

Polyurethane Latex

STUART P. SUSKIND,* *Research Division, W. R. Grace and Co.,
Clarksville, Maryland*

Synopsis

A technique has been developed for preparing stable, film-forming, polyurethane latices without the use of emulsifying agents. The reaction of an alkyl diethanolamine with a stoichiometric excess of an isocyanate terminated prepolymer yields a relatively low molecular weight urethane which is readily dispersed with 3% aqueous acetic acid. When small amounts of triethanolamine are employed as a third reactant, the self-emulsifiable urethane is branched. In either case, water diffuses into the suspended globules of the latex and chain-extends the urethane to a linear or crosslinked high polymer via reaction with isocyanate endgroups. Upon drying, the creamy, white latices yield strong, elastic films which exhibit low swelling when immersed in water for extended periods. Cationic polyurethane latices were prepared from both polyester- and polyether-based materials, and, in general, the expected structure-property relationships were obtained. A major stabilizing factor in these polyurethane latices is the positive charge on the particles arising from the tertiary amine salts. The latices were compatible with nonionic pigmenting and thickening agents, and they could be blended with a nonionic poly(vinyl acetate) emulsion.

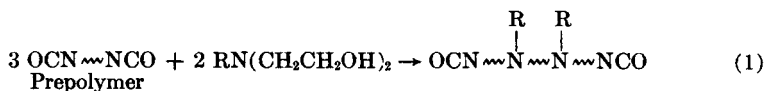
INTRODUCTION

Urethane polymers are finding wide and increasing application in foams, elastomers, coatings, and fibers. Although best known for their excellent tensile properties, load-bearing capacity, and resistance to abrasion, weather, and chemicals, they may be prepared with a wide range of structural modifications and properties. The commercial status of polyurethanes has been realized, though, only through the availability of cheaper raw materials and improved fabrication techniques. The latter has been especially important where the high reactivity and toxicity of isocyanates have presented problems in safe handling and storage stability. Urethane systems which can be easily processed with conventional equipment are still being developed. Thus, the isocyanate-terminated prepolymers and millable urethane gums, thermoplastic polyurethanes, moisture-curing and two-component solvent-based systems, and "blocked isocyanate" techniques have each contributed in at least one respect to the goals of safety, storage stability, and ease of handling.

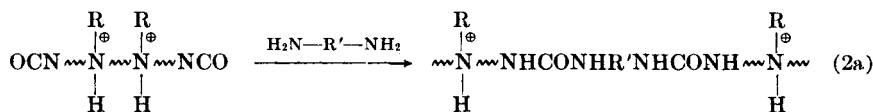
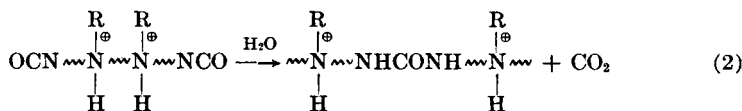
* Present address: Chemstrand Research Center, Durham, North Carolina.

Synthetic polymer latices are used in large volumes for surface coatings, binders, and adhesives. Not only are they safer and less expensive than solvent-based polymers, but they may also be formulated with higher solids content over a wide range of viscosities. The polyurethane latex described here combines the outstanding properties of this polymer with the convenience of a water-based system. This cationic latex is prepared from a self-emulsifiable urethane without the aid of conventional emulsifiers. Tough, elastic films, which exhibit very low swelling in water, are formed by evaporation of the volatile components of the latex.

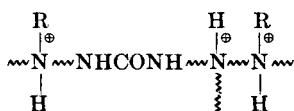
The isocyanate-terminated prepolymer shown in eq. (1) is the reaction product of a polyester or polyether diol with an excess of tolylene diisocyanate. Partial chain-extension of the prepolymer with an alkyl diethanolamine according to eq. (1) yields a relatively low molecular weight urethane bearing tertiary amino groups and still capable of undergoing chain-lengthening reactions. When triethanolamine is included as a third reactant, maintaining the NCO:OH ratio at 1.5, the product has an isocyanate functionality greater than two.



