)-phosphonium salt to introduce allyl groups into the cellulosic component, and subsequently halogenating, preferably brominating, the allyl groups thus introduced.

15 Claims, No Drawings
3,765,837

FLAME RETARDANT FINISH FOR POLYESTER/COTTON BLENDS

The present invention pertains to a process for decreasing the flammability of textile materials, and more particularly of textiles comprising cellulosic fibers preferentially in conjunction with nitrogen-free thermoplastic fibers such as polyesters or polyolefins.

The problem of textile flammability has been of interest for many years, and many approaches have been proposed to the solution of this problem. Many processes are known for decreasing the flammability of textile materials, and some among these have attained commercial importance. However, known processes are generally effective only for those textile materials or fabrics made entirely from one type of fiber—in most instances cellulose. For example, treatment with organophosphorus compounds is known to decrease the flammability of cellulose textiles, and insolubilization of appropriate phosphorus-containing reagents in or on cellulose textiles can impart flame-retardant properties that withstand a great number of launderings, dry cleanings, or other cleaning procedures.

In view of the recent commercial importance attained by fabrics made from blend yarns, and particularly of polyester/cellulose fabrics, consideration has also been given to processes intended to decrease their flammability. The problem of imparting flame-retardant properties to textile materials containing more than one fiber, and more specifically polyester and cellulose fibers (in blends or mixtures) has proved to be of enormous complexity. When flame-retardant chemicals known to be effective on cellulose fibers are added to such fabrics, the flammability of the treated material is generally not decreased. In fact, the treated fabric in some instances burns more readily than the untreated one because, after ignition, molten polyester continues to burn in and around the cellulose fibers (even though these have been rendered non-combustible by the flame-retardant treatment) instead of dripping away from the flame, and the entire structure is consumed. Several investigators have documented these observations (e.g., W. Kruse and K. Filipp, Melland Textilber, 49, 203 (1968); and W. Kruse, Melland Textilber, 50, 460 (1969)) and various interpretations have been proposed for the observed phenomena. It has been postulated that flame-retardant polyester/cellulose can be obtained only when appropriate flame-retardant chemicals are present in or on both fibers (e.g., G. C. Tesoro & C. H. Meiser, Tex. Res. J., 40, 430 (1970); and P. Linden, S. B. Sello, H. S. Skovronek, Proceedings Annual Meeting I.C.F.F., New York, Dec. 1970) and that it would not be possible to obtain flame-retardant polyester/cellulose fabrics of adequate performance by modifying the cellulose with flame-retardant chemicals while leaving the polyester component essentially unchanged. Attempts to treat fabrics with chemicals or combinations of chemicals that could be insolubilized in or on both fibers have led to unsatisfactory results, primarily because the chemical inertness of polyester necessitates the use of high concentrations of reagents in chemical systems which form polymeric coatings on fiber surfaces, which coatings inevitably impair the flexibility, breathability, and hand of the treated textiles. Accordingly, there is a great need in the industry for processes to decrease the flammability of polyester/cellulose fabrics, and more generally of fabrics made from cellulosic fiber in conjunction with non-nitrogenous thermoplastic fiber.

Copending application Ser. No. 140,256, filed May 4, 1971 by Giuliana C. Tesoro, and now abandoned, describes the unexpected discovery that it is possible to impart flame-retardant properties to polyester/cellulose fabrics by processes modifying the cellulose fiber component while leaving the polyester component essentially unchanged. The modification of the cellulose component is carried out by (a) treatment with a reagent containing unsaturation, and (b), in a subsequent step, halogenation (preferably bromination) of the unsaturated groups introduced. The reagent containing unsaturation may also contain, in the same molecule, elements known to have flame retardant effectiveness in cellulose polymers such as phosphorus (phosphine, phosphonate, phosphonium, etc.) and, optionally, nitrogen (amide, amine, etc.). On the other hand, the incorporation of such “flame-retarding elements” can be carried out as a subsequent step (c). When halogen is introduced into the cellulose component as shown in the process of said earlier application, the amount of additional flame-retarding compound (e.g. organophosphorus) needed is lower, and its effect on fabric properties is reduced. The overall result is to obtain a polyester/cellulose textile in which the cellulose contains compounds of halogen (bromine), phosphorus, and (optionally) nitrogen in such amounts as to cause the flammability of the textile to be significantly decreased without substantial impairment of other properties. The extent of decrease in flammability will depend on the amounts of flame-retardant chemicals present in the cellulose, on the ratios of flame-retarding elements introduced, and also on the percentage of cellulose present in the polyester/cellulose substrate and available for modification. In many situations, it is possible to obtain self-extinguishing polyester/cellulose fabrics—or fabrics which pass a severe flammability test (Vertical Test — AATCC—34—1969) with amounts of insolubilized flame-retardants comparable to the amounts needed to attain self-extinguishing behavior on 100 percent cellulose fabrics. The object of the present invention is thus to provide novel processes by which the flammability of both 100 percent cellulose and blended cellulose textiles, such as polyester/cellulose and polyolefin/cellulose textiles, can be decreased, the effect being durable to laundering, dry cleaning, and other conditions of use.

