

Blocked Isocyanate-Terminated Prepolymers in a Delayed-Cure Durable-Press Finish for Wool. Influence of Isocyanate and Blocking Group Structure on Reactivity*

G. B. GUISE, G. N. FREELAND, and G. C. SMITH, *CSIRO Division of Textile Industry, Belmont, Victoria 3216, Australia*

Synopsis

A series of prepolymers containing terminal blocked isocyanate groups was prepared by reaction of isocyanate-terminated prepolymers [derived from a poly(propylene oxide) diol (MW = 2000) or a triol (MW = 3000) and different diisocyanates] with various blocking agents. Their curing rates with a polyepoxide crosslinking agent were measured to assess their suitability for a delayed-cure durable-press treatment for wool. The curing rates varied over a wide range, but commonly used blocking groups such as phenols, caprolactam, β -diketones, and alcohols were not sufficiently reactive for the intended application, although others, e.g., oximes and certain blocking agents containing a basic center such as N,N-diethylhydroxylamine, hydroxypyridines, and hydroxyquinolines, had the required reactivity. Blocking by 1,3-dipolar cycloaddition of nitrones was examined, but the reactivities were too low. Prepolymers containing blocked aromatic isocyanates were more reactive than those containing blocked aliphatic isocyanates. Difunctional butanone oxime-blocked prepolymers cured slightly more slowly than analogous trifunctional prepolymers.

INTRODUCTION

Reactions of isocyanates are widely used to crosslink and chain extend polymers.¹ The main feature of isocyanate chemistry is their high reactivity toward nucleophiles, e.g., reaction with alcohols to form urethanes occurs readily (particularly in the presence of catalysts) at room or slightly higher temperatures, and this is the basis of polyurethane technology.¹ However, in certain situations this high reactivity, particularly toward water, can be a problem. As water is difunctional, chain extension or crosslinking results. The reactivity can be reduced by conversion to derivatives, known as blocked or masked isocyanates, which do not react with water at ambient temperature but at higher temperatures either re-form the parent isocyanate or undergo displacement reactions, e.g., with alcohols to form urethanes^{1,2} (Fig. 1). Common blocking agents are phenols, β -diketones, lactams, oximes, etc.¹⁻³ There is an extensive patent literature² on the applications of prepolymers containing blocked isocyanate groups, but little has been published about their curing chemistry or on comparisons of various types of blocking agent.

Some years ago, CSIRO developed⁴ a durable-press finish for wool in which garments were treated with an isocyanate-terminated prepolymer derived from a poly(propylene oxide) triol and an aliphatic diisocyanate [see reaction (i), Fig.

* Presented in part at the 9th Australian Polymer Symposium, Tanunda, South Australia, February, 9-12, 1977.

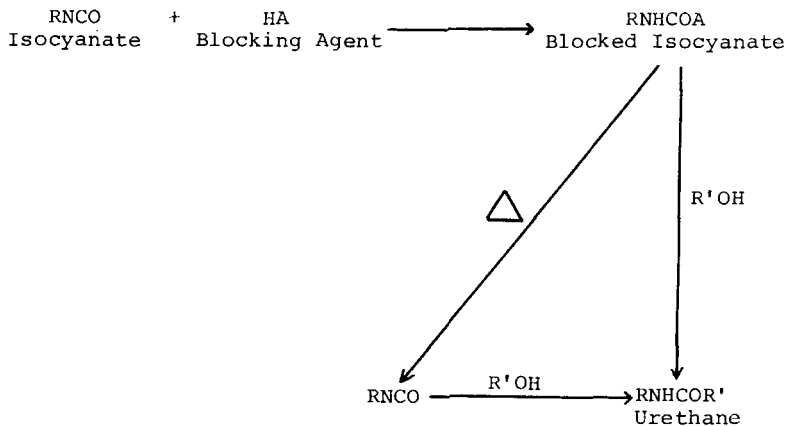


Fig. 1. Reactions of blocked isocyanates.