The partially extended urethane is then added with high-speed mixing to 3% aqueous acetic acid; an emulsion forms immediately. Curing of the polymer occurs in the latex as water diffuses into the soft globules and reacts with the isocyanate endgroups [eq. (2)].^{1,2} Alternatively, a water-soluble diamine may be added to the fresh latex as the chain-extending agent [eq. (2a)].



The urethanes which were partially extended with a mixture of an alkyl diethanolamine and triethanolamine were composed of both linear and branched units terminating in isocyanate groups. During the chain-extension step in the latex, these units were combined into a crosslinked network:



EXPERIMENTAL

Materials

Multrathane R-14 (Mobay Chemical Co.), a linear poly(ethylene adipate) diol had an acid number of 1.5 and a hydroxyl number of 51-58. The polypropylene oxide diol was Actol 22-110 (Allied Chemical Corp.), molecular weight 1000. Prepolymers were prepared from these diols with an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate (Mondur TD 80, Mobay Chemical Co.). The commercial isocyanate terminated urethane prepolymers were: Formrez P-611 (Witco Chemical Co.) polyester-based prepolymer; Adiprene L-167 (E. I. du Pont de Nemours and Co., Inc.) poly(oxytetramethylene)-based prepolymer; and Multrathane F-196 (Mobay Chemical Co.) poly(oxypropylene)-based prepolymer.

The alkyl diethanolamines were *tert*-butyldiethanolamine (Rohm and Haas), methyldiethanolamine (Union Carbide Chemicals Co.), and *n*-butyldiethanolamine (Aldrich Chemical Co.). Triethanolamine was a Fisher reagent chemical.

A 20% aqueous solution of polyvinylpyrrolidone (General Aniline and Film Corp., K-90) having an average molecular weight of 360,000 was used as a post-stabilizer.

Preparation of Polyester-Urethane-Urea Latices I-V

A 2-liter flask equipped with a thermometer, air stirrer, and a Dean-Stark water trap surmounted by a condenser was charged with 400 g. (0.4 equiv.) of polyester diol and 300 ml. of toluene. A small amount of water was distilled from the solution along with 160 ml. of toluene. The solution was then stirred with 69.6 g. (0.8 equiv.) of tolylene diisocyanate for 3 hr. at 100-110°C. (In experiment II a prepolymer solution with a lower isocyanate content was prepared with 0.6 equiv. of tolylene diisocyanate.) The methyl diethanolamine (plus triethanolamine in III and IV) was added and stirred with the prepolymer solution for 2 hr. at 60-70°C. The quantities of diol and triol were calculated to react with two thirds of the isocyanate end groups. Next the partially extended urethane was poured over a period of 3-5 min. into 400 ml. of a 3% acetic acid solution stirred with a Sorvall Omni-mixer (Ivan Sorvall, Inc.)

A solution of 38 g. 20% polyvinylpyrrolidone in 50 ml. of water was added to the fresh latex, and slow stirring was continued for 3 hr., during which time a layer of foam appeared on the surface. (In latex IV, 8.2 g. of *m*-tolylenediamine dissolved in 50 ml. of water was added to the freshly prepared latex.) The latices were degassed with a rotary evaporator under reduced pressure and then filtered through a 100-mesh screen.

In experiment V the partial chain extension of 2.62 kg. of Formrez P-611 dissolved in 525 ml. of toluene with 228.5 g. of *tert*-butyldiethanolamine was monitored with a Brookfield viscometer (Model LVT). Reaction times (minutes), temperatures and viscosities (poises) were: 50, 64.5°C., 200;

90, 58.5°C., 470; and 135, 56.0°C., 470, indicating that the diol was completely reacted in 1.5 hr.

