Dipolar Solvents in Polyurethane Foams

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Synopsis

A number of catalytic solvents have been discovered for the polyurethane foaming process. These solvents include *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), formamide, and a number of others. The catalytic effectiveness of a given solvent appears to be dependent on its dipole moment, water solubility, and the size or bulkiness of the groups which are attached to the carbonyl carbon or sulfur atom of the amides and sulfoxides, respectively. Steric effects play a very important role in controlling the catalytic efficiency of these solvents. A mechanism is proposed for the catalytic action of these solvents in the polyurethane reaction.

INTRODUCTION

The incorporation of various dipolar solvents into a foam formulation was undertaken in an effort to determine the catalytic effects of these materials in the overall polyurethane flexible foaming process.
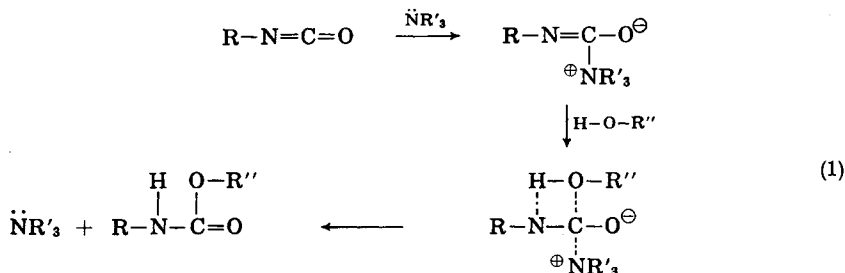
The use of dipolar solvents as reaction media in organic syntheses has been common practice for decades. However, the use of these dipolar compounds for the specific purpose of reaction catalysis is of rather recent origin. Zaugg and his co-workers have, for example, reported a marked accelerating effect of *N,N*-dimethylformamide (DMF) on the alkylation of enolate anions.[1] Kittila has published a review on the catalytic applications of DMF and *N,N*-dimethylacetamide (DMAC).[2] In the same vein, the literature has been reviewed for dimethyl sulfoxide (DMSO) as a catalytic reaction medium by the Crown Zellerbach Corporation.[3] Parker has recently published an excellent review on the topic of dipolar aprotic solvents and their effects on the properties of anions.[4]

The exact nature of dipolar solvent catalysis in an organic reaction mechanism is a rather complicated subject. Ingold's approach to this subject is one of the stabilization of a transition state intermediate by the solvent in question.[5] In general, if two uncharged reacting species form a charged transition state intermediate, then the presence of a dipolar solvent would stabilize this charged intermediate considerably more than a nonpolar solvent. The overall effect of this transition state stabilization would be an increase in the reaction rate.
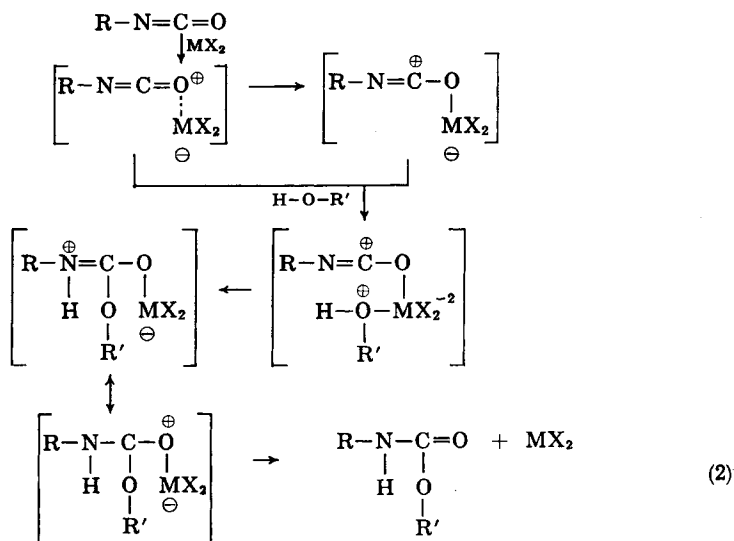
In the case of polyurethane chemistry, a number of workers such as Britain and Gemeinhardt[6] have proposed just such a case as described

above. A highly charged transition state was postulated for both the amine- and metal-catalyzed isocyanate–hydroxyl reaction, as shown in eqs. (1) and (2).

Amine-catalyzed:

$$R-N=C=O \xrightarrow{\ddot{N}R'_3} \begin{array}{c} R-N=C-O^\ominus \\ | \\ {}^{\oplus}NR'_3 \end{array}$$

$$\Big\downarrow {}_{H-O-R''}$$

$$\ddot{N}R'_3 + \begin{array}{c} H \;\; O-R'' \\ | \;\;\;\; | \\ R-N-C=O \end{array} \quad\longleftarrow\quad \begin{array}{c} H-O-R'' \\ \vdots \\ R-N-C-O^\ominus \\ {}^{\oplus}NR'_3 \end{array} \tag{1}$$

Metal-catalyzed:

$$R-N=C=O$$
$$\Big\downarrow MX_2$$

$$\left[\begin{array}{c} R-N=C=O^\oplus \\ \vdots \\ MX_2 \\ \ominus \end{array} \right] \longrightarrow \left[\begin{array}{c} {}^{\oplus} \\ R-N=C-O \\ | \\ MX_2 \\ \ominus \end{array} \right]$$

$$H-O-R' \Big\downarrow$$

$$\left[\begin{array}{c} {}^{\oplus} \\ R-N=C-O \\ | \;\; | \;\; | \\ H \;\; O \;\; MX_2 \\ | \;\; \ominus \\ R' \end{array} \right] \longleftarrow \left[\begin{array}{c} {}^{\oplus} \\ R-N=C-O \\ {}^{\oplus}| \\ H-O-MX_2^{-2} \\ | \\ R' \end{array} \right]$$

$$\updownarrow$$

$$\left[\begin{array}{c} {}^{\oplus} \\ R-N-C-O \\ | \;\; | \;\; | \\ H \;\; O \;\; MX_2 \\ | \;\; \ominus \\ R' \end{array} \right] \quad\rightarrow\quad \begin{array}{c} R-N-C=O \;\; + \;\; MX_2 \\ | \;\; | \\ H \;\; O \\ | \\ R' \end{array} \tag{2}$$