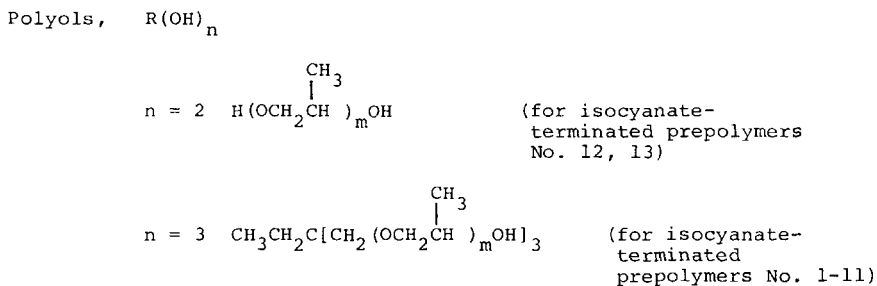
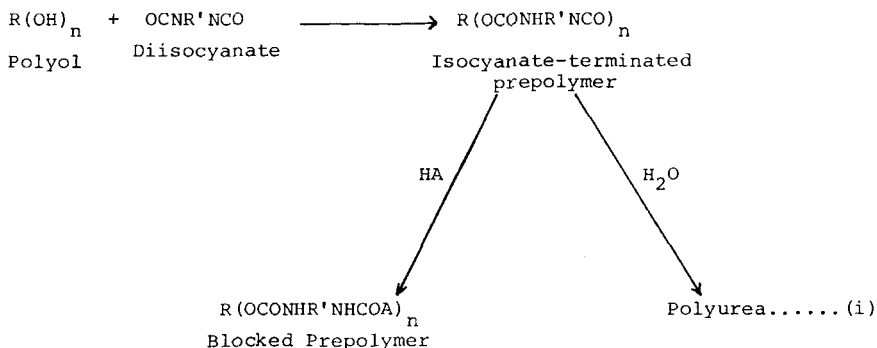


Fig. 2. Preparation and reactions of isocyanate-terminated prepolymers.

2]. The isocyanate-terminated prepolymer cured with moisture to form a crosslinked polyurea coating on the fibers that shrink resisted the wool and held the creases in place while they were being permanently set in steam. Premature reaction of the isocyanate-terminated prepolymer with water resulted in poor durable-press performance. Fleischfresser and Freeland⁵ found that this problem could be avoided by blocking the isocyanate groups, which also allowed a delayed-cure treatment.

In the delayed-cure durable-press treatment, fabric is treated, and then, after

a delay of perhaps a year or more, garments are made up, pressed, heated to cure the blocked prepolymer, and finally hung in saturated steam to permanently set the creases. The heat-cured prepolymer containing blocked isocyanate functions in the same way as the moisture-cured isocyanate-terminated prepolymer, namely, to shrink resist the wool and to hold cohesively set creases until these are permanently set. The overall result in both cases is a durable-press finish, i.e., garments are produced which, after laundering, do not shrink, retain sharp creases, and do not need ironing.

To find the most suitable prepolymer structure for use in this delayed-cure treatment, the influence of structure on durable-press performance is being studied systematically. Durable-press performance in wool garments requires the fabric to be shrink resisted and set in some particular configuration. However, because the blocked prepolymers investigated were prepared from isocyanate-terminated prepolymers known^{6,7} to shrink resist wool, and because setting conditions for wool are well known,^{4,5} these two factors were not studied in the present work.

Only curing rates and the ability of the blocked prepolymers to prevent loss of crease definition during the setting operation were evaluated. A detailed study of the durable-press performance of some of the prepolymers with satisfactory curing rates will be reported later.⁷

EXPERIMENTAL

Preparation and Blocking of Isocyanate-Terminated Prepolymers

The preparation (Fig. 2) of isocyanate-terminated prepolymers 1, 2, and 4 to 13 from a polyol and a diisocyanate has been described previously.^{6,8} The polyol used to make isocyanate-terminated prepolymers 1 to 11 was a poly(propylene oxide) triol, MW = 3000 (Desmophen 3400, Bayer); and for isocyanate-terminated prepolymers 12 and 13, the polyol was a poly(propylene oxide) diol, MW = 2000 (Voranol P2000, Dow). The isocyanate-terminated prepolymers were then blocked by heating with 10% excess blocking agent in dry toluene under nitrogen until the isocyanate infrared absorption disappeared.

The butanone oxime-blocked prepolymers derived from isocyanate-terminated prepolymers 1, 2, etc., were designated 1A, 2A, etc.

To prepare the butanone oxime-blocked prepolymer 3A, 2,4-tolylene diisocyanate (34.8 g, 0.20 mole) was dissolved in toluene (200 ml), and butanone oxime (17.4 g, 0.20 mole) was added. The temperature rose to 45°C during the addition. This solution was kept overnight at room temperature, and the solvent was removed under vacuum below 50°C. The product (13.0% NCO) was reacted with Desmophen 3400 (147 g, 0.05 mole) for 8 hr at 100°C under nitrogen.

Durable-Press Experiments

Full details have been given elsewhere.^{4,5} A plain-weave worsted wool fabric (210 g/m²) which had been scoured with soap and sodium carbonate was treated, unless otherwise stated, with a mixture of 4% blocked prepolymer, 0.4% Epikote 1001 (Shell, a bisphenol-A diglycidyl ether), 0.04% Annulex PBA 15 (Wm. Pearson, a hindered phenolic antioxidant), and 0.01% dibutyltin dilaurate. The treatment was by impregnation with 70% by weight of an emulsion prepared by

emulsifying a 10% toluene solution of the above materials with a nonionic surfactant mixture.