It is a further object of the present invention to decrease the flammability of blended cellulose and particularly of polyester/cellulose textiles by introducing the flame-retardant chemicals solely or primarily into the cellulose component, leaving the polyester or other fiber essentially unchanged. The objects of the invention can be attained by treating 100 percent cellulose, blended cellulose or particularly polyester/cellulose fabric with an allylurea, e.g. allyl-, diallyl-, and/or triallylureas combined either chemically or in physical admixture with a phosphine-aromaticdehyde condensate, optimally a tetraakis(hydroxy-methyl)phosphonium chloride or phosphate, optionally further fixing the reagents by curing with ammonia, and thereafter brominating the product at the allyl groups.

The processes of the present invention can be used to obtain flame-retardant textiles suitable for many end uses (apparel, furnishings, industrial, military, etc.).
The following types of substrates are among those suitable for practicing the process of the invention:

a. Woven, knitted, or nonwoven fabrics made from 100 percent cotton or from blended yarns, particularly of polyester/cotton, in which the cotton content is at least 20 percent;

b. Fabrics made from blended yarns containing polyester and regenerated cellulose (rayon, modified rayon) in which the regenerated cellulose content is at least 20 percent;

c. Woven fabrics made from 100 percent cellulose yarns (cotton or regenerated cellulose) in the warp or filling direction, and 100 percent polyester, or polyester/cellulose blend yarns in the other direction;

d. Knitted fabrics made from plied yarns in which cellulose yarns are combined with polyester filaments.

Generally speaking, the cellulose content of the substrate should be at least 20 percent and preferably 35 percent or more in order for the process to be effective.

The allylureas suitable for carrying out the process of the invention comprise compounds having the formula

$$CH_2=CHCH\ddot{N}CH=CHCONH_2$$

where X and X' may be hydrogen or an allyl, or lower alkyl, e.g. methyl, or ethyl radical, or where the two groups taken together may constitute an ethylene or substituted ethylene group

$$CH\ddot{N}CH=CHCONH_2$$

where R and R' are hydrogen, or lower alkyl, e.g. methyl or ethyl; i.e.,

$$CH\ddot{N}CH=CHCONH_2$$

The preferred urea is allylurea itself,

$$CH\ddot{N}CH=CHCONH_2$$

Other suitable ureas include N,N-diallylurea, N,N'-diallyleurea, triallylurea, N-allyl-N-methylurea, N-allyl-N'-methyleneurea, N-allyl-N'-ethyleurea, and N-allylethyleneurea, and the like.

The phosphine/formaldehyde condensates useful in the process of this invention comprise tetrais(hydroxymethyl)-phosphonium tetrais(hydroxymethyl)-salts such as the chloride, bromide, iodide, sulfate, fluoride, acetate, and diacetyl phosphate, or mixtures thereof; tris(hydroxymethyl)phosphine; tris(hydroxymethyl)phosphine oxide; and other like derivatives. The preferred condensate is tetrais(hydroxymethyl)phosphonium chloride, referred to hereinafter as THPC.