If the reaction scheme proposed by Britain and Gemeinhardt or more recently by Smith[7] were correct, then dipolar solvents would be expected to accelerate the polyurethane polymerization reaction. Moreover, these dipolar solvents would be expected to be catalytic towards the polyurethane foaming reaction, even though many of these compounds are powerful solvents for the foamed elastomer. The present study with dipolar solvents in polyurethane foams apparently confirms the concept of a highly charged transition state intermediate as postulated above. This confirmation was not complete, however, as all solvents with a high dipole moment did not increase the reaction rate in the foaming process. Certain dipolar compounds were found to be markedly catalytic while others were not. The catalytic selectivity of a number of these solvents in the polyurethane

foaming process was quite unexpected. This subject will be discussed more fully in a later section of this paper.
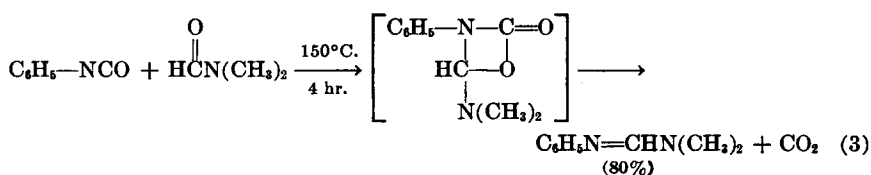
The use of various solvents for the making of polyurethane elastomers, coatings, and fibers is old to the polyurethane art. The use of dipolar solvents as an integral part of a flexible foam formulation is new, and it was observed that certain dipolar compounds, such as dimethyl sulfoxide and N,N-dimethylformamide, will not only catalyze the foaming reaction, as evidenced by the decrease of bun rise time with increasing solvent concentration, but these compounds (solvents) will greatly extend the operating range of the metal catalyst for a given polyol system.

In a recent review by Saunders and Frisch, it was concluded that the use of dipolar solvents in a polyurethane reaction would be expected to provide a slower overall rate.[8] It was further pointed out, in support of this conclusion, that in extreme cases these dipolar solvents may even react with the isocyanate used as in the cases of DMF, DMAC, and DMSO.

Saunders and Frisch apparently based their conclusion on the kinetic work of Ephraim and co-workers,[9] who found a 71-fold decrease of the rate of the phenyl isocyanate-methanol reaction when the solvent was changed from toluene to acetonitrile. These observations were confirmed generally by a number of other workers, though not in the same degree.[8b]

Amides and sulfoxides do indeed react with isocyanates, but these reactions occur at relatively high temperatures and over long periods of time. Contrast these conditions with the approximate 90 sec. time period required to make a polyurethane flexible foam.

Weiner[10] has reported the reaction of N,N-dimethylformamide and phenyl isocyanate, at 150°C. for 4 hr., to yield carbon dioxide and an amidine.

$$C_6H_5-NCO + H\overset{O}{\overset{\|}{C}}N(CH_3)_2 \xrightarrow[4\ hr.]{150°C.} \begin{bmatrix} C_6H_5-N-C=O \\ HC-O \\ N(CH_3)_2 \end{bmatrix} \longrightarrow$$

$$C_6H_5N=CHN(CH_3)_2 + CO_2 \quad (3)$$
$$(80\%)$$

An example of an isocyanate–sulfoxide reaction was reported by Sorenson[11] for the reaction of benzoic acid and phenyl isocyanate in refluxing dimethyl sulfoxide (190°C.) for 16 hr.

$$ArNCO + ArCOOH \xrightarrow[190°/16\ hr.]{(CH_3)_2SO} ArNHCOOCOAr \xrightarrow{(CH_3)_2SO}$$

$$(ArNHCO_2^{\ominus})\ [(CH_3)_2S \rightarrow OCOAr^{\oplus}] \rightarrow$$

$$ArNHCOOH + \begin{bmatrix} O \\ CH_3-S \rightarrow O\overset{\|}{C}Ar \\ CH_2 \end{bmatrix}$$
$$Ar\overset{\downarrow}{N}H_2$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$ArNHCONHAr \qquad CH_3SCH_2OCOAr \quad (4)$$
$$(70\%\ isolated) \qquad (50\%\ isolated)$$
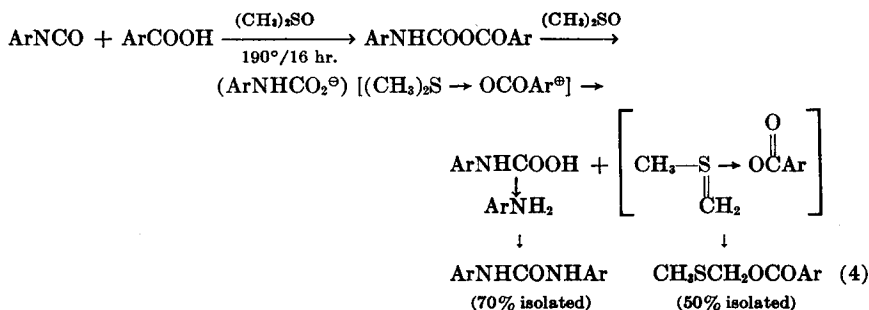
For purposes of reference, a compilation of the electric moments of a number of compounds is found in Table I. The compounds listed are representative of the various classes of organic compounds evaluated as catalysts in the making of polyurethane flexible foams.