Treated samples were then subjected to the following sequence. Step 1: The samples were dried for 2 min at 130°C in a Konrad Peter dryer. Step 2: The samples were creased by folding in half and steam pressing. Step 3: The creased samples were heated for various times in an oven. Step 4: The creases were permanently set^{4,5} by hanging the samples with the creases vertical and not constrained in any way, while being subjected to a setting cycle of 30 min of heating at 90°C followed by steaming for 2 hr in saturated steam.

The crease angle was measured as previously^{5,6} and the flexural rigidity determined according to BS 3356:1961 (the value for untreated fabric was 10 mN-mm). If there was no polymer present or if the polymer had not been cured in step 3, this sequence caused the creases to open out to about 120°. If the polymer cured, lower crease angles were obtained. The previous work^{4,5} has shown that if the crease angle was below 60° after the above sequence, the durable-press performance after washing would be satisfactory provided the shrink resistance was adequate. The curing times quoted below are the minimum heating times in step 3 at a particular temperature, required to give a crease angle below 60°. Curing will mainly occur in step 3 of the above sequence but some will occur during the drying in step 1 and the 90°C preheating in step 4. If curing was completed during step 1, the creases were unsatisfactory.

RESULTS AND DISCUSSION

The main objective of this investigation was to optimize the curing rates of the polymers. Their reactivity should be sufficiently low to avoid premature curing during the drying step that follows the initial fabric treatment and also should allow for as long a delay as possible between the fabric treatment and curing of the garments. However, the curing rate should not be so slow that excessive heating is needed for the final curing as this may damage the wool. In other words, the difference between high- and low-temperature curing rates should be as large as possible, a requirement which has also been noted² for other applications of prepolymers containing blocked isocyanate groups. For the intended delayed-cure durable-press treatment, a satisfactory curing rate was considered to be one that allowed a delay of at least a year at 20°C between the initial treatment and final curing, and also one that cured within 30 min at 120°C.

The curing times (Table I) of the various blocked prepolymers were measured in durable-press crease-holding experiments. In a study⁷ in which the fabric flexural rigidity (i.e., stiffness) was determined after various extents of curing, the curing time corresponded to a point where the flexural rigidity leveled off after a significant rise from the untreated value. This suggests that the curing time corresponds to a gel time.

Crosslinking of the isocyanate-terminated prepolymers on wool involves urea formation from the reaction of the isocyanates with water. However, with the prepolymers containing blocked isocyanates, crosslinking will be much more complex. The isocyanates formed will react with the hydroxyl groups and possibly the epoxides of the crosslinking agent; and as unblocking occurs at 120°C, the thermal reactions of isocyanates such as dimerization, trimerization, or formation of allophanates or biurets may also occur.¹ The observed curing

TABLE I
Influence of Isocyanate Reactivity in Prepolymers Derived from Polyols and Diisocyanates Blocked with Butanone Oxime

Isocyanate-terminated prepolymer	Diisocyanate and source ^a	Blocking reaction temp., ^b °C	Curing time of blocked prepolymer at				Flexural rigidity, ^c mN-mm, Fabric A
			60°C	100°C	120°C	140°C	
			Triol MW = 3000				
1 ^d	Diphenylmethane diisocyanate (MDI) (Isonate 143L, Upjohn)	20	20 hr	30 min	15 min	10 min	42
2 ^d	2,4-Tolylene diisocyanate (TDI) (Desmodur T100, Bayer)	70	10 hr	15 min	10 min	5 min	39
3 ^e	2,4-Tolylene diisocyanate (TDI) (Desmodur T100, Bayer)	e	24 hr	20 min	15 min	10 min	38
4 ^d	65% 2,4- and 35% 2,6-Tolylene diisocyanate (Desmodur T65, Bayer)	60	20 hr	10 min	5 min	5 min	36
5 ^d	Xylylidene diisocyanate (70% <i>m</i> , 30% <i>p</i>) (T.C.I., Japan)	60	>2 wk	2 hr	1 hr	30 min	29
6 ^d	2-Methoxycarbonylpentamethylene diisocyanate (Lysine diisocyanate, Toray)	60	>2 wk	2 hr	1.5 hr	30 min	33
7 ^d	Hexamethylene diisocyanate (HDI) (Desmodur H, Bayer)	60	1 mo	2 hr	1 hr	30 min	33
8 ^d	2,2,4-(and 2,4,4-)Trimethylhexamethylene diisocyanate (Vebe)	80	>2 wk	2 hr	1 hr	30 min	29
9 ^d	1-Isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (Isophorone diisocyanate, Vebe)	60	>2 wk	2 hr	1.25 hr	30 min	31
10 ^d	Bis(4-isocyanatocyclohexyl)methane (Hylene W, du Pont)	70	3 wk	1 hr	45 min	20 min	23
11 ^d	Bis(3-methyl-4-isocyanatocyclohexyl)methane (BASF)	60	>2 wk	2 hr	1 hr	30 min	41
	Difunctional Polymers from Poly(propylene Oxide) Diol MW = 2000						
12 ^d	2,4-Tolylene diisocyanate (TDI) (Desmodur T100, Bayer)	70	40 hr	20 min	15 min	10 min	29
13 ^d	Hexamethylene diisocyanate (HDI) (Desmodur H, Bayer)	60	5 wk	2 hr	1 hr	45 min	29

^a Prepolymers 1-10 arranged in decreasing order of isocyanate reactivity.²

^b Reaction time 3-4 hr.

