Durable-Press Cotton with Improved Retentions of Strength and Abrasion Resistance via N-Methylolpolyethyleneurea D.P. 2

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Synopsis

Diethylenetriamine was reacted with urea to form a noncyclic analog of ethyleneurea (one of the lowest members of a series of linear polyethyleneureas) which was characterized spectroscopically. Its reaction with formaldehyde to yield the N-methylol derivative (N-methylolpolyethyleneurea, degree of polymerization 2; NMP-2) was investigated. The polymerization characteristics of the NMP-2 were studied and compared with those of N-methylol derivatives of cyclic ethyleneurea (related structurally) and melamine (related polyfunctionally). The NMP-2 was applied to cotton fabrics by a pad–dry–cure process with $Al_2(OH)_5Cl\cdot2H_2O$ as the polymerization crosslinking catalyst. Fabrics treated with the experimental reagent developed high levels of resilience (durable press appearance) and were characterized by significantly higher than conventional levels of retained strength and abrasion resistance. Analyses by electron microscopy of fibers treated with NMP-2 and with the predominant conventional reagent, dimethyloldihydroxyethyleneurea, are reported. Attractive performance properties are discussed and attributed, at least in part, to rapid polymerization accompanying, or in advance of, etherification of cellulosic hydroxyl groups.

INTRODUCTION

Imparting durable-press properties to all-cotton fabrics with conventional crosslinking agents results in substantial losses in strength and abrasion resistance. In a recent study, Bertoniere and Rowland[1] applied N-methylolpolyethyleneureas (degree of polymerization, D.P., 7 and 14) to cotton fabric in a pad–dry–cure process to generate attractive levels of resilience. Higher than conventional levels of retained strength and abrasion resistance were realized with these multifunctional polymeric reagents. Currently we are reporting the results of a study of a low molecular weight member of this series, N-methylolpolyethyleneurea, D.P. 2 (NMP-2).

EXPERIMENTAL

Materials

Diethylenetriamine was purchased from Eastman Kodak Company. Urea and formalin were from the Fisher Scientific Company. Dimethylolurea was prepared by the procedure of Einhorn and Hamburger.[2] Dimethyloldihydroxyethyleneurea (DMDHEU) was purchased as Fixapret CP 40 from BASF Wyandotte Corporation. Trimethylolmelamine was purchased under the trade name Resloom HP from the Monsanto Chemical Company. The highly meth-

ylated hexamethylolmelamine was Aerotex 23S from American Cyanamid Company. The $Al_2(OH)_5Cl \cdot 2H_2O$ was from the Armour Pharmaceutical Company. The softening agent was Velvetol OE, a 17% solids emulsion of polyethylene from Quaker Chemical Corporation. The nonionic wetting agent was Triton X-100 from Rohm & Haas Company.

The cotton fabrics employed were 80 × 80 printcloth, 3/1 white twill, and 3/1 khaki twill weighing 0.122, 0.268, and 0.271 kg/m^2, respectively. These fabrics were desized, scoured, and bleached prior to use. The white twill required an additional "deoiling" treatment.

Preparation of Polyethyleneurea

The polyethyleneurea, D.P. 2, was prepared as a 50% (by weight) aqueous solution. Diethylenetriamine (333 g, 3.23 moles) was placed in a 3-liter round-bottomed flask. Water (750 ml) and a 10% molar excess of urea (640 g, 10.66 moles) were added, the mixture was stirred until a homogeneous solution formed, and then it was refluxed for 48 hr. The condenser was rinsed with distilled water periodically to remove a white solid that collected on the cool surface. The reaction mixture was poured into a large crystallizing dish. The product crystallized slowly from the syrupy residue left after slow evaporation of the water. The crystalline product (53%) was isolated by removal of the syrup with hot ethanol. The compound was recrystallized from ethanol/water 1/1 (v/v) (mp 203–204°C). When heating was continued slightly beyond the melting point, the compound decomposed with evolution of ammonia.

ANAL. Calcd. for $C_7H_{16}O_3N_6$: C, 36.20; H, 6.94; N, 36.19; MW, 232.24. Found: C, 36.41; H, 7.01; N, 35.81; MW, 239.