TABLE I
Electric Moments of Various Compounds

Compound	Electric moment μ, D.	Reference
Dimethyl sulfoxide	4.3	12
Diethyl sulfoxide	3.85	13
Diphenyl sulfoxide	4.05	13
Diisobutyl sulfoxide	3.9	12
Formamide	3.86	14
N,N-Dimethylformamide	3.82	2a
Acetamide	3.90	14
N,N-Dimethylacetamide	3.79	15
Propionamide	3.85	14
Benzamide	3.84	14
2-Pyrrolidinone	4.2	16
1-Methyl-2-pyrrolidinone	4.1	17
Oxazolidone	5.1	16
Urea	4.56	18
Thiourea	4.89	18
Cyanamide	4.52	19
Diisopropylcyanamide	4.76	19
Dicyanamide	8.16	19
Tetrahydrothiophene 1,1-dioxide	4.69	20
Acetone	2.72	21
2-Butanone	2.75	21
Benzaldehyde	2.77	21
Acetonitrile	3.37	21
Methacrylonitrile	3.69	21
Benzonitrile	4.05	21
Nitrobenzene	3.99	21
o-Nitroanisole	4.81	21
m-Xylene	0.37	21

EXPERIMENTAL

Dipolar Compounds

The dipolar compounds used in this study were commercial grade materials obtained through standard laboratory supply houses. There appeared to be very little difference between specially purified and commercially available reagents in their catalytic response to the polyurethane reaction. For example, commercial grade DMF was found to be virtually free from amine impurities by its alkalinity analysis, and, the catalytic response of specially purified DMF (2 hr. reflux over P_2O_5 followed by distillation) was comparable with the commercial grade material (Table IV).

The dipolar compounds were in all cases considered as inert additives and evaluated as such in a standard flexible foam formulation (Table II).

TABLE II
Polyurethane Fexible Foam Formulation

Component	Wt., g.
Polyol (NIAX triol LG-56)[a][b]	100
Tolylene diisocyanate (80/20)[b]	44.6[c]
Water	3.50
Silicone L-520[d]	2.00
N,N,N',N'-Tetramethyl-1,3- butanediamine	0.10
Stannous octoate	Indicated in Tables
Additive	Indicated in Tables

[a] NIAX triol LG-56: a 3000 average molecular weight triol, an adduct of 1,2-propylene oxide to glycerol, made by the Union Carbide Corporation.

[b] Tolylene diisocyanate (80/20): a commercial grade of tolylene diisocyanate comprising an 80/20 mixture of the 2,4 and 2,6 isomers of tolylene diisocyanate, made by the Mobay Chemical Company.

[c] 5% excess for a 56-hydroxyl no. polyol.

[d] Silicone L-520: a flexible foam surfactant made by the Union Carbide Corporation.

The solvent additive was usually premixed with the polyol prior to foaming. However, the solvent may be mixed with any of the other formulation components prior to, or during, the foaming operation without appreciable variance in foam rise time or difference in final foam properties. The foaming procedure is found below.

Catalysis by an additive compound is indicated by a decrease in foam bun rise time over the control. The compounds evaluated in this study are tabulated under their respective chemical group classes. NIAX triol LG-56, a polyoxypropyl triol having an average molecular weight of 3000, was the polyol used for these evaluations (Tables III–IX).

Foaming Procedure

The polyol, silicone surfactant, water, N,N,N',N'-tetramethyl-1,3-butane-diamine (unless otherwise noted), and solvent catalyst (unless otherwise noted) were mixed, using an air-driver stirrer, in a 2-liter stainless steel beaker for a period of 55 sec. The metal catalyst was then added, and the mixture stirred for an additional 5 sec. before the isocyanate was added. Stirring was continued for a 5–8 sec. time period, after which time this mixture was poured into a cardboard mold, whereupon the mass foamed to its full height (rise time defined as time from first adding the isocyanate to the end of bun rise). The foam was then cured overnight at room temperature before testing.

Foam Testing Procedures

The foam samples were tested according to standard ASTM methods.

Normalized ILD

This is the load bearing value at unit density, obtained by dividing the 25% ILD figure by the foam density.

TABLE III

Sulfoxides: $\begin{array}{c} R_1 \\ \diagdown \\ R_2 \end{array} S \rightarrow O$

Sulfoxide	R_1	R_2	Sn oct, phr	Hand foam rise times (for various compound concns. in formulation), sec.						
				0.0 phr	2.5 phr	5.0 phr	7.5 phr	10 phr	15 phr	20 phr
Dimethyl sulfoxide	CH₃—	CH₃—	0.30	88	—	—	—	68	—	—
Tetramethylene sulfoxide[a]	—CH₂CH₂CH₂CH₂—		0.40	74	72	66	61	57	53	53[b]
Diisobutyl sulfoxide	(CH₃)₂CHCH₂—	(CH₃)₂CHCH₂—	0.30	88	—	—	88	67	—	—
Di-n-butyl sulfoxide	CH₃(CH₂)₃—	CH₃(CH₂)₃—	0.30	88	—	—	—	72	—	—
Di-p-tolyl sulfoxide[c]	H₃C—⟨phenyl⟩	H₃C—⟨phenyl⟩	0.30	88	—	—	—	94	—	—
Di-4-chlorophenyl sulfoxide[c]	Cl—⟨phenyl⟩	Cl—⟨phenyl⟩	0.30	88	—	—	—	94	—	—
Dibenzyl sulfoxide[c]	⟨phenyl⟩—CH₂—	—CH₂—⟨phenyl⟩	0.30	89	—	—	124	—	—	—
Diphenyl sulfoxide[c]	⟨phenyl⟩	⟨phenyl⟩	0.30	89	—	—	>500	—	—	—
Bis(2-hydroxyethyl) sulfoxide[d]	HO(CH₂)₂	HO(CH₂)₂	0.35	78	—	100[e]	—	120[e]	—	—

[a] Solid dissolved in polyol, cooled to 25°C., then foamed.
[b] Foam badly split.
[c] Solid dissolved in polyol, cooled to 25°C., some solid pptd. out of soln., foamed as such.
[d] Added as a solid, foamed as such.
[e] Foam was a shrinker.

DISCUSSION OF RESULTS

Solvent Catalysts

An examination of the data in Tables III–IX allows several general conclusions.

Compounds which show catalysis have a dipole moment of 3.7 or more Debye units, and generally have great water solubility.