^c Cured at 120°C.

^d Produce from reaction of polyol and diisocyanate reacted with butanone oxime.

^e Product from reaction of butanone oxime and diisocyanate reacted with polyol (see experimental section).

times will presumably reflect the time it takes for these various reactions to cause gelation. But in view of the possibility of a number of competing and consecutive reactions, it was not surprising that the observed curing times did not parallel the known reactivities of different types of isocyanates or of a particular isocyanate with different reactants.

Influence of Isocyanate Reactivity with Butanone Oxime Blocking Group

The isocyanate-terminated prepolymers of the present study cured with moisture on wool at widely differing rates.⁶ However, when blocked with butanone oxime, the same series of prepolymers showed much less variation, and the curing times (Table I) fell into two groups. The faster curing group were prepolymers 1A to 4A, in which the isocyanates were attached to aromatic rings, whereas the slower group were all based on aliphatic isocyanates.

The difference between the unblocked and blocked prepolymers could reflect the fact that different crosslinking reactions were involved. Alternatively, with the blocked prepolymers, free isocyanates may not be involved in the rate-determining step or may not be actual intermediates in the curing reactions. Also, steric effects may not have the same influence on blocked and free isocyanates. Steric effects are well known¹ to be an important factor in determining the reactivity of isocyanates, for example, the 2-position of TDI is less reactive than the 4-position, and cyclohexyl isocyanate is less reactive than *n*-hexyl isocyanate.¹ However, blocked hindered isocyanates might be more reactive than unhindered ones due to relief of steric strain during unblocking. Examples (see Table I) of such a reversal of relative rates are the prepolymers derived from MDI and TDI. MDI-terminated prepolymers are more reactive than those derived from TDI,¹ but the reverse was the case with the butanone oxime-blocked prepolymers 1A and 2A. Also, prepolymers 7 and 10, terminated with hexamethylene diisocyanate and bis(4-isocyanatocyclohexyl)methane, respectively, when applied to wool and exposed to air, required 1.5 and 21 days, respectively, for shrink resistance to develop at 20°C,⁶ whereas the butanone oxime-blocked prepolymer 10A was more reactive than prepolymer 7A.

The butanone oxime-blocked prepolymer based on 2,4-tolylene diisocyanate was prepared in two ways. Prepolymer 2A was prepared (as in Fig. 2) by reacting the diisocyanate with the polyol and then blocking the product. Prepolymer 3A was prepared by partially blocking TDI and reacting the product with the polyol. As a consequence of steric effects, the blocking groups should be expected to be mainly in the 2-position in prepolymer 2A but in the 4-position in prepolymer 3A. The result of this should be that the blocked prepolymer 2A should unblock more readily than prepolymer 3A, and such an effect was observed (Table I).

Another effect can be seen if the curing rates (Table II) in the presence and absence of catalyst are compared. The curing rates of the less reactive aliphatic isocyanates appear to be changed to a much greater extent by the addition of catalyst. Possible explanations are differences in the relative rates of unblocking and subsequent reactions such as urethane formation. With less reactive¹ aliphatic isocyanates, crosslinking reactions are probably rate limiting, and hence the catalyst has a significant effect, whereas with reactive isocyanates (such as TDI and MDI) unblocking is probably rate limiting, and so the catalyst has little effect.

TABLE II
Influence of Catalyst on Curing Rates of Butanone Oxime-Blocked Isocyanate-Terminated Prepolymers

Butanone oxime-blocked prepolymer no.	Parent diisocyanate	Curing times (120°C)	
		No catalyst	0.01% DBTDL ^a
1A	diphenylmethane diisocyanate	1 hr	15 min
2A	2,4-tolylene diisocyanate	15 min	10 min
7A	hexamethylene diisocyanate	>24 hr	1 hr
10A	bis(4-isocyanatocyclohexyl)methane	24 hr	45 min

^a DBTDL = Dibutyltin dilaurate.