Preparation of Polyether-Urethane-Urea Latices VI-IX

In experiment IX a mixture of 400 g. (0.8 equiv.) polypropylene ether glycol, 104.4 g. (1.2 equiv.) of tolylene diisocyanate, and 0.1 g. stannous octoate (catalyst T-9, Metal and Thermit Corp.) was stirred for 4 hr. at 80-90°C. The resulting isocyanate-terminated prepolymer was dissolved in 125 ml. of toluene and then allowed to react with 15.8 g. (0.266 equiv.) of methyldiethanolamine for 2 hr. at 60-70°C. The product was emulsified with 550 ml. of 3% acetic acid solution giving a white, creamy latex which was stirred with 40 g. K-90 for several hours and then degassed and filtered.

Latexes VI, VII, and VIII were prepared from commercially available polyether prepolymers by means of the foregoing experimental procedures.

Preparation of Films

The data shown in Table I were obtained from films prepared by allowing the latices to dry overnight within a 9 × 12 in. frame of plastic tape on glass lubricated with Fluoro Glide (Chemplast, Inc.). Excess latex was removed from the frame with a metal rod by using light pressure. The dried films, 10-15 mils. thick, were dusted with talc and heated in an oven at 75°C. for 24 hr.

RESULTS AND DISCUSSION

Physical Properties of Films

Emulsions I-IV (Table I) were prepared from a Multrathane R14-tolylene diisocyanate prepolymer. Whereas I and II are linear polymers deriving a large measure of their strength from intermolecular attractions among urea, urethane, and ester groups, films from III and IV are chemically crosslinked, as evidenced by solvent swell values. As anticipated, the triethanolamine employed in the partial chain-extension step served ultimately as a source of primary crosslinking in the polymer. In emulsion IV a diamine curing agent, *m*-tolylenediamine, was added to the freshly prepared latex. Due to the higher reactivity of amines relative to water with isocyanates, chain extension occurred in the latex predominately via reaction (2a).

The higher tensile properties of IV when compared to III may be attributable to the higher urea and aromatic content obtained with the diamine curative. It was not unexpected to find that polyester- and polyoxytetramethylene-based films (I-VII) had higher tensile properties than those derived from propylene oxide (VIH and IX).³ The major structural difference between VIII and IX is their urea (—NHCONH—) contents, which were 1.1 and 0.76%, respectively.

TABLE I
Physical Properties of Films Cast from Polyurethane Latexes

	I		II		III ^a		IV ^a		V		VI		VII ^a		VIII		IX	
	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex	Latex
Prepolymer	Multirathane R 14—TDI		Multirathane R 14—TDI		Multirathane R 14—TDI		Formerz P-611		Adiprene L-167		Adiprene L-167		F-196		Multirathane Acetol 22-110-TDI			
Prepolymer NCO content, %	3.6	1.9	3.6	3.6	3.6	3.6	6.1	6.3	6.3	6.3	6.3	6.3	6.3	5.0	5.0	3.3	3.3	3.3
Partial chain-extension	3.4 ^c	1.7 ^c	2.2 ^c	2.2 ^c	2.2 ^c	2.2 ^c	8.8 ^d	5.9 ^e	4.4 ^e	4.4 ^e	4.4 ^e	4.4 ^e	4.4 ^e	6.4 ^e	6.4 ^e	3.9 ^e	3.9 ^e	3.9 ^e
Alkyldiethanolamine, pph ^b	—	—	0.96	0.96	0.96	0.96	—	—	1.3	1.3	1.3	1.3	1.3	—	—	—	—	—
Triethanolamine, pph ^b	920	1052	996	996	2258	2258	1225	1042	2229	2229	2229	2229	2229	597	597	392	392	392
Film properties:																		
Tensile strength, psi	165	245	135	135	210	210	170	190	200	200	200	200	200	120	120	94	94	94
Modulus, psi	300	400	220	220	350	350	220	215	300	300	300	300	300	180	180	130	130	130
100%	700	645	735	735	807	807	1028	863	676	676	676	676	676	918	918	1175	1175	1175
300%	48	61	53	53	60	60	58	59	63	63	63	63	63	53	53	40	40	40
Elongation, %	—	13	9	9	12	12	—	3	3	3	3	3	3	2	2	24	24	24
Hardness (Shore A-2)	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	36	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved	—	—	—	—	—
Taber abrasion (CS-17 wheel), mg./1000 cycles	—	—	165	165	520	520	950	—	270	270	270	270	270	—	—	—	—	—
THF soluble, wt.-% ^g	—	—	—	—	2.6	2.6	—	—	—	—	—	—	—	—	—	—	—	—
THF swell, wt.-% ^g	—	—	—	—	1.9	1.9	—	—	—	—	—	—	—	—	—	—	—	—
Water soluble, wt. % ^h	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Water swell, wt. % ^h	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