Characterization of the Polyethyleneurea

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 247 grating infrared spectrophotometer. The proton magnetic resonance (PMR) spectra were taken on a Varian A-60 NMR spectrometer, with D_2O as the solvent and DSS as an internal standard. The ESCA were run on a Varian IEE 15 spectrometer equipped with a magnesium anode. Mass spectra were determined on a Perkin–Elmer MS 270. Molecular weights and elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Methylolation Studies

The extent of reaction of formaldehyde with polyethyleneurea D.P. 2, cyclic ethyleneurea (2-imidazolidinone), and urea as a function of time was determined by following the free formaldehyde content of reaction mixtures with the method employed by Reid et al.[3] in a similar investigation of carbamates. The reaction mixtures included 37.5 g of the urea derivative (15% by weight), 0.4 g $Ca(OH)_2$, 1 mole formaldehyde per —NH_2 group (—NH in the case of 2-imidazolidinone), and sufficient water to bring the total weight to 250 g. The mixture was shaken at 35°C and sampled for free formaldehyde after 0.5, 1, 2, 3, 4, and 24 hr. The pH of these reaction mixtures fell within a very narrow range (11.2–11.6). The

results are expressed as the percentage of the total formaldehyde that is bound to the nitrogen compound.

Preparation of the N-Methylol Derivatives

One mole of formaldehyde per —NH_2 group was employed in the methylolation[3] of the polyethyleneurea. It (270 g, 1.16 mole) was dissolved in 949-g water (to give 25% NMP-2 solution) and 281-g formalin (104.5-g CH_2O, 3.48 moles), and then 5-g $Ca(OH)_2$ was added and the reaction mixture stirred overnight at room temperature. At the end of this period, the pH of the mixture was reduced to approximately 7 by bubbling CO_2 through the solution and removing the solid $CaCO_3$ by vacuum filtration. Such solutions have remained stable at room temperature for one year.

Polymerization Studies

Gel times as a function of concentration and pH (HCl) were determined at 50°C. The sudden increase in viscosity was recorded on a Brookfield Rheolog viscometer.

Fabric Treatment

In order to realize add-ons of 9%–11% NMP-2 or 6%–9% DMDHEU, these durable-press reagents were applied from pad baths containing 12%–17% NMP-2 or 8%–17% DMDHEU, 1% softener, and 0.1% wetting agent. $Al_2(OH)_5Cl\cdot2H_2O$ was incorporated at a level of 20% of the resin solids. The fabric samples, 0.25 × 0.64 m, were padded by two dips and two nips under approximately 18 kg roll pressure. The fabrics were dried on pin frames in a forced-draft oven at 70°C and subsequently cured for 3 min at 160°C. Cured samples were tested after one machine washing (permanent press cycle, wash water 100°F, with 80-ml 25% Triton X-100 solution as the detergent) and tumble drying for 30 min.

Fabric Evaluation

Add-ons were determined on air-equilibrated samples of fabric. Durable-press ratings were assigned to tumble-dried fabric by comparison to three-dimensional durable-press replicas according to AATCC test method No. 124-1975. Conditioned and wet wrinkle recovery angles (WRAs) were measured with the Monsanto tester, ASTM D-1295-67, and a modification thereof, respectively. Breaking strength and elongation were determined by the strip (1 in.) method ASTM D-1682-64. Elmendorf tearing strength was measured by the ASTM D-1424-63 method. Stoll-flex and accelerotor weight loss abrasion resistance were measured by the ASTM D-1175-71 method. Tearing strength, breaking strength, elongation, and Stoll-flex abrasion resistance were measured in the fill direction.
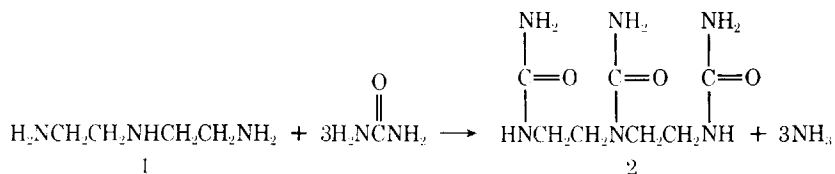
Changes in fiber morphology were followed by transmission electron micrographs of (1) ultrathin cross sections of fibers before and after immersion in 0.5M cupriethylenediamine hydroxide (cuene) for 30 min[4–6] and (2) ultrathin sections of fibers, which were prepared by a modification of the methacrylate expansion

technique to separate the fiber wall into layers.[5-7] Fiber surfaces were examined with an International Scientific Instruments scanning electron microscope.