The allylureas and the phosphine/formaldehyde condensates may be reacted with cellulose fibers either in the form of mixtures with each other or as essentially 1:1 precondensates. A preferred combination is the 1:1 precondensate of allylurea made with an equimolar or a slightly greater than equimolar proportion of THPC, the structure of which condensate is believed to be predominantly

$$CH_2=CHCH\ddot{N}CH=CHCONH_2$$

Precondensates of this general type, but derived from urea and lacking the essential allyl groups of our invention, are described in U. S. Pat. No. 2,983,623, as is also the process for fixing the precondensate to cotton with an ammonia cure, an optional additional step in the process of our invention.

The methods and conditions employed for obtaining the flame-retardant textiles of the present invention depend, in part, on the substrate and chemical system employed, and on the level of performance required. Cellulose/polyester fabrics, believed to be the substrates most benefitted by the invention, may be treated with a variety of allylureas and phosphate/formaldehyde condensates, these latter being either physically mixed or chemically precondensed, by padding from aqueous solutions, drying, curing in the presence or absence of ammonia, and optionally washing to remove constituents not firmly fixed to the substrate fabric. Drying and curing conditions can be widely varied depending on the textile and treating agents analyzed. However, drying conditions of 90°-100°C for 1-10 minutes and curing at 150°-275°C for 2-10 minutes can be given as illustrative.

Although either or both may preferably be used under certain conditions, it is not believed that the ammonia cure or the use of a precondensate is always essential. One fact which has emerged is that unless a precondensate is formed, the bath life of the mixture of an allylurea and a phosphine/formaldehyde condensate may be rather short. The course of the invention also seems to be adversely affected by excessively acidic conditions in certain formulations, precipitation from the treating solutions for instance having been observed at times if the pH was lower than about 5. Addition of alkali to near neutrality overcomes this tendency when it is observed. Excessively alkaline conditions are also generally to be avoided because they are known to cause decomposition of THPC and related salts. One skilled in the art will be able to adapt these variables of reaction conditions to specific combinations by simple experimentation within the scope of the invention.

Catalysts are not believed necessary in the invention, but neither is their use meant to be excluded from the scope.

The reagents added to cellulose during the padding/cure phase serve as a means for durable incorporation of nitrogen and phosphorus into the fabric, meanwhile providing a site for later addition of bromine to the carbon-carbon double bond of the allyl group. Using the precondensate of THPC and allylurea (Formula IV) as an example, one may postulate initial attachment through an ether-like linkage to cellulose as follows:

$$[CH_2=CHCH\ddot{N}CH=CHCONH_2]Cl^-$$

$$CH_2=CH=CHCONH_2$$
The pendant allyl groups in the cellulose ether are then halogenated by treatment with a solution of elemental halogen under mild conditions. Bromine is the preferred halogen for a number of reasons: it is an effective flame-retardant element, it reacts rapidly with the unsaturated groups, and it does not attack, discolor or impair the cellulose component in the substrate. The bromine may be dissolved in water or in an inert organic solvent. The concentration of bromine, the time and temperature of the bromination reaction, and the medium employed are not critical and may be determined in each case by appropriate experiments.

A surprising feature of this invention is the fact that, as shown in the examples, it provides products which pass the strenuous vertical flammability test, AATCC 34-1969, at comparatively low levels of P, N, and Br content.

One of the major advantages of the process of the invention is that covalently-bound bromine is introduced readily and uniformly throughout the modified cellulose fibers. This cannot be done by employing brominated reagents for the cellulose modification, since limitations in the solubility and penetration of such brominated reagents generally result in the reagent being concentrated on fiber surfaces, with consequent unsatisfactory efficiency, and poor durability of the treatment in laundering, in cleaning, and in use.

The evaluation of the flammability of treated textiles is conveniently and accurately carried out by the "Limiting Oxygen Index (LOI) Method" as described in several recent publications (e.g., Isaac - J. Fire & Flammability, I, 36-47 (1970)). The higher the LOI, the lower the flammability. LOI values above .240-.260 are believed to reflect self-extinguishing behavior in vertical flammability tests such as AATCC 34-1969 and are thus indicative of satisfactory flame-retardant properties in use.

Except when otherwise indicated, test fabrics were 100 percent cotton sheeting, 3.75 oz/yd², 95 x 84 count, and 50/50 polyester/cotton sheeting, 3.68 oz/yd², 96 x 88 count. Samples for treatment were usually about 17 x 20 inches.