^a Average molecular weight per branch point calculated from triol content of polymer was 12000.

^b Parts per hundred prepolymer.

^c Methyl diethanolamine.

^d *tert*-Butyl diethanolamine.

^e *n*-Butyl diethanolamine.

^f Tensile strength, elongation, and moduli, ASTM 412D.

^g 10-mil film immersed 3 days at 24°C.

^h 10-mil film immersed 7 days at 24°C.

Interpretation of the data in Table I in terms of structure-property relationships is of limited significance, since the degree of particle coalescence leading to film consolidation is an unknown, yet important, factor affecting the physical properties of these latex-derived films.

Although a small amount of polyvinylpyrrolidone was added to the emulsions to enhance their mechanical stability, no emulsifying agents were used in the preparations. The low water swell values shown in Table I are consistent with the proposal that volatilization of the acetic acid during the drying cycle yields a polyurethane which no longer contains the hydrophilic amine acetate groups. A commercial urethane latex E-204 (Wyandotte Chemicals Corp.) prepared with nonionic surfactants is reported to yield films which gain 19% by weight of water when immersed at 25°C. for 7 days.⁴

The dried urethane latices had good wet and dry adhesion to glass, metals, wood, paper, masonry, and fabrics. By applying freshly prepared latex to these substrates the chain-extension reactions occur on the surface resulting in markedly stronger adhesive bonds.

Latex Properties

Some of the physical properties of these polyurethane latices are shown in Table II. The average particle size was estimated by microscopic examination of diluted samples. The particles were spherically shaped with some appearing to have occlusions of water or gas. Downward creaming, noticeable after several days, is probably due to the presence of particles larger than 3μ in each latex. This thick sediment was easily redispersed by stirring.

TABLE II
Latex Properties

Latex	Total solids, %	Viscosity, cpoise ^a	pH	Avg. particle size, μ
I	40	385	4.5	2-3
II	41	25	3.0	—
III	44	122	3.4	2-3
IV	45	102	3.5	3-4
V	52	320	3.4	2-3
VI	44	112	3.6	1-2
VII	45	310	3.6	1-2
VIII	43	25	3.1	1-2
IX	41	29	3.4	1

^a Brookfield Model LVT.

A measure of the latex stability undoubtedly arises from the positive charge on the particles which in one case amounted to 86 mv. Both the tertiary amines in the urethane backbone and the acetic acid in the water phase were found to be essential components in this system. When 1,4-

butanediol was substituted for the alkyldiethanolamine in eq. (1), the product could not be emulsified with aqueous acetic acid. Although emulsifiers were not required in the preparations, the addition of 1.5 phr polyvinylpyrrolidone to the latices resulted in a noticeable improvement in rub stability. Hydroxyethylcellulose was found to be an effective thickener and also improved the mechanical stability at levels of 0.5–1.0 phr. The emulsions could be pigmented with titanium dioxide or with Aquablack K (Columbian Carbon), a nonionic dispersed carbon black. Sodium hydroxide, sodium bicarbonate, ammonium hydroxide, and a calcium carbonate slurry caused coagulation as did temperatures above 60°C.; however, the urethane latices were compatible with a nonionic poly(vinyl acetate) emulsion.

The partially extended urethanes diluted with toluene were readily poured into the emulsifying bath. No attempts were made to remove this solvent from the latex; however, when heptane was used in a duplicate of IX, it was volatilized with a rotary evaporator under reduced pressure.