RESULTS

Polyethyleneurea

Synthesis of the polyethyleneurea 2 by reaction of urea with the diethylenetriamine (1) proceeded smoothly with the evolution of ammonia as anticipated from the well-studied reactions of urea with simple amines.[9-11] The equation for this reaction is illustrated below:

$$H_2NCH_2CH_2NHCH_2CH_2NH_2 + 3H_2N\overset{\overset{\displaystyle O}{\|}}{C}NH_2 \longrightarrow$$

$$\underset{1}{} \qquad \underset{2}{HN\overset{\overset{\displaystyle NH_2}{|}}{C}H_2CH_2N\overset{\overset{\displaystyle NH_2}{|}}{C}H_2CH_2NH} + 3NH_3$$

Conversion of amine to substituted urea was easily followed via PMR spectra, as the methylene protons adjacent to amine nitrogen in 1 resonate approximately δ 0.6 upfield from those adjacent to urea nitrogen. The PMR spectra of 1 and 2, the polyethyleneurea derived from it, are presented in Figure 1 to demonstrate the complete conversion of amine to urea nitrogen. The ESCA of 2 confirmed the presence of nitrogen, oxygen, and carbon in sp^3 and sp^2 hybridized states.
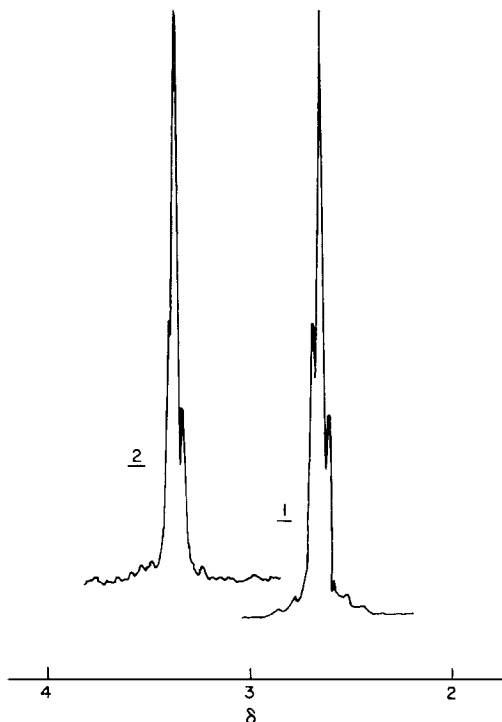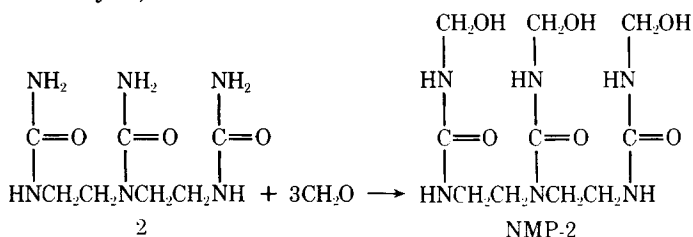

Fig. 1. Proton magnetic spectra of diethylenetriamine (1) and the polyethyleneurea D.P. 2 (2) derived from it. Spectra were taken in D_2O with DSS as internal standard.

The expected absorbances at 3440, 3350 (NH) and 1650, 1590 (C=O) cm^{-1} were evident in the infrared spectra. No molecular ions were observed in the mass spectra. Prominent peaks in the mass spectra of this dimer occurred at 60, 44, and 43 m/e. The spectral evidence is consistent with the proposed structure 2. The method of synthesis and molecular weight determination provide the strongest evidence for the molecular size.