The bulkiness of the groups attached to the nitrogen or sulfur atom determines the catalytic effectiveness of the amides and sulfoxides, respectively.
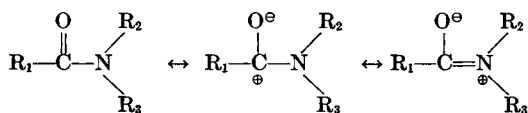
In general, the smaller the group the more effective the compound is as a catalyst. Thus, at a 10 phr level, the catalytic efficiency of the formamide series was as follows: formamide > N-methylformamide > N,N-dimethylformamide > no solvent present or N,N-diethylformamide > N-methylformanilide > N-formylpiperidine (Table IV). A similar trend was indicated for the catalytic effectiveness of the sulfoxide series: dimethyl sulfoxide or tetramethylene sulfoxide > di-n-butyl sulfoxide > diisobutyl sulfoxide or no solvent present > dibenzyl or diaromatic sulfoxides (Table III). This steric trend was apparent for the cyclic amides (Table VII). In the series where R_1 was —$CH_2CH_2CH_2$—, the catalytic effectiveness was in the order of (R_2): H— > CH_3— > CH_2=CH—. The steric effect in ring size was also apparent in the cyclic amides, where the catalytic effectiveness was in the order of +(CH_2)_3 > +(CH_2)_5. This steric effect was also exhibited in the formyl toluidine series. In this case, the position of the ring methyl group exerts its bulk effect and subsequent reduction of catalytic effectiveness in the order of *ortho* or *meta* > *para* (Table VI). The urea series also shows a bulk or steric effect, the catalytic effectiveness being in the order of: H_2N— > $(CH_3)HN$— > $(CH_3)_2N$— (Table VIII). The bulkiness of the group attached to the amide carbon atom also determines the catalytic effectiveness of the compound. On comparing the data for formamide, acetamide, propionamide, and benzamide, the decrease in catalytic effectiveness is not as readily apparent as comparing the N-methyl derivatives of these alkyl amides. In the latter case, the series is clearly H— > CH_3— > CH_3CH_2— for the order of the catalytic effectiveness.

Mechanism of Catalysis: Amides and Sulfoxides

From the observations above, a postulation of catalysis for both the amides and sulfoxides is possible.
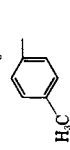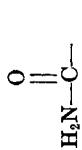
First it would be well to examine the extreme resonance structure for the amide, sulfoxide, and isocyanate molecules.
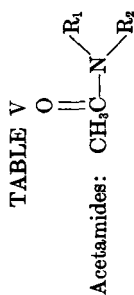
Amide:

TABLE IV

Formamides: $\underset{\displaystyle HCN}{\overset{\displaystyle O}{\|}}\diagdown\!\!\!\begin{smallmatrix}R_1\\R_2\end{smallmatrix}$

| Formamides | R_1 | R_2 | Sn oct, phr | Hand foam rise times (for various compound concns. in formulation), sec. | | | | | | | | | | |
				0.0 phr	2.5 phr	5.0 phr	7.5 phr	10 phr	15 phr	20 phr	25 phr	30 phr	40 phr	50 phr
Formamide	H—	H—	0.30	89	67	57	—	54	56	—	—	—	—	—
N-Methylformamide	CH₃—	H—	0.40	72	57	50	—	45	46	49	53	57	64	71
N-Ethylformamide	CH₃CH₂—	H—	0.30	89	—	76[a]	—	71[a]	69[a]	—	—	—	—	—
	C_6H_5—	H—	0.35	76	—	74[a]	—	69[a]	66[a]	—	—	—	—	—
Formanilide	C_6H_5—	H—	0.30	86	—	84	—	85	85[a]	—	—	—	—	—
N,N-Dimethylformamide[b,c]	CH₃—	CH₃—	0.35	91	—	85[a,c]	—	82[a,c]	—	74[a,c]	—	—	—	—
	CH₂CH₃—		0.30	85	—	80[a,b]	—	76[a,b]	—	69[a,b]	—	—	—	—
N,N-Diethylformamide	CH₂CH₃—	CH₃CH₂—	0.30	83	—	—	—	100[a]	—	—	—	—	—	—
N-Methylformanilide	C_6H_5—	CH₃—	0.30	83	—	87[a]	—	92[a]	—	—	—	—	—	—
N-Formylpiperidine	—CH₂CH₂CH₂CH₂CH₂—		0.40	72	—	114	—	123	123[a]	—	—	—	—	—

Compound	Structure												
N-Formyl-o-toluidine	H—	0.30	80	—	79	—	80[a]	80[a]	—	—	—	—	—
N-Formyl-m-toluidine	H—	0.40	72	—	71	—	73	76	—	—	—	—	—
N-Formyl-p-toluidine	H—	0.30	80	—	76	—	77	80	—	—	—	—	—
Formylhydrazine	H₂N— H—	0.35	76	—	>300[d]	—	—	—	—	—	—	—	—
		0.40	72	—	—	—	>300[d]	—	—	—	—	—	—
N,N-Diphenylformamide		0.30	80	—	—	85	—	—	—	—	—	—	—
Formylurea	H₂N—C(=O)— H—	0.30	80	—	>500[d]	—	—	—	—	—	—	—	—

[a] Foam badly split.
[b] Purified by refluxing over P_2O_5 for 2 hr., followed by distillation at atmospheric pressure.
[c] Commercial grade.
[d] Total bun collapse.

TABLE V

Acetamides: $CH_3C(=O)-N\begin{smallmatrix}R_1\\R_2\end{smallmatrix}$

Acetamide	R_1	R_2	Sn oct. phr	Hand foam rise times (for various compound concns. in formulation), sec.						
				0.0 phr	2.5 phr	5.0 phr	7.5 phr	10.0 phr	15 phr	20 phr
Acetamide[a]	H—	H—	0.30	82	69	67	—	68	74	76
N-Methylacetamide	CH₃—	H—	0.30	83	—	73	—	68[b]	74[b]	67[b]
N,N-Dimethylacetamide	CH₃—	CH₃—	0.40	74	—	170[b]	—	180[b]	—	—
N,N-Diethylacetamide	CH₃CH₂—	CH₃CH₂—	0.30	82	—	—	—	135[b]	—	—
Acetanilide[a]	⬡	H—	0.30	82	—	100	—	110	120	—

a Added as a solid, foamed as such.
b Foam badly split.