Influence of Blocking Group on Curing Rate

The effect of the blocking group was investigated with prepolymers derived from an aliphatic (hexamethylene) diisocyanate (Table III) or an aromatic (2,4-tolylene) diisocyanate (Table IV). Very significant differences in curing rates were found, e.g., some gelled during the blocking reaction, others cured during the preliminary drying of 2 min at 130°C, whereas others did not appear to cure after 4 hr of heating at 120°C. The cured, treated fabrics differed significantly in stiffness (see flexural rigidity results in Tables III and IV), suggesting differences in the extent of crosslinking in the cured polymer.

In view of the complexity of the curing of the blocked prepolymers it was not surprising that there was little relationship between the curing times and the rate of the blocking reaction (as judged from the conditions required for reaction with the blocking agent). This could also indicate that unblocking is not the rate-determining step in curing. Also, if the mechanism⁹ of additions to isocyanate groups is considered, at least two steps, an addition followed by a subsequent proton transfer, must be involved; but in spite of this, in many cases the blocking/unblocking of isocyanates has been treated as a simple reversible equilibrium. The rate of the blocking reactions of isocyanates, as with other nucleophilic additions to carbonyl groups, should be related to the base strength of the nucleophile, i.e., reaction of HA with a proton. However, the unblocking reaction should depend on the electron-withdrawing ability of the group A, which should correlate with the acid strength of HA, i.e., the ability of HA to lose a proton. Thus, with a series of blocking groups, acid and base strengths will not necessarily follow the same order. For example, for reaction with the isocyanates, the order amine \gg alcohol \approx phenol would be expected; but for the unblocking reaction, the order is phenol \gg alcohol \geq amine. However, in the present study exceptions to this order were noted, e.g., isocyanate-terminated prepolymer 2 blocked with di-*n*-butylamine was more reactive than expected.

Prepolymers blocked with the commonly used blocking groups, such as phenols, β -diketones, caprolactam, and alcohols, were not sufficiently reactive (see above) for this delayed-cure durable-press application. The blocking groups that gave satisfactory curing times, such as oximes, N,N-diethylhydroxylamine, hydroxypyridines, hydroxyquinolines, and pyrazolinones, possess a common structural feature, namely, an —OH group (or a group capable of enolization) and a basic nitrogen function. However, some compounds with these features, e.g., 2-diethylaminoethanol and N-methyl-N-phenylethanolamine, were unsatisfactory, as were compounds containing an —NH₂ group together with a basic

TABLE III
Influence of Blocking Group in Prepolymers Derived from Hexamethylene
Diisocyanate (Isocyanate-Terminated Prepolymer 7)

Blocking group	Block- ing reaction temp., °C	Block- ing reaction time, hr	Curing time at				Flexural rigidity, mN-mm (curing temp., °C)	
			60°C	100°C	120°C	140°C		
Oximes								
Acetoxime	70	0.2	>1 mo	4 hr	2 hr	1 hr	40 (120)	
Butanone oxime	60	3	1 mo	2 hr	1 hr	30 min	33 (120)	
Cyclohexanone oxime	70	3	>1 mo	4 hr	3 hr	2 hr	28 (120)	
Phenols, Enols, etc.								
Phenol	100	24 ^a	>2 mo	4 hr	2 hr	1.5 hr	19 (120)	
<i>m</i> -Cresol	100	24 ^a	>2 mo	>4 hr	3 hr	2 hr	29 (140)	
<i>o</i> -Chlorophenol	100	24 ^a	>2 mo	4 hr	2 hr	1.5 hr	28 (120)	
<i>p</i> -Toluene thiol	100	4	4 day	>4 hr	4 hr	1 hr	41 (140)	
Ethyl acetoacetate	80	4 ^b	>2 mo	>4 hr	>4 hr	3 hr	14 (140)	
Alcohols, Amines								
Di- <i>n</i> -butylamine	20	0.1	2 mo	—	>2 hr	15 min	20 (140)	
2,2,2-Trifluoroethanol	60	4 ^c						
<i>N</i> -Hydroxyphthalimide	60	3	3 days	2 hr	1 hr	1 hr	47 (120)	
<i>N,N</i> -Dimethylhydrazine	20	3	>2 mo	—	—	>4 hr	15 (140)	
<i>N</i> -Hydroxysuccinimide	65	1	cures during preliminary drying					
Compounds Containing Basic Nitrogens								
<i>N,N</i> -Diethylhydroxylamine	20	16	3 days	45 min	15 min	10 min	48 (120)	
2-Hydroxypyridine	60	12	cures during preliminary drying					
3-Hydroxypyridine	60	11	10 hr	20 min	15 min	10 min	46 (120)	
4-Hydroxypyridine	60	2 ^c						
Pyridine <i>N</i> -oxide	70	24 ^e						
8-Hydroxyquinoline	70	14	2 days	20 min	15 min	10 min	33 (120)	
8-Hydroxyquinaldine	60	4	3 days	30 min	10 min	5 min	23 (120)	
6-Chloro-2-hydroxypyridine	70	10 ^d						
3-Hydroxypyridine <i>N</i> -oxide	65	2 ^c						
2-Mercaptopyridine	60	6			4 hr			
3-Methyl-1-phenyl-2-pyrazolin-5-one	80	24	24 hr	20 min	15 min	10 min	37 (120) ^f	
3-Methyl-2-pyrazolin-5-one	80	3	8 days	2 hr	1 hr	30 min	38 (120) ^f	
<i>N</i> -Phenylhydroxylamine	20	72	>7 days		>1 hr	1 hr	—	
2-Diethylaminoethanol	20	16			>4 hr	4 hr		
<i>N</i> -Ethyl- <i>N</i> -phenylethanolamine	20	16			>4 hr	3 hr		
2-Mercapto-1-methylimidazole	60	20			1.5 hr			
1,3-Dipolar Compounds								
Nitrone III	20	16			>1 hr	>2 hr		
Nitrone IV	100	2 ^e						
Other Compounds								
Dimethyl phosphite	100	4	>2 mo	>4 hr	4 hr	4 hr	23 (120)	
Caprolactam	80	6	>2 mo	—	>4 hr	1 hr	34 (140)	
Acetohydroxamic acid	40	4	5 days	2 hr	45 min	30 min	40 (120)	
<i>p</i> -Toluenesulfonamide	100	8 ^e						
Diethylbarbituric acid	60	6 ^d						
Thioglycolic acid	20	120 ^c	cures during preliminary drying					
Thioacetic acid	20	120			>4 hr			
Thiobenzoic acid	20	120	1 mo		>4 hr			
Acetone phenylhydrazone	20	240 ^c						
<i>p</i> -Toluenesulfonic acid	60	10 ^c						