Reactions with Formaldehyde

The utility of this compound as a polymerization crosslinking agent for cotton cellulose depends upon its conversion to the N-methylol derivative by reaction with formaldehyde, as illustrated below:

$$
\begin{array}{ccc}
 & & CH_2OH \quad CH_2OH \quad CH_2OH \\
 & & | \qquad\quad | \qquad\quad | \\
NH_2 \quad NH_2 \quad NH_2 & & HN \qquad HN \qquad HN \\
| \qquad\; | \qquad\; | & & | \qquad\quad | \qquad\quad | \\
C{=}O \quad C{=}O \quad C{=}O & & C{=}O \quad C{=}O \quad C{=}O \\
| \qquad\; | \qquad\; | & & | \qquad\quad | \qquad\quad | \\
HNCH_2CH_2NCH_2CH_2NH \; + \; 3CH_2O & \longrightarrow & HNCH_2CH_2NCH_2CH_2NH \\
2 & & NMP\text{-}2
\end{array}
$$

This reaction is normally conducted under basic conditions with Ca(OH)$_2$.[8] The extent of reaction of 2 with formaldehyde at high pH was determined as a function of time, and its behavior was compared with that of unsubstituted urea and the cyclic ethyleneurea (2-imidazolidinone). Results are presented in Figure 2. A limiting level of 80%–90% bound formaldehyde was reached within the first hour. The urea unit in 2 had reactivity toward formaldehyde that was essentially equivalent to urea and cyclic ethyleneurea at this pH. A 10% NMP-2 pad bath contains 0.3%–0.6% free formaldehyde.
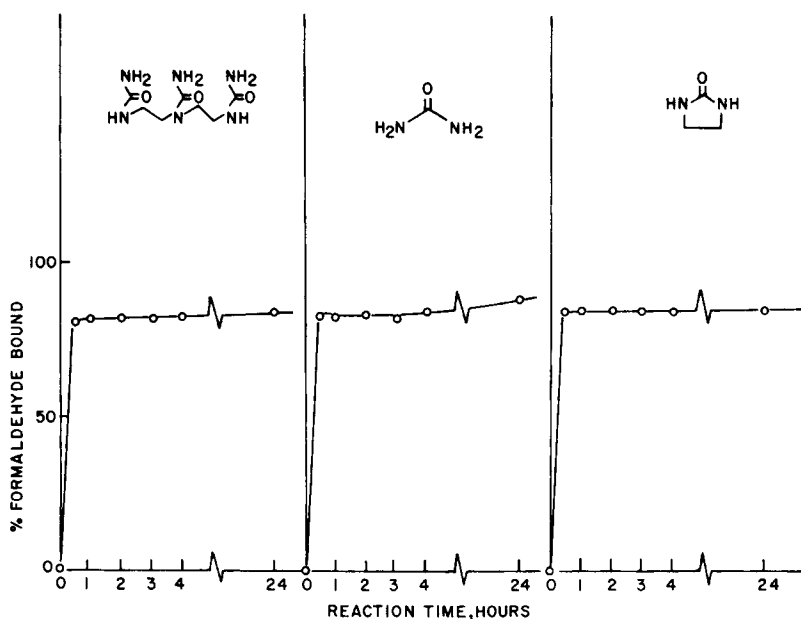

Fig. 2. Extent of methylolation of NMP-2, urea, and cyclic ethyleneurea at pH 11.2–11.6.

Polymerization Studies

Polymerization of NMP-2 was characterized in terms of gel time at 50°C, measured as a function of concentration and pH of solution. Results are illustrated in Figure 3 along with corresponding data for trimethylolmelamine (TMM). The functionality of the latter is similar to that of NMP-2, and its use in textile modification is well established. With both compounds at all pHs investigated, the gel time decreased as the solids content of the reaction mixture increased. The time required for gelation of NMP-2 decreased as the pH was lowered from 4 to 3 to 2. In contrast, the gel time of TMM increased when the pH was lowered from 3 to 2, determinations at pH 4 not having been made because TMM was insoluble at this and higher pHs. Whereas roughly similar behavior was observed at pH 3 for NMP-2 and TMM, the former gelled in 3%–4% of the time required by the latter at pH 2.

