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# Polyols based on isocyanates and melamines and their applications in 1K and 2K coatings☆

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ABSTRACT

Polyurethane polyols (PUPOs) and melamine polyols (MEPOs), invented by AkzoNobel Coatings, offer valuable alternatives to the commonly used polyester and acrylic polyols and new formulating tools for the development of novel coatings. The resin chemistry is based on the predominantly selective reactivity of α,β- and α,γ-diols with commonly used polyisocyanate and melamine formaldehyde crosslinkers. The resulting low molecular weight, hydroxyl functional resins are suitable for use in low VOC coatings. By choosing the appropriate crosslinker, diol, and modifier, the chemical structures of these resins can be altered to obtain the desired properties of the coatings. Synthesis methods for novel PUPOs and MEPOs and properties of one component and two component coatings containing them are described.


## 1. Introduction

Conventional one component (1K) acrylic melamine coatings for automotive OEM applications have been used for a number of years and, for the most part, have met automotive specifications. With the increasing demands of the OEMs for improved weathering performance in the 1980s, these coatings could not meet the newer requirements for resistance to acid etch. The launch of two component (2K) urethane coatings allowed coating suppliers to pass the acid etch requirement and offer improved overall performance. Some end-users, however, were not ready to retrofit their assembly plants with 2K equipment and were reluctant to use polyisocyanates. Polyurethane polyols (PUPOs) provided the means to incorporate the many advantages of 2K urethanes into 1K melamine coatings.

The practical synthetic method and the applications of PUPOs in coatings have been established over the last 20 years. Early attempts to prepare PUPOs were based on the reaction of polyisocyanates with a large excess of diol [1]. Unreacted diol was subsequently removed by vacuum distillation after all of the isocyanate was consumed. This inconvenient post-reaction step was costly and prohibited the practical applications of this process for manufacturing PUPOs. Another method for preparing PUPOs relied on the ring opening reaction of cyclic carbonates with amines [2]. The limited commercial availability of multifunctional amines and cyclic carbonates restricted the use of these types of PUPOs in coatings. The pioneering work of J. Gardon, F. Walker, P. Uhlianuk, and S. Loper in the late 1980s and early 1990s described a novel method to produce polyurethane polyols using stoichiometric quantities of certain diols [3–6]. They discovered that α,β- and α,γ-diols predominantly react single-ended with isocyanates as described in Fig. 1. Using conventional polyisocyanate crosslinkers and α,β- and α,γ-diols, they were able to produce low molecular weight PUPOs with at least three hydroxyl functionalities. One component PUPO melamine coatings were superior in acid etch resistance to traditional acrylic melamine coatings [6].

Recently, the concept of the predominantly single-ended reaction between α,β- and α,γ-diols and polyisocyanates was applied to the reaction of these diols with melamine formaldehyde