The durability of flame-retardant properties to laundering or other cleaning procedure is easily evaluated by exposing the treated textiles to appropriate washing or cleaning procedures and checking the LOI after exposure. Analytical determination of halogen and of other elements introduced in the cellulose modification can also be used to establish that the desired flame-retardant elements are firmly bound to the cellulose molecules, and retained after exposure to laundering and other conditions.

The following examples are illustrative of the invention described:

**EXAMPLE 1**
N,N'-diallylurea was prepared for use in Example 5. A solution of 49.4 g (0.51 mole) of diallylamine, 70 g (0.51 mole) of phenyl carbamate, and 500 ml of benzene was refluxed for 20 hours. The solution was stripped on a rotary evaporator, and the residue was taken up again in benzene. The solution was washed three times with 100-ml portions of 15 percent NaOH, dried overnight over sodium sulfate, filtered, and again stripped on the evaporator, leaving 41 g, 56 percent yield, of N,N'-diallylurea, melting 63°-65°C.

**Analysis:**
Calc'd: C 60.00, H 8.57, N 20.00 percent
Found: C 60.04, H 8.65, N 20.81 percent
The NMR spectrum supported the desired structure, and no impurity bands were observed.

**EXAMPLE 2**
N,N'-diallylurea was prepared for use in Example 5. To a solution of 171 g (3.0 moles) of allylamine, 303.6 g (3.0 moles) of triethylamine, and one liter of benzene in a three-liter flask was added, dropwise and below 30°C, 234.9 g (1.5 moles) of phenyl chloroformate. After 30 minutes more of stirring, the precipitated amine hydrochloride was filtered off, and the filtrate was refluxed for 24 hours. When its infrared spectrum indicated that reaction was incomplete, the mixture was treated with another 57 g (1 mole) of allylamine and refluxed 17 hours longer, at which point the spectrum indicated complete reaction. The solution was washed three times with 400-ml portions of 15 percent sodium hydroxide, dried over sodium sulfate, filtered, and stripped on the rotary evaporator. The residue weighed 196 g, 93.3 percent yield, melting 93°-94°C.

**Analysis:**
Calc'd: C 60.00, H 8.57, N 20.00 percent
Found: C 59.62, H 8.46, N 20.34 percent

**EXAMPLE 3**
An aqueous 80 percent solution of THPC (223 g, 0.94 mole) was stirred into 75 g, 0.75 mole, of allylurea (Aldrich Chemical Company) in 180 ml of water, and the mixture was refluxed for one hour and cooled. NMR analysis indicated that conversion of the allylurea to its 1:1 THPC precondensate had been essentially quantitative, the excess THPC remaining unreacted.

**EXAMPLE 4**
Refluxing, as in Example 3, a solution of 74.5 g of 80% THPC, 35 g of the N,N'-diallylurea of Example 1, and 60 g of water yielded a solution whose NMR analysis indicated substantially quantitative conversion to the 1:1 THPC-N,N'-diallylurea precondensate.

**EXAMPLE 5**
Refluxing, as in Example 3, a solution of 298 g of 80% THPC, 137 g of the N,N'-diallylurea of Example 2, and 240 g of water yielded a solution whose NMR analysis indicated only about a 55 percent conversion to the desired 1:1 THPC-N,N'-diallylurea precondensate, the remainder of the solution appearing to be unreacted starting materials.

**EXAMPLE 6**
A 200-g portion of the allylurea-THPC precondensate of Example 3 was diluted with 134 ml of water and the solution was used as a pad bath for samples of 100 percent cotton and 50/50 polyester/cotton sheeting. The samples, 16.5 x 20 inches, initial weight determined after overnight conditioning at 65 percent relative humidity, were padded twice at 30 psi roll pressure to wet pickups of about 70 percent, dried four minutes at 93°C, wrapped on stainless steel cylinders and exposed to gaseous ammonia for 10 minutes, and then soaked in 10 percent aqueous ammonia for 10 minutes. After this the samples were washed in one liter of water containing 5 g of soap and 2 g of 30% H₂O₂, first at 40°-50°C for 10 minutes, then in fresh peroxide and soap solution at 90°-95°C. For 10 minutes longer, rinsed in hot water, dried two minutes at 120°C, and finally conditioned overnight at 65% R.H. before final weighing, analysis, and testing. Portions of each sample were padded with water, soaked for 30 minutes in 350 g of chloroform containing a large excess of bromine, rinsed in cold water, washed for 12 minutes with water containing 0.01% detergent in a home washing machine set on "warm," tumble-dried, and conditioned
3,765,837

