

A One-Component Sealant Based on 1,3-Dipoles*

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Synopsis

An unusual one-component sealant based on a moisture cure has been developed. The chemistry involves the reaction of a 1,3-dipole (a difunctional nitrile oxide) with a dipolarophile (an unsaturated polymer); a difunctional hydroximoyl chloride, which forms a nitrile oxide on reaction with a latent base, reacts with the polymer on exposure to moisture by forming isoxazoline crosslinks. The hydroximoyl chloride was prepared from a *bis*(chloroketone) (e.g., 4,4'-*bis*(chloroacetyl)diphenyl ether), by reaction with nitrous acid; this avoided the use of expensive dialdehydes, as well as hydroxylamine. The preferred latent base was barium oxide, and almost any unsaturated polymer could be used. Such a system, stable indefinitely when dry, crosslinked rapidly when exposed to atmospheric moisture. Since water is generated when the initially formed barium hydroxide reacts with the hydroximoyl chloride, only catalytic amounts are required, and thick beads cure completely; skinning causes problems with other moisture-curable systems.

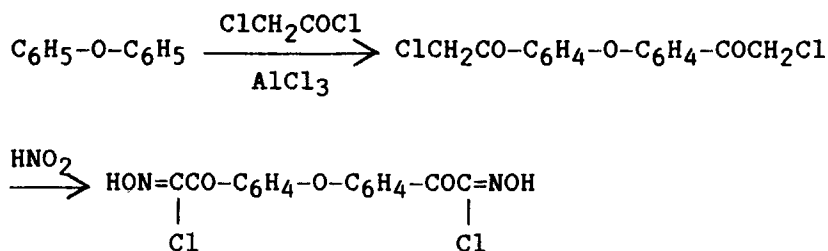
A sealant is any material placed in a joint opening, generally for the purpose of weatherproofing the building.¹ The classic drying oil-filler putty, quite satisfactory for sealing glass in window frames, cannot meet the requirements of present construction methods, in which a building skeleton of steel or concrete is wrapped in a separate envelope or curtain wall; each section must be sealed to prevent leakage at the joints.

Numerous sealants are available, but each type has its disadvantages. Polymer solutions shrink as solvent is lost. Nonsolvent types depend on crosslinking low-molecular weight polymers after insertion into the joint. Two-component systems must be mixed on site, frequently by unskilled labor under adverse conditions. A number of one-component sealants are available which depend on moisture for crosslinking; thick beads are a problem, however, because surface skimming prevents moisture penetration, which leads to slow or incomplete cures.

This project was initiated in order to determine if polyfunctional 1,3-dipoles could be prepared and used to crosslink polymers containing dipolarophiles. Polyfunctional nitrile oxides,² nitrile imines,³ nitrones,⁴ sydnones,⁵ and aziridines⁶ (or their precursors) were prepared and shown to act as crosslinking agents for unsaturated polymers (many polyfunctional sulfonyl azides and azidoformates had also been prepared, but these have been used primarily as nitrene precursors^{7,8}). Consideration of both economics and reactivity led us to choose nitrile oxides and their hydroximoyl chloride precursors, in spite of

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the known predilection of nitrile oxides to dimerize to furoxans in the absence of reactive dipolarophiles.⁹ Since the polyaldehyde starting materials are both difficult and expensive to prepare (only glyoxal and glutaraldehyde are available on an industrial scale), we decided to investigate carbonylhydroximoyl chlorides, prepared from ketones, instead, even though the corresponding nitrile oxides are too reactive to isolate. An added advantage was the elimination of hydroxylamine as a reactant. The starting ketones were prepared by a Friedel-Crafts reaction of aromatic hydrocarbons with chloroacetyl chloride, as illustrated here with diphenyl ether:¹⁰



Scheme 1

Other aromatics were also used (Table I).