TABLE VI

Propionamides: $CH_3CH_2C(=O)-N\langle {}^{R_1}_{R_2}$
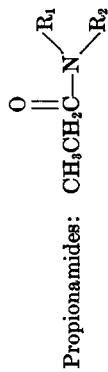
Propionamide	R_1	R_2	Sn oct, phr	Hand foam rise times (for various compound concns. in formulation), sec.						
				0.0 phr	2.5 phr	5.0 phr	7.5 phr	10.0 phr	15 phr	20 phr
Propionamide[a]	H—	H—	0.30	83	—	53[b]	—	50[b]	53[b]	—
N-Methylpropionamide	CH₃—	H—	0.30	86	—	85	—	84	88	112[b]
N,N-Dimethylpropionamide	CH₃—	CH₃—	0.30	86	—	90	—	93[b]	94[b]	—

[a] Added as a solid, foamed as such.
[b] Foam badly split.

TABLE VII

Cyclic Amides: R_1—(ring with)—N—R_2, $C{=}O$

Cyclic amide	R_1	R_2	Sn oct, phr	Hand foam rise times (for various compound concns. in formulation) sec.						
				0.0 phr	2.5 phr	5.0 phr	7.5 phr	10.0 phr	15 phr	20 phr
2-Pyrrolidinone	$-CH_2CH_2CH_2-$	$H-$	0.30	81	—	54[a]	—	44[a]	37[a]	37[a]
1-Methyl-2-pyrrolidinone[b,c]	$-CH_2CH_2CH_2-$	CH_3-	0.30	89	—	83[b]	—	74[b]	71[a,b]	—
	$-CH_2CH_2CH_2-$	CH_3-	0.35	82	—	71[c]	—	67[c]	—	64[a,c]
1-Vinyl-2-pyrrolidinone	$-CH_2CH_2CH_2-$	$CH_2{=}CH-$	0.40	98	—	93	—	96[a]	93[a]	—
2-Oxazolidone[d]	$-CH_2CH_2O-$	$H-$	0.30	86	—	87	—	91[a]	—	—
2-(1H)-Pyridone[d]	$-CH{=}CH-CH{=}CH-$	$H-$	0.30	83	—	77	—	76	—	—
2-Oxohexamethyleneimine[d]	$-CH_2CH_2CH_2CH_2CH_2-$	$H-$	0.30	83	—	62	—	58	55[a]	56[a]

[a] Foam badly split.
[b] Purified by refluxing over P_2O_5 for 2 hr., followed by distillation at atmospheric pressure.
[c] Commercial grade.
[d] Added as a solid, foamed as such.

Sulfoxide:

Isocyanate:

$$R—N=C=O \leftrightarrow R—\underset{\ominus}{N}—\underset{\oplus}{C}=O \leftrightarrow R—N=\underset{\oplus}{C}—\underset{\ominus}{O}$$
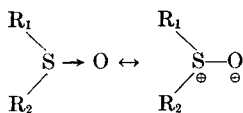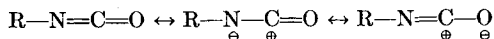
An inspection of these structures for the amide and sulfoxide groups indicates, in both cases, a resonance hybrid having a partial negative charge (high electron density) on the oxygen atom. Whereas the resonance hybrid for an isocyanate molecule has a partial positive charge (high electron deficiency) on the carbon atom in the —NCO group.

The proposed mechanism for the amide and, or, sulfoxide catalysis in a polyurethane reaction is outlined in eqs. (5).

(5)
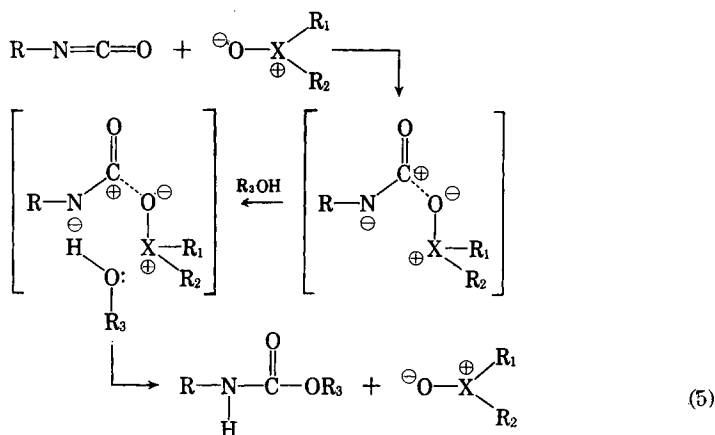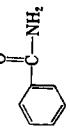
The oxygen atom of the amide or sulfoxide first coordinates on the isocyanate carbon, thus aiding in the generation and stabilization of a negative charge on the isocyanate nitrogen atom. The water or alcohol reactant must then approach this transition state to yield its proton to the negatively charged nitrogen. The electrons on the hydroxyl oxygen might then coordinate with the positively charged X atom (carbon or sulfur), to form a six-membered ring transition state, before the reaction goes to completion. The groups attached to either the sulfur or nitrogen atom [sulfoxides or amides, respectively, represented by XR_1R_2 in the mechanism of eq. (5)], would provide steric bulk, thus interfering in the approach of the hydroxyl group. The larger these groups are, the less effective would be the solvent catalyst.