The author is indebted to Dr. J. L. Harper, Dr. C. L. Kehr, and Dr. T. R. Steadman of these laboratories for their inspiring discussions in the field of urethane chemistry; to Dr. P. K. Isaacs for measuring the particle charge using a micro electrophoresis cell; and to Dr. J. J. Godfrey for reading and commenting on the manuscript, and is grateful also for the experimental assistance of Messrs. D. Goldup, W. Dennis, and R. Daffin.

References

1. Hill, F. B., Jr. (to du Pont), U.S. Pat. 2,726,219 (December 6, 1955).
2. Mallonee, J. E. (to du Pont), U.S. Pat. 2,968,575 (January 17, 1961).
3. Saunders, J. H., *Rubber Chem. Technol.*, **32**, 1275 (1960).
4. *Experimental Urethane Latex E-204*, Bulletin, Wyandotte Chemicals Corporation, July 15, 1963.

Résumé

On décrit une technique pour préparer des réseaux de polyuréthanes stables et fournissant des films sans l'utilisation d'agents émulsifiants. La réaction d'une diéthanolamine alcoylée avec un excès stœchiométrique d'un prépolymère d'isocyanate terminé fournit un uréthane de poids moléculaire relativement bas, qui est facilement dispersé avec de l'acide acétique à 3% en solution aqueuse. Quand on emploie de petites quantités de triéthanolamine comme troisième réactif, l'uréthane auto-émulsifiable est ramifié. Dans l'un et l'autre cas, l'eau diffuse entre les globules en suspension du latex et la chaîne s'étend en un polymère linéaire ou réticulé via une réaction avec les groupements terminaux isocyanates. Par séchage, les réseaux blancs crémeux donnent des films élastiques résistants qui présentent un faible gonflement quand ils sont plongés dans l'eau pendant de longues périodes. Les réseaux de polyuréthanes cationiques sont préparés à partir du polyester et du polyéther, et en général, on a obtenu les relations prévues entre la structure et les propriétés. Un facteur stabilisant important dans ces réseaux de polyuréthanes est la charge positive sur les particules provenant des sels d'ammine tertiaire. Les réseaux sont compatibles avec les agents de pigmentation non-ioniques et avec les agents épaississants, et ils pourraient être mélangés avec une émulsion d'acétate de polyvinyle non-ionique.

Zusammenfassung

Ein Verfahren zur Darstellung stabiler, filmbildender Polyurethanlatizes ohne Verwendung von Emulgatoren wurde entwickelt. Die Reaktion eines Alkyldiäthanolamins mit einem stöchiometrischen Überschuss eines Präpolymeren mit Isocyanatendgruppe liefert ein relativ niedermolekulares Urethan, welches mit 3%iger wässriger Essigsäure leicht dispergiert werden kann. Bei Verwendung kleiner Mengen von Triäthanolamin als dritter Komponente ist das spontan emulgierende Urethan verzweigt. In jedem Fall diffundiert Wasser in die suspendierten Latexkügelchen und verlängert über eine Reaktion mit den Isocyanatendgruppen die Urethanketten zu einem linearen oder verzweigte Hochpolymeren. Beim Trocknen liefern die pastenartigen, weissen Latizes feste elastische Filme, welche bei langzeitigem Eintauchen in Wasser nur geringe Quellung zeigen. Kationische Polyurethanlatizes wurden aus Stoffen auf Polyester- und Polyätherbasis dargestellt; im allgemeinen wurden die erwarteten Beziehungen zwischen Struktur und Eigenschaften erhalten. Die Hauptfaktoren für die Stabilisierung sind in diesen Polyurethanlatizes die positive, von den tertiären Aminsalzen herrührende Ladung der Teilchen. Die Latizes waren mit nichtionischen Pigmenten und Verdickungsmitteln verträglich und konnten mit einer nichtionischen Polyvinylacetatemulsion gemischt werden.

Received December 23, 1964