It was readily demonstrated that a *bis*(nitrile oxide), for example, terephthalobis(nitrile oxide)(4), or a nitrile oxide precursor plus base, would crosslink a variety of unsaturated polymers (Table II). It was found in this work that several latent bases—barium oxide, calcium nitride, aluminum carbide—could be mixed with hydrated salts, an unsaturated polymer, and a hydroximoyl chloride without crosslinking the polymer at room temperature; reaction took place only on heating.¹¹

With these results in hand, we decided to develop a one-component sealant based on a moisture cure. It was demonstrated that a mixture of an unsaturated polymer, a polyfunctional carbonylhydroximoyl chloride (1-3), and barium oxide, if rigorously dried, was stable indefinitely at room temperature, but would crosslink on exposure to atmospheric moisture. It was quite surprising to find that the best physical properties of the cross-linked polymer were obtained when stoichiometric ratios of hydroximoyl chloride to olefinic

TABLE I
Bis(arylglyoxylohydroximoyl Chlorides)

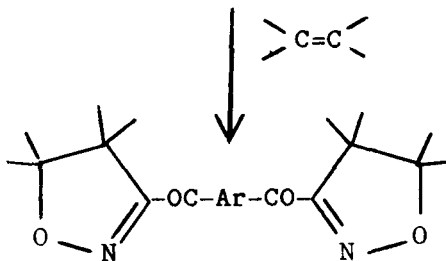
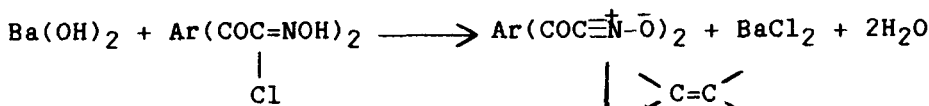
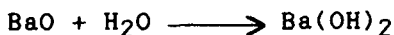
| Ar | HON=CCO—Ar—COC=NOH | | Analysis | | | | |
|--|--------------------|----|----------|------|------|------|------|
| | Cl | Cl | C | H | N | Cl | |
| | m.p., °C | | | | | | |
| (1) 4,4'-O(C ₆ H ₄) ₂ | 189–190 | | theory | 50.4 | 2.64 | 7.35 | 18.6 |
| | | | found | 50.6 | 2.90 | 7.71 | 18.2 |
| (2) 4,4'-CH ₂ (C ₆ H ₄) ₂ | 171–172 | | theory | | | 7.39 | 18.7 |
| | | | found | | | 7.47 | 18.4 |
| (3) 4,4'-(C ₆ H ₄) ₂ | 214 | | theory | 52.6 | 2.76 | 7.67 | 19.4 |
| | | | found | 53.0 | 2.95 | 7.70 | 19.4 |

TABLE II
Polymer Crosslinking with Nitrile Oxides

| Nitrile oxide or precursor | Polymer | Base | Conditions for cross-linking |
|--|---|--|--------------------------------|
| 4 | <i>cis</i> -1, 4-Polybutadiene | — | 20 min at 25°C (in benzene) |
| 4,4'-C ₆ H ₄ (C=NOH) ₂ Cl | Propylene oxide/allyl glycidyl ether copolymer | Et ₃ N (gas) | 7 hrs at 25°C |
| 1 | Oxyethylene ether of bisphenol A/maleic polyester | CaN ₂ /Na citrate · 2H ₂ O | 10 min at 160°C |
| 2 | Polyethylene glycol/maleic polyester | BaO/Na ₂ MoO ₄ · 2H ₂ O | 10 min at 110°C |
| 3 | Styrene/butadiene rubber | BaO/Na ₂ MoO ₄ · 2H ₂ O | 10 min at 110°C |

unsaturation were used. Thus, there appeared to be little, if any, furoxan formation; apparently the very high viscosity of these systems prevented nitrile oxide dimerization.

The addition of filler, a thixotropic agent, an adhesion promoter, and a stabilizer resulted in a one-component, moisture-curable sealant with excellent physical properties.¹² Unlike other moisture-curable systems, penetration of water into the sealant is not required, since the initially formed barium hydroxide generates water upon reaction with the hydroximoyl chloride.



ISOXAZOLINE CROSS-LINKS

Scheme II

A sealant based on this chemistry was used in the construction of a laboratory building at the Hercules Research Center; it has given excellent service.

EXPERIMENTAL

Terephthalo-bis(hydroximoyl chloride). Nitrosyl chloride was passed into a suspension of 19.8 g of terephthalaldehyde dioxime) in 500 mL of ether at 0°C until the material dissolved and the green color, formed initially, disappeared. Removal of the solvent and recrystallization of the residue from ether/hexane yielded 5.9 g of product, m.p. 177.5-179°C.