In support of this mechanism was the observation that a stable polyurethane flexible foam could be made without metal or amine catalysts,

TABLE VIII
Ureas, Acrylamides, and Miscellaneous Amides and Thioamides

Compound	Compound structure	Sn oct, phr	Hand foam rise times (for various compound concns. in formulation), sec.						
			0.0 phr	2.5 phr	5.0 phr	7.5 phr	10.0 phr	15 phr	20 phr
Ureas									
Urea[a] (1)	$H_2N-C(=O)-NH_2$	0.30	86	—	66	—	67	66	—
N,N'-Dimethylurea[a]	$H_3C-N(H)-C(=O)-N(H)-CH_3$	0.30	82	—	76	—	77	76	—
Tetramethylurea	$(H_3C)_2N-C(=O)-N(CH_3)_2$	0.30	82	—	78	—	—	—	—
Acrylamides									
Acrylamide[a]	$CH_2=CH-C(=O)-NH_2$	0.30	86	—	76[b]	—	68[b]	68[b]	—
Methacrylamide[a]	$CH_2=C(CH_3)-C(=O)-NH_2$	0.30	86	—	72[b]	—	68[b]	66[b]	—

Compound	Structure								
N,N-Dimethylacrylamide	$CH_2=CH-C(=O)-N(CH_3)_2$	0.30	86	—	84	—	85	91[b]	—
N,N-Diallylacrylamide	$CH_2=CH-C(=O)-N(CH_2-CH=CH_2)_2$	0.30	86	—	85	—	94	93	—
Miscellaneous Amides and Thioamides									
Benzamide[a]	$C_6H_5-C(=O)-NH_2$	0.30	83	—	115[c]	—	130[b]	180[c]	—
Ethyl Carbamate	$CH_3CH_2O-C(=O)-NH_2$	0.30	80	—	77	—	79[b]	80[b]	—
Thioacetamide[a]	$CH_3-C(=S)-NH_2$	0.30	82	—	>500[d]	—	—	—	—
Thiourea[a]	$H_2N-C(=S)-NH_2$	0.30	82	—	82	—	86	—	—

[a] Added as a solid, foamed as such.
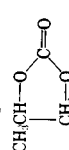[b] Foam badly split.
[c] Foam was a shrinker.
[d] Total bun collapse.

TABLE IX
Miscellaneous Organic Compounds

Compound	Compound structure	Sn oct, phr	Hand foam rise times (for various compound concns. in formulation), sec.						
			0.0 phr	2.5 phr	5.0 phr	7.5 phr	10 phr	15 phr	20 phr
Nitriles									
Acetonitrile	CH_3-CN	0.40	74	—	94[a]	—	120[a]	—	—
Acrylonitrile	$CH_2=CH-CN$	0.35	83	95[a]	120[a]	—	—	—	120[b]
Methacrylonitrile	$CH_2=C-CN$ CH_3	0.30	86	87	100	—	144[b]	—	—
Nitro compounds:									
Nitromethane	CH_3-NO_2	0.35	82	—	>500[b]	—	>500[b]	—	—
Nitrobenzene	$-NO_2$ (benzene ring)	0.40	79	—	>500[b]	—	>500[b]	—	—
Sulfones									
Dimethyl sulfone	$(CH_3)_2SO_2$	0.35	83	—	83	—	93[a]	—	—
Butadiene sulfone	SO_2 (ring)	0.35	83	—	83	—	100[a]	—	—
Tetrahydrothiophene 1,1-dioxide	SO_2 (ring)	0.35	82	—	82	—	93[a]	—	—
Sulfides									
Tetrahydrothiophene	S (ring)	0.30	86	—	89[a]	—	96[a]	107[b]	—
Thiophene	S (ring)	0.30	87	—	91[a]	—	108[a]	119[b]	—

Cyanamides									
Cyanamide[c]	0.30	82	—	>500[b]	—	—	—	—	—
Dimethylcyanamide	$(CH_3)_2N-CN$	0.30	82	—	84	—	93[a]	—	100[b]	—
Diethylcyanamide	$(CH_3CH_2)_2N-CN$	0.30	82	—	86[a]	—	93[a]	—	—	—
Diisopropylcyanamide	$[(CH_3)_2CH]_2N-CN$	0.30	82	—	130	—	130	—	150	—
Dicyanamide[c]	$H_2N-C-NH-CN$	0.35	78	—	83	—	83	—	83	83
Miscellaneous compounds									
o-Xylene	0.40	84	—	115[a]	—	120[a]	—	125[a]	136[b]
	0.40	95	—	107[a]	—	116[a]	—	—	117[b]
	1.60	52	—	54	—	60	—	—	55[a]
Acetone	$(CH_3)_2C=O$	0.40	74	—	94[b]	—	110[b]	—	—	—
Propylene carbonate	0.40	74	—	90	—	105[a]	—	—	—
2,5-Dihydrofuran	0.30	87	—	120[a]	—	>500[b]	—	>500[b]	—
Hexamethyl phosphoramide	$[(CH_3)_2N-]_3P=O$	0.35	82	72	79[d]	—	—	—	—	—
Formamide acetate[c]	$NH=CH-NH_2 \cdot CH_3CO_2H$	0.30	86	—	150	—	180	—	210	—

[a] Foam badly split.
[b] Total bun collapse.
[c] Added as a solid, foamed as such.
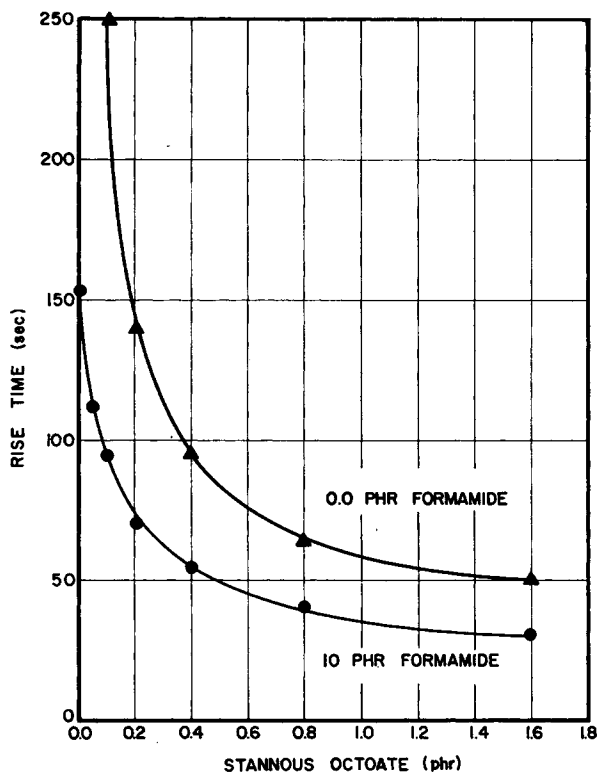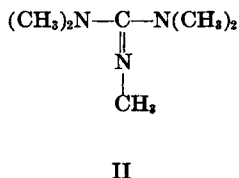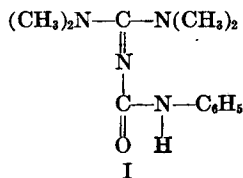[d] Severe bun shrinkage.