Precipitative rather than homogeneous gelation was observed for dimethylolurea when a 10% solution (maximum solubility 12%[12]) was acidified with dilute HCl at room temperature. Precipitative gelation was also observed with the highly methylated hexamethylolmelamine. This reaction occurred less rapidly at room temperature than that of dimethylolurea, thus the effect of concentration and pH upon the precipitative gel time at 50°C could be deter-
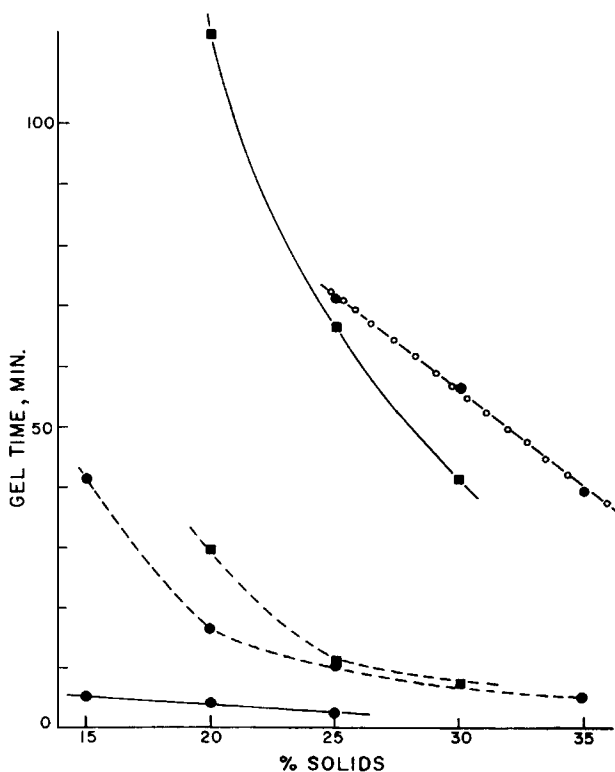

Fig. 3. Gelation of NMP-2 (circles) and trimethylolmelamine (squares) at 50°C. Solid, broken, and dot-dash lines indicate pH 2, 3, and 4, respectively. Gel times are not given when less than 2 min (30% and 35% NMP-2 at pH 2), when the time scale was exceeded (15% and 20% NMP-2 at pH 4, 15% TMM at pH 2 and 3), or when the mixture was not completely soluble (35% TMM at pH 2 and 3, all concentrations at pH 4).

mined. In contrast to the homogeneous gelation observed for trimethylolme-
lamine, precipitative gelation of the methylated hexamethylolmelamine occurred
faster in dilute than in concentrated solution and faster at higher than at lower
pHs. No gelation or change in viscosity was observed when a 30% solution of
dimethyloldihydroxyethyleneurea (DMDHEU) was held at 50°C at pH 2 for 24
hr. The principal reaction of the latter within the cotton fiber is believed to be
crosslinking rather than resinification.

Reaction of NMP-2 with Cellulose

NMP-2 was evaluated as a polymerization crosslinking agent on cotton fabrics
versus DMDHEU, the preferred industrial crosslinking agent. Three different
fabrics were studied to ensure representative results for lightweight and mod-
erately heavyweight fabrics. The percentages of applied reagent fixed in the
fabrics were 73%–80% and 80%–95% for DMDHEU and NMP-2, respectively.
Results are summarized in Figure 4.

Although specific values vary significantly from one fabric to another for each
textile property, consistent differences between the two reagents are evident.
Both reagents conferred high and essentially comparable durable-press ap-
pearance ratings on all three fabrics, the NMP-2 samples showing a slight su-
periority. On the other hand, conditioned and wet WRAs were generally higher
for the DMDHEU fabrics. In retentions of breaking strength, elongation, and
tearing strength, the NMP-2 fabrics were consistently better by 16%–25%,
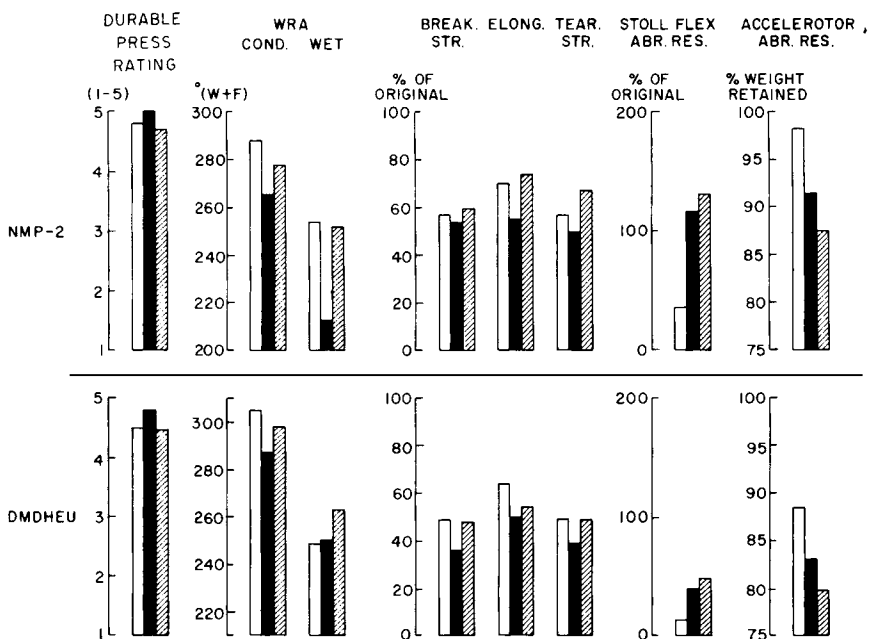9%–37%, and 16%–37%, respectively. In both tests for abrasion resistance, the