TABLE 2

<table>
<thead>
<tr>
<th>Treatment of 100% Cotton and 50/50 Polyester/Cotton Sheeting with THPC-N,N-diallylurea Precondensate, Ammonia, and Bromine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before bromination</td>
</tr>
<tr>
<td>Percent add-on</td>
</tr>
<tr>
<td>100% cotton</td>
</tr>
<tr>
<td>Do</td>
</tr>
<tr>
<td>50/50 polyester/cotton</td>
</tr>
</tbody>
</table>

overnight as before. Results of treatment and testing of these samples are given in Table 1.

TABLE 1

<table>
<thead>
<tr>
<th>Treatment of 100% Cotton and 50/50 Polyester/Cotton Sheeting with THPC-allylurea Precondensate, Ammonia, and Bromine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before bromination</td>
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<tr>
<td>50/50 polyester/cotton</td>
</tr>
</tbody>
</table>

Despite the analytical evidence, in Example 5, that the precondensation may not have proceeded to completion, bromination of the fabrics treated with the reaction mixture produced a marked increase in flame-retardance. Also, both here and in Example 7 it is believed remarkable that the samples passed the vertical test at such low levels of P, N, and Br.

EXAMPLE 9

In an experiment similar to but differing in both composition and absence of ammonia cure from that of Example 6, a pad bath was prepared containing 25% THPC (solids), 13 percent allylurea, and 5% Na_2HPO_4, adjusted to pH 6. Samples of 50/50 polyester/cotton sheeting were padded, dried, cured, treated with peroxide, laundered, brominated, and again washed, all as in the earlier example. All but portions of the samples for analysis were then laundered 10 more times. The results are shown in Table 4.

TABLE 4

<table>
<thead>
<tr>
<th>Laundering Tests on 50/50 Polyester/Cotton Treated with Buffered THPC and Allylurea, Followed by Oxidation and Bromination</th>
</tr>
</thead>
<tbody>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>18.8</td>
</tr>
<tr>
<td>19.6</td>
</tr>
</tbody>
</table>
These results show unusually high LOI measurements after bromination, virtually complete retention of phosphorus and nitrogen throughout the operations, and an unusual capacity for passing the vertical test after laundering. The fall of the LOI after 10 launderings still leaves it at a relatively high level, this fall being apparently the result of a partial loss of bromine.

**EXAMPLE 10**

In this example the ammonia cure was omitted, the allylurea and the phosphine/formaldehyde condensate were not precondensed, and a condensate known commercially as "Pyroset TPK," a product of the American Cyanamid Company, was substituted for THPC. The exact formula for Pyroset TPK has not been published, but analysis indicates it to contain tetrakis(hydroxymethyl)phosphonium cations and PO₄⁻³, HPO₄⁻², and/or H₂PO₄⁻ anions. The product is sold as an aqueous solution containing approximately 70 percent solids.

A pad bath was made up from 30 parts of Pyroset TPK, 15 parts of allylurea, 0.1 part of nonylphenoxypolyethyleneoxyethanol detergent, and 55 parts of water. The solution was divided into two lots of 17 X 20-inch pieces of 50/50 polyester/cotton and 100 percent cotton sheeting at 30 psi roll pressure, dried four minutes at 93°C, cured three minutes at 175°C, and laundered in the washing machine as in Example 6. Half of the samples were then divided into two with 10 percent H₂O₂ at 30 psi and again laundered. The samples, after separation of appropriate segments for analysis, were then padded with water, brominated in chloroform, and laundered, as in Example 6. Analysis and testing of the samples gave the results shown in Table 5.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Treatment of 100% Cotton and 50/50 Polyester/Cotton Sheet with Pyroset TPK and Allylurea, Followed by Bromination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric</td>
<td>Before bromination</td>
</tr>
<tr>
<td></td>
<td>Percent</td>
</tr>
<tr>
<td>100% cotton</td>
<td></td>
</tr>
<tr>
<td>Unoxidized</td>
<td>17.0</td>
</tr>
<tr>
<td>Oxidized</td>
<td>17.0</td>
</tr>
<tr>
<td>50/50 polyester/cotton</td>
<td></td>
</tr>
<tr>
<td>Unoxidized</td>
<td>14.6</td>
</tr>
<tr>
<td>Oxidized</td>
<td>14.6</td>
</tr>
</tbody>
</table>