Terephthalo-bis(nitrile oxide)(4). A solution of 5 g terephthalo-bis(hydroximoyl chloride) in 80 mL methanol at 0°C was treated with 4.23 g of triethylamine in 15 mL of methanol for 1 h. The resulting slurry was filtered, washed twice with methanol, and dried, yielding 3.17 g of nitrile oxide. Anal. calcd. for $C_8H_4N_2O_2$: C, 60.0; H, 2.52. Found: C, 59.8; H, 2.90.

4,4'-Oxy-bis(phenylglyoxylohydroximoyl chloride)(1). A suspension of 32.3 g of 4,4'-bis(chloroacetyl)diphenyl ether in 200 mL of diethyl ether was saturated with dry hydrogen chloride. To this was added 42 g of 70% isoamyl nitrite dropwise with stirring. A clear solution was formed, which crystallized on standing. The solvent was evaporated and the residue washed several times with small portions of ether, yielding 31.8 g of **1**, m.p. 188°C. Recrystallization from ether/pentane gave a product m.p. 189-190°C. **2** and **3** were prepared in a similar fashion (Table I).

Sealants. A polyurethane was prepared by reacting a poly(propylene oxide) adduct of 1,2-propanediol (MW 2,000) with toluene diisocyanate (TDI) at a molar ratio of 2 : 3, and then end-capped with allyl alcohol; the product had a molecular weight of about 5,000 and an olefin functionality of 1.81 by infrared. Similarly, a poly(propylene oxide) adduct of trimethylolpropane (MW 4,000) was reacted with TDI at a molar ratio of 1 : 3, and then end-capped with 3 moles of allyl alcohol; the product had a molecular weight of about 5,000 and a functionality of 2.86. In a roller-type mill, in the absence of moisture, 95 parts diolefin and 5 parts triolefin were blended with 6.5 parts of **2**, 5 parts BaO, 15 parts TiO₂, 50 parts talc, and 5 parts bentonite. The resulting paste was stable for at least 6 months if all the ingredients were dry, and a 1/8-inch bead crosslinked within 24 h on exposure to the atmosphere at 50% relative humidity.

To a solution of 100 parts of propylene oxide-allyl glycidyl ether copolymer, having a molecular weight of 12,000 and containing 97 mole% propylene oxide and 3 mole% allyl glycidal ether, in 100 parts of anhydrous tetrahydrofuran was added 10 parts **1**, and the solvent was evaporated. The residue was mixed in a roller-type mill with 7.5 parts BaO, 30 parts TiO₂ and 5 parts bentonite clay. The resulting paste was similar to the polyurethane sealant described above in both stability and cure properties.

References

1. J. P. Cook, *Construction Sealants and Adhesives*, Wiley-Interscience, New York 1970, p. 1.
2. D. S. Breslow, U.S. Patent 3,390,204 (1968).
3. D. S. Breslow, U.S. Patents 3,418,285 (1968); 3,832,399 (1974); 4,247,474 (1981).
4. D. S. Breslow, U.S. Patent 3,390,133 (1968).
5. D. S. Breslow, U.S. Patent 3,448,063 (1969).
6. D. S. Breslow, U.S. Patent 3,828,024 (1974).
7. W. Lwowski, Carbonylnitrenes, and D. S. Breslow, Sulfonylnitrenes, in *Nitrenes*, W. Lwowski, Ed., Wiley-Interscience, New York, 1970, Chapters 6 and 8, respectively.

8. D. S. Breslow, "Industrial Applications," in *Azides and Nitrenes*, E. F. V. Scriven, Ed., Academic Press, New York, 1984, Chapter 11.
9. C. Grundmann and P. Gruenanger, *Nitrile Oxides*, Springer, New York, 1971.
10. D. S. Breslow, U.S. Patents 3,504,017 (1970); 3,670,023 (1972).
11. K. Brack, U.S. Patent 3,454,506 (1969).
12. J. C. Richards III, *Adhesives Age* (July 1970) 22.

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