Fig. 1. Effect of stannous octoate concentration on foam rise time at a constant form-amide concentration (no other catalysts used in formulation).

using 10 phr formamide in the formulation (Fig. 1). A stable foam could not be made without formamide or other catalysts.

The recent observation by Flynn and Nenortas[22] of the greater catalytic activity of the carbanilide of 1,1,3,3-tetramethylguanidine (I) over penta-methylguanidine (II), towards a urethane reaction, might be explained by the catalytic contribution of the amide group present in I.

$$(CH_3)_2N—C—N(CH_3)_2$$
$$\|$$
$$N$$
$$|$$
$$C—N—C_6H_5$$
$$\| \quad |$$
$$O \quad H$$
$$I$$

$$(CH_3)_2N—C—N(CH_3)_2$$
$$\|$$
$$N$$
$$|$$
$$CH_3$$
$$II$$

The polyurethane foaming reaction appears to be highly specific as to the types of compounds which will be both catalytic and compatible with the foam system. Nitro compounds were extremely efficient in their poisoning effects toward stannous catalysts, and to a lesser extent, were the nitriles, sulfides, ketones, sulfones, cyanamides, and nonpolar solvents.

The catalytic solvents of this study are generally considered as nonbasic. Formamide, for example, has been reported to be a weaker base than water.[21]

It was found that impurities contained in the compounds under study generally did not contribute to the catalytic response.   For example, it was shown that in the case of tetramethylene sulfoxide (Table III), both the corresponding sulfone and sulfide were noncatalytic (Table IX).

Utility and Properties of Solvent-Containing Foams

Three catalytic solvents were studied in detail for their properties and utility in polyurethane flexible foams; namely, formamide, dimethyl sulfoxide, and N,N-dimethylformamide.
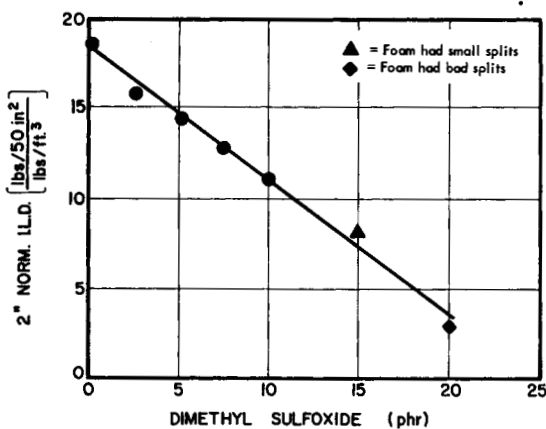

Fig. 2. Effect of dimethyl sulfoxide concentration on normalized indentation load deflection.
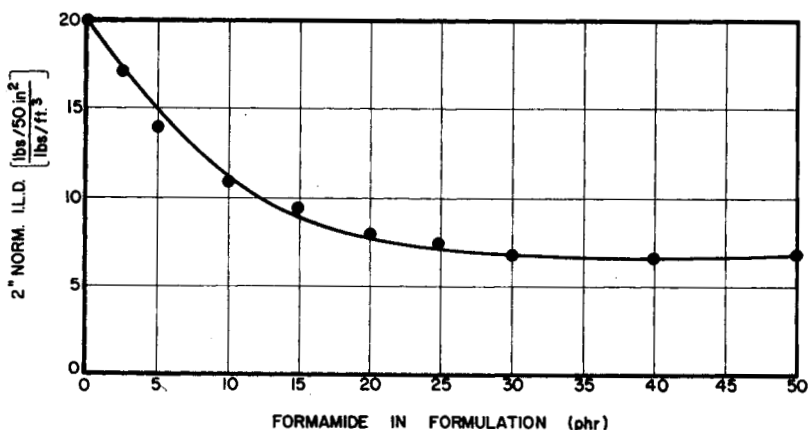

Fig. 3. Effect of formamide concentration on normalized indentation load deflection.
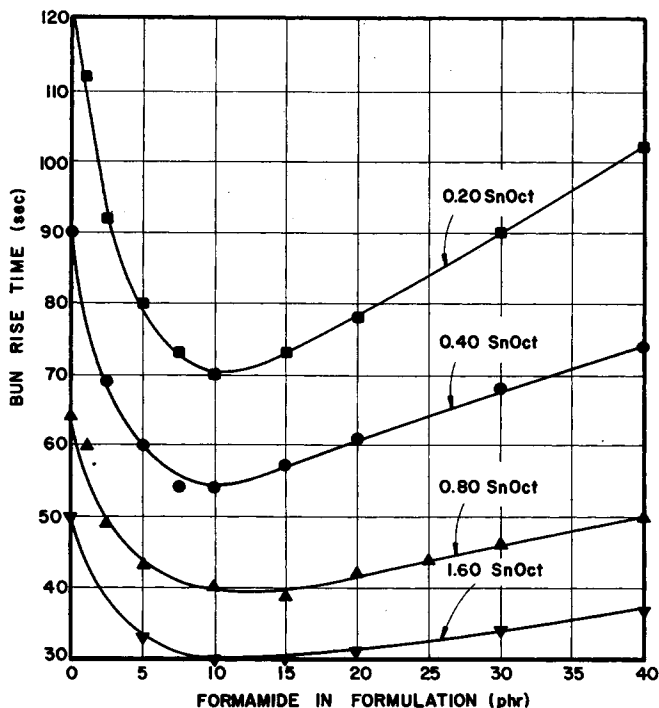
Fig. 4. Effect of various levels of stannous octoate on bun rise time and formamide concentration (no amine catalyst in formulation).