The results, although rather scattered, show marked increases in flame-retardance as the result of addition of Pyroset TPK, allylurea, and bromine. It will be recognized that various other modifications may be made in the invention in addition to those described above. Hence, the scope of the invention is limited only by the following claims wherein:

What is claimed is:

1. A process for decreasing the flammability of a textile comprising cellulosic fiber which comprises treating the textile with an allylurea of the formula

$$\text{CH}_2=\text{C-CH}_2\text{O H}$$

where X and X' are hydrogen, an allyl or lower alkyl or, taken together, constitute the group

$$\text{R}\text{R'}$$

where R and R' are hydrogen or lower alkyl and a phosphine/formaldehyde condensate selected from the group consisting of tetrakis(hydroxymethyl)-phosphonium hydroxide, a tetrakis(hydroxy methyl)-phosphonium salt, tris(hydroxymethyl)phosphine and tris(hydroxymethyl)phosphine oxide whereby allyl groups are introduced into said cellulosic fibers, and subsequently halogenating the allyl groups thus introduced, said treatment involving the use of a solution which contains a member of the group consisting of (a) a condensate produced by reacting the allyl urea with an equimolar or slightly greater than equimolar proportion of the phosphorus/formaldehyde condensate and (b) a solution containing a physical admixture of the allyl urea and the phosphine/formaldehyde condensate wherein the respective materials are present in equimolar proportion or the phosphine/formaldehyde condensate is present in slightly greater than equimolar proportion.

2. The process of claim 1 wherein the allylurea and phosphine/formaldehyde condensate are used together in physical admixture.

3. The process of claim 1 wherein the allylurea and phosphine/formaldehyde condensate are used together in precondensate form.

4. The process of claim 1 wherein the allylurea is allylurea itself.

5. The process of claim 1 wherein the allylurea is N,N-diallylurea, N,N'-diallylurea, triallylurea, N-allyl-N-methylurea, N-allyl-N'-methylurea, N-allyl-N'-ethylurea or N-allylethyleneurea.

6. The process of claim 1 wherein the phosphine/formaldehyde condensate is tetrakis(hydroxymethyl)-phosphonium chloride.

7. The process of claim 1 wherein the textile is treated with a 1:1 precondensate of allylurea and tetrakis(hydroxymethyl)phosphonium chloride.

8. The process of claim 1 wherein the textile comprises a cellulosic/polyester blend.

9. The process of claim 1 wherein the textile comprises a blend of cellulosic fiber and a different nitrogen-free thermoplastic fiber.

10. The process of claim 1 wherein the halogenating is brominating.

11. The process of claim 1 wherein the textile is treated with the allylurea and phosphine/formaldehyde condensate by padding with an aqueous solution containing the allylurea and the condensate, followed by drying and curing.

12. The process of claim 11 wherein curing is carried out in the presence of ammonia.

13. The process of claim 11 wherein the textile is washed after curing.

14. The process of claim 11 wherein the aqueous solution has a pH of at least about 5.

15. The textile obtained by the process of claim 1.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) Ben F. Aycock and Giuliana C. Tesoro

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

1) Column 3, lines 56-58 should read .......comprise tetrakis(hydroxymethyl)phosphonium hydroxide; tetrakis(hydroxymethyl)phosphonium salts such as......

2) Column 8, in the Table 3 heading, insert a prime mark in the word --THPC-N,N'-diallylurea--.

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. J. MARSHALL DAIN
Attesting Officer Commissioner of Patents
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