^a Dibutyltin dilaurate catalyst present.

^b Potassium *tert*-butoxide catalyst.

^c Gelled during reaction.

^d Gelled after two days' storage.

^e No reaction.

^f Treated fabric samples developed a pinkish coloration after curing.

TABLE IV
Influence of Blocking Group in Prepolymers Derived from 2,4-Tolylene Diisocyanate
(Isocyanate-Terminated Prepolymer 2)

Blocking group	Blocking reaction temp., °C	Blocking reaction time, hr	Curing time at				Flexural rigidity, mN-mm (curing temp., °C)
			60°C	100°C	120°C	140°C	
Acetoxime	70	0.2	1 day	15 min	10 min	5 min	35 (120)
Butanone oxime	60	6	10 hr	15 min	10 min	5 min	39 (120)
Cyclohexanone oxime	70	2	1 day	30 min	20 min	15 min	47 (120)
Cyclopentanone oxime	60	4	cures during preliminary drying				
Acetophenone oxime	70	2	2 days	1 hr	45 min	15 min	42 (120)
Benzophenone oxime	70	4	5 days	2 hr	1 hr	30 min	24 (120)
di- <i>n</i> -butylamine	20	0.1	7 days	2 hr	1 hr	15 min	45 (140)
Ethanol	20	48	—	—	—	>4 hr	—
<i>t</i> -Butanol	100	4	—	—	—	2 hr	—
2-Aminopyridine	20	4	—	—	—	>4 hr	—
2-Mercaptobenzothiazole			gel formed during blocking reaction				
Nitrone III	20	8			>1 hr	1 hr	—
Nitrone IV	100	2			>1 hr	>2 hr	—
N-Phenylhydroxylamine	20	72			>1 hr	>2 hr	—

tertiary amino group, e.g., 2-aminopyridine and *N,N*-dimethylhydrazine. The basic nitrogen may facilitate crosslinking by catalyzing the isocyanate-alcohol reaction or isocyanate polymerization (reactions that are base catalyzed¹) or may facilitate unblocking. From a kinetic study of some benzophenone oxime-blocked isocyanates, Levine and Fech¹⁰ postulated a cyclic intramolecular reaction (Fig. 3) in which the elimination of an isocyanate was facilitated by participation of the basic group. Similar base-catalyzed eliminations of carbamate esters to isocyanates are known.¹¹ Similar intramolecular or intermolecular reactions may occur with other blocking groups containing basic nitrogens.

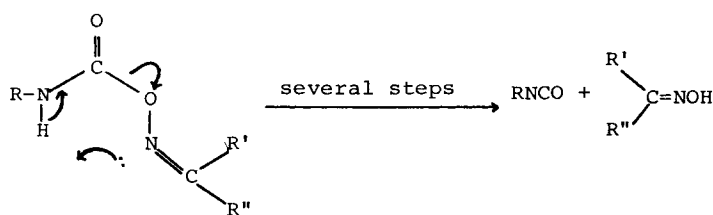


Fig. 3. Intramolecular unblocking reaction.