Fig. 4. Textile properties of fabrics treated with NMP-2 and DMDHEU. Fabrics are identified
by bars (left to right): printcloth, solid white; white twill, dotted black; Khaki twill, hatched. Re-
spective add-ons to the three fabrics were 11.0%, 10.2%, and 8.7% NMP-2 and 5.8%, 8.8%, and 8.8%
DMDHEU.

NMP-2 fabrics were superior to the DMDHEU fabrics by substantial margins.

NMP-2 is unique in conferring a very high durable-press appearance rating but relatively low wrinkle recovery angles. Such results are suggestive of slower, delayed wrinkle recovery in NMP-2 fabrics. That such is at least partially the case is indicated by the extent to which conditioned wrinkle recovery angle increases as a function of time (Table I). Fabrics treated with NMP-2 recovered only 80% of the 16-hr WRA almost instantly, compared to 90% for those modified with DMDHEU. Conditioned WRA is only one measure of resilience, and only an approximate relationship between durable-press appearance rating and WRAs is realized when both conditioned and wet WRAs are considered.[13]

Microscopic Analyses

Examination of fiber surfaces with the scanning electron microscope revealed no resin deposition with DMDHEU but some unevenly distributed surface polymer from NMP-2. Heavy resin deposition on fiber surfaces was noted earlier in a study of wet fixation,[14] a technique that also yields fabrics with improved strength retention.[15] The surface deposition with N-methylolpolyethyleneurea was very light, especially by comparison to that observed for samples modified by wet fixation with N-methylolmelamines. In the latter case, large deposits with significant interfiber bonding were observed, whereas there was no evidence of interfiber bonding with NMP-2.

The behavior of whole fibers and ultrathin cross sections of treated samples in $0.5M$ cuene was observed in the light microscope and the transmission electron microscope, respectively. Whole fibers taken from fabric treated with DMDHEU were unaffected by $0.5M$ cuene after 30 min, whereas moderate swelling was observed with fibers treated to a higher level with NMP-2. Similar results were obtained when thin cross sections were exposed to the cuene solution. In the case of the DMDHEU fabrics, there was no evidence of dissolution and very little swelling; both swelling and dissolution were observed for the sample treated with NMP-2. When thin cross sections of fibers that had been subjected to methacrylate expansion were observed in the transmission electron microscope, specimens from NMP-2 fabrics expanded in a pattern that was somewhat coarser than that characteristic of unmodified cotton, whereas no expansion was

TABLE I
Conditioned Wrinkle Recovery Angle [°(W + F)] as Function of Time

Time, min[a]	Printcloth		White Twill		Khaki Twill	
	NMP-2	DMDHEU	NMP-2	DMDHEU	NMP-2	DMDHEU
0[b]	241	295	227	266	210	287
1	274	308	252	277	248	298
2.5	281	310	264	281	255	306
5	287	312	269	284	260	307
30	293	318	273	286	266	307
60	297	320	274	288	269	307
960	302	324	278	291	274	310

[a] Time lapse after removal of weight and placement in tester; standard method requires reading after 5 min.
[b] Initial reading taken immediately after placement in tester designated 0 min.

observed in the sample crosslinked with DMDHEU. The microscopic studies indicate a more open, less tightly crosslinked structure for fabric treated with NMP-2.