Dimethyl Sulfoxide (DMSO). The polyurethane foam data show the load bearing ability to be inversely proportional to the concentration of the DMSO contained therein (Fig. 2).

TABLE X
Effect of DMF at a 10:1 Ratio of DMF to Stannous Octoate[a]

Dimethyl formamide, phr	0	10	15	20	30	40	50	100	150
Stannous octoate, phr	0.40	1.00	1.50	2.00	3.00	4.00	5.00	10.00	15.00
Rise time, sec.	84	45	37	33	29	31	33	60	70
Tensile, psi	14.7	15.8	16.6	13.9	16.5	17.8	23.9	5.28	6.40
Elongation, %	119	174	185	160	206	210	250	170	138
Density, pcf	1.71	1.57	1.53	1.54	1.52	1.57	1.70	2.75	5.03
2 in. ILD, lb./50 in.^{2}									
25%	34.9	18.4	16.6	13.4	10.8	8.7	7.9	—	—
65%	64.3	37.8	33.2	27.5	22.1	19.0	20.6	—	—
Resiliency, %	37	36	34	35	32	37	38	—	—
Foam quality	OK	OK	OK	OK	OK	OK	OK	b	b

[a] Polyol used was NIAX triol L9-56.
[b] Open cells but severe shrinkage on standing.

Formamide (FA). The response of foam properties to formamide concentration was most unusual. The foam load properties decreased with increasing formamide concentration (Fig. 3). The data show a minimum of foam rise time occurring at about 10 phr formamide level, with or without a tertiary amine present in the formulation and at various constant levels of metal catalyst (Fig. 4). Moreover, this rise time minimum is constant with variations of formulation components, such as water (Fig. 5), polyol composition, amount of TDI, or silicone surfactant. Other solvents in this study which exhibited an apparent rise time minimum at a
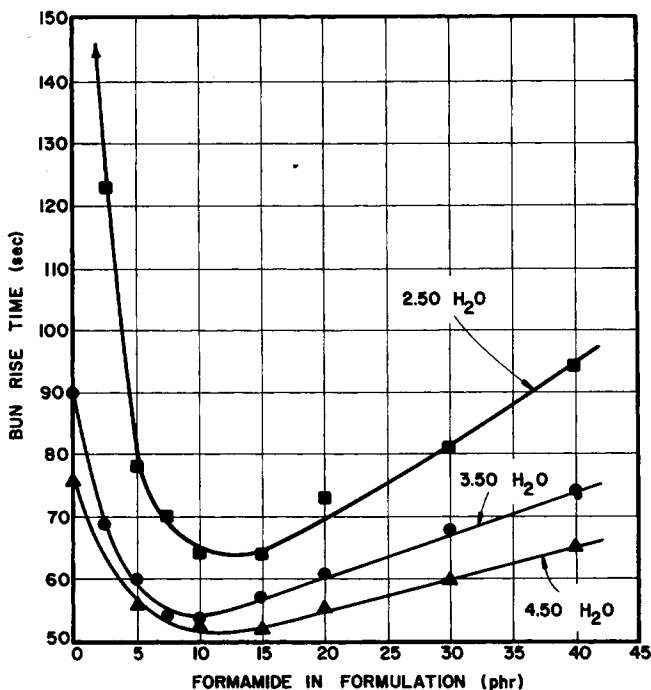

Fig. 5. Effect of various levels of water on bun rise time and formamide concentration (no amine catalyst in formulation).

constant metal catalyst level include: propionamide, N-methylpropion-amide, acetamide, and N-methylacetamide.

N,N-Dimethylformamide (DMF). The foam catalyst operating range of any given polyol composition may be greatly extended with the use of a 10 to 1 ratio of DMF to metal catalyst. Stable foams have been made, for example with up to 150 phr DMF and 15.0 phr stannous octoate in the formulation (Table X).

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Résumé

Un certain nombre de solvants catalytiques a été découvert pour la fabrication de mousse de polyuréthanne. Ces solvants sont le *N,N*-diméthylformamide (DMF), le diméthylsulfoxide (DMSO), le formamide et d'autres encore. L'efficacité catalytique d'un solvant donné semble dépendre de son moment dipolaire, de sa solubilité dans l'eau, du volume ou de l'encombrement des groupes qui sont attachés au carbone carbonylé ou à l'atome de soufre des amides et sulfoxydes respectivement. Les effets stériques jouent un très grand rôle dans le contrôle de l'efficacité catalytique de ces solvants. Un mécanisme est proposé pour l'action catalytique de ces solvants dans la réaction des polyuréthannes.

Zusammenfassung

Für den Polyurethan-Schäumungsprozess wurde eine Anzahl katalytischer Lösungsmittel entdeckt. Dazu gehören *N,N*-Dimethylformamid (DMF), Dimethylsulfoxyd (DMSO), Formamid und eine Reihe anderer Stoffe. Die katalytische Wirksamkeit eines gegebenen Lösungsmittels scheint von seinem Dipolmoment, seiner Wasserlöslichkeit und der Grösse oder Raumbeanspruchung der Gruppen, welche sich am Carbonylkohlenstoff oder Schwefelatom der Amide bzw. Sulfoxyde befinden, abzuhängen. Sterische Effekte spielen für die katalytische Wirksamkeit dieser Lösungsmittel eine sehr bedeutende Rolle. Ein Mechanismus für die katalytische Wirkung dieser Lösungsmittel bei der Polyurethanreaktion wurde vorgeschlagen.