Influence of Prepolymer Functionality

As curing involves a polyfunctional condensation, the functionality of the reactants would be expected to influence the extent of reaction at the gel point and the extent of crosslinking, which should be reflected in changes in curing times and the properties of the cured polymer. Table I shows some results for prepolymers derived from a poly(propylene oxide) diol, MW = 2000, and a triol, MW = 3000. In both cases the difunctional prepolymers had longer curing times, reflecting the greater extent of reaction required for gelation.¹² This may provide a useful means to vary curing rates. In contrast, in experiments⁷ with a series of bisphenol-A diglycidyl ether crosslinking agents of different molecular weights and hence different hydroxyl functionalities, very little change in curing time was observed provided the ratio of crosslinking agent by weight was constant, although there was a slight increase at very low polyepoxide concentrations.

Blocking by 1,3-Dipolar Cycloaddition Reactions

Isocyanates are usually blocked by reversible addition of compounds containing an acidic hydrogen atom, i.e., compounds of structure HA (Fig. 1). Another isocyanate addition that is known to be reversible^{13,14} is 1,3-dipolar cycloaddition (see Fig. 4), but this does not appear to have been used for blocking

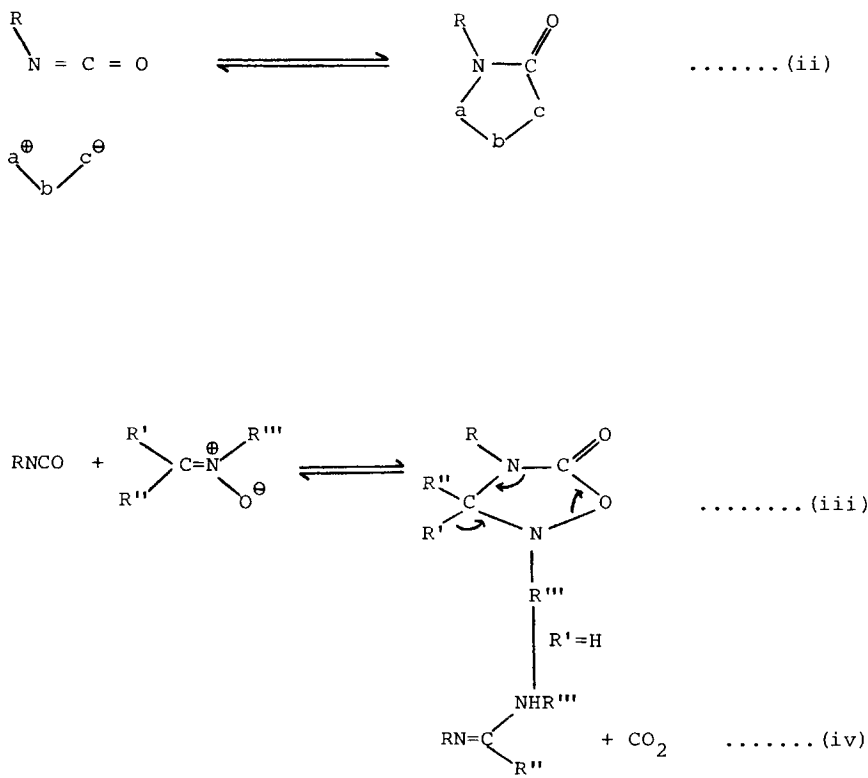


Fig. 4. Blocking of isocyanate-terminated prepolymers by 1,3-dipolar cycloadditions.

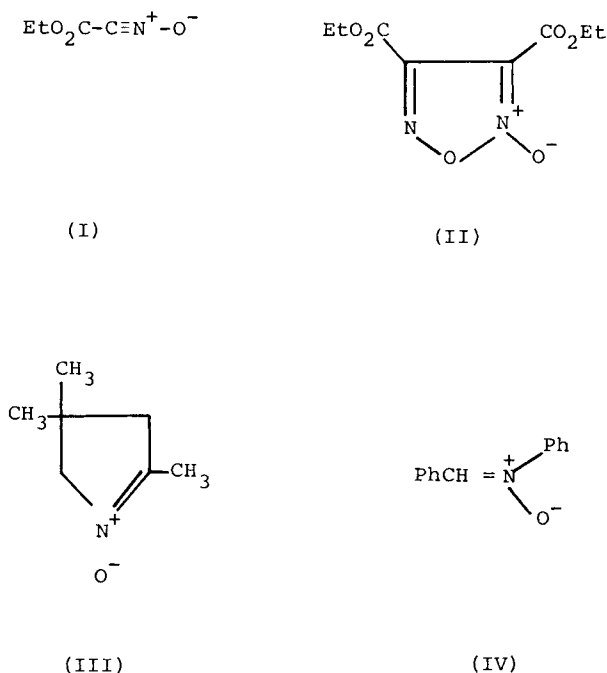


Fig. 4. (Continued from previous page.)