DISCUSSION

Polyethyleneurea D.P. 2 and NMP-2

Polyethyleneurea D.P. 2 was readily prepared from thermal reaction of diethylenetriamine with urea. The structure of this crystalline product was verified by various analytic methods. This polyamide underwent methylolation at pH 11.2–11.6 to form NMP-2 at a rate and to an equilibrium very similar to those of urea and cyclic ethyleneurea. NMP-2, which has approximately 2.5 N-methylol units per molecule (remaining 0.5 mole formaldehyde is unbound) and 5+ reactive —NH groups, polymerized rapidly to a network polymer when adjusted to pH 4 or lower. As measured by gel times at 50°C, NMP-2 was less sensitive to acid than dimethylolurea and polymerized more rapidly than TMM. In all cases, NMP-2 formed a homogeneous gel in aqueous solutions, whereas dimethylolurea formed a gel that separated from the aqueous system; this precipitative gelation was also observed to occur in the case of a highly methylated hexamethylolmelamine. No evidence was obtained for gel formation from DMDHEU.

Cotton Reacted with MNP-2

Textile performance properties of cotton fabric treated with NMP-2, in comparison to those of the same fabrics treated with DMDHEU, may be summarized as follows: (a) High and comparable levels of durable press appearance ratings were realized with the two types of reagents, accompanied by (b) lower conditioned and wet wrinkle recovery angles for NMP-2 fabrics and (c) significantly higher levels of retained strength and abrasion resistance for the fabrics modified with NMP-2. Microscopic examination of the samples taken from these fabrics revealed small amounts of surface deposits on the NMP-2 fabric. Responses of fibers to methacrylate expansion and to cuene studies indicated a more open, less tightly crosslinked microstructure for the cotton treated with NMP-2.

Early methods for imparting easy care properties to the cotton fabrics involved urea–formaldehyde, which is capable of both polymerization and crosslinking to cellulose. The extent to which each occurs is complex and catalyst dependent.[16-19] At present, the most common durable press reagents are based on the cyclic ethyleneurea type of structure, e.g., DMDHEU, whose principal mode of reaction is cellulosic crosslinking. Such treatments, unfortunately, result in severe losses in strength and abrasion resistance. These losses are reduced significantly when DMDHEU is applied in combination with N-methylolmelamines in a two-step process designated "wet fixation."[15] It was suggested that the improved retention of strength and abrasion resistance could be attributed to the gradual deposition of polymer in the form of a network structure in the less accessible regions of the fiber during the fixation period.[20] Improved retention of strength and abrasion resistance were also observed when oligomeric N-methylolpolyethyleneureas D.P. 7 and 14 were applied to cotton, both alone

and in combination with DMDHEU, in a pad–dry–cure process.[1]   These results lent further credence to the proposal that a network polymeric crosslink was a key factor.

NMP-2 is one of the lowest members of the N-methylolpolyethyleneurea series. By applying NMP-2 to cotton, we again observed improved retentions of strength and abrasion resistance.   In this case, however, the reagent, at least at time of application, is relatively low in molecular weight.   It is clear that NMP-2 forms a network polymer readily, but controllably.   Resistance of NMP-2-treated cotton fibers to dissolution and swelling in cuene indicates that some reaction between the network polymer and cellulose has occurred.   The fact that this reaction is limited is indicated by the greater swelling observed for NMP-2-treated fibers than for DMDHEU-treated fibers.   Additionally, there was a suggestion that some cellulose in NMP-2-treated fibers might actually be dissolved by the action of cuene.   The layering or expansion that was observed upon methacrylate treatment of NMP-2-treated fibers provides further indication of a crosslinked system that is considerably less collapsed than that characteristic of DMDHEU.   To our knowledge, an N-methylol crosslinking reagent that confers high durable-press appearance rating to cotton while still allowing the microstructure to swell in cuene and to expand during the methacrylate treatment is completely unique.

At this time it appears that there is an intimate relationship among the polymerization crosslinking characteristics of NMP-2, the relatively open, loose crosslinking system that is developed in the microstructure of the cotton fiber, the combination of high durable-press appearance rating and high retentions of strength and abrasion resistance in NMP-2 fabric, the relatively low WRAs of NMP-2 fabric, and the low rate of wrinkle recovery.

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