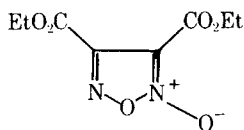
isocyanate-terminated prepolymers. A possible advantage of this type of blocking reaction for use in delayed-cure durable-press treatments is that it may increase the difference between the curing rates at high and low temperatures. Wicks² has considered the thermodynamics of unblocking; an increased rate difference between high and low temperatures should be given by a high activation energy and/or a large positive entropy of activation. The last factor would be expected to be the case in the unblocking of cyclic 1,3-dipolar adducts [reaction (iii), Fig. 4].

Most 1,3-dipolar compounds are either difficult to prepare or are unstable. We found that the reportedly¹⁵ stable nitrile oxide I was in fact the furoxan II by comparison of the infrared spectrum (nujol) with that reported¹⁸ for II and the lack of bands in the region of $2000\text{--}2600\text{ cm}^{-1}$ characteristic of nitrile oxides.¹⁹ The furoxan II did not react with phenyl isocyanate, even when heated in the presence of tertiary amines.

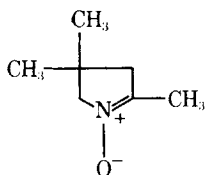
Nitrones form cyclic adducts^{13,14} with isocyanates [reaction (iii), Fig. 4]. The adducts from ketonitrones on heating re-form isocyanates, but those from aldonitrones (particularly pyridine N-oxides) may also decarboxylate [reaction (iv), Fig. 4]. The nitrones III,¹⁶ prepared in two steps from mesityl oxide, and IV¹⁷ derived from N-phenylhydroxylamine were examined. These reacted readily with isocyanate-terminated prepolymers, but the curing times were too low for durable-press use (see Tables III and IV).



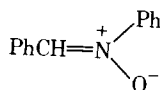
I



II



III



IV

CONCLUSIONS

In the present study directed at finding prepolymers containing blocked isocyanate groups suitable for use in a delayed-cure durable-press process, the curing times were assessed by measuring the ability to hold creases in wool fabric during steam setting. The prepolymer structure, particularly the nature of the blocking group, had a significant influence on the rate of curing and also on the extent of crosslinking, as judged by the differences in stiffness of the treated fabrics (see flexural rigidity results in the tables). Satisfactory curing times (i.e., slow rates at low temperature and curing time of about 30 min at 120°C) for the intended delayed-cure durable-press treatment were only obtained with certain blocking agents, in particular, oximes and certain agents containing a hydroxyl group and a basic nitrogen. More detailed investigation of these prepolymers will be reported at a later stage.⁷

In general, it was not possible to predict curing times at a particular temperature from the prepolymer structure or from curing times at another temperature. To obtain specific curing rates, it was necessary to change empirically the prepolymer structure and other variables, such as catalyst or crosslinking agent concentration. This situation will most likely be the case in other applications of prepolymers containing blocked isocyanate groups.

REFERENCES

1. J. G. Saunders and K. C. Frisch, "Polyurethanes: Chemistry and Technology, Vols. I and II, Interscience, New York, 1962.
2. Z. W. Wicks, *Prog. Org. Coat.*, **3**, 73 (1975).
3. S. Petersen, *Liebigs Ann.*, **562**, 205 (1949).
4. H. D. Feldtman and B. E. Fleischfresser, *Text. Inst. Ind.*, **8**, 249 (1970).
5. B. E. Fleischfresser and G. N. Freeland, *Text. Inst. Ind.*, **14**, 291 (1976).
6. G. B. Guise and M. A. Rushforth, *J. Soc. Dyers Colour.*, **91**, 305 and 325 (1975).
7. G. B. Guise and G. N. Freeland, *J. Text. Inst.*, to appear.
8. G. B. Guise, *J. Appl. Polym. Sci.*, **21**, 3427 (1977).
9. D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.*, **4**, 231 (1975).
10. A. W. Levine and J. Fech, *J. Org. Chem.*, **37**, 1500 and 2455 (1972).
11. A. Williams and K. T. Douglas, *Chem. Rev.*, **75**, 627 (1975).
12. G. B. Guise and M. A. Rushforth, *J. Soc. Dyers Colour.*, **91**, 389 (1975).
13. H. Ulrich, *Cycloaddition Reactions of Heterocumulenes*, Academic Press, New York, 1967, pp. 189-197.
14. E. Van Loock, *Ind. Chim. Belg.*, **39**, 661 (1974).

15. J. Kalvoda and H. Kaufmann, *J. Chem. Soc., Chem. Comm.*, 210 (1976).
16. R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2084 (1959).
17. O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, 78, 3363 (1956).
18. N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, 77, 4238 (1955).
19. R. H. Wiley and G. J. Wakefield, *J. Org. Chem.*, 25, 546 (1960).

Received August 30, 1977

Revised November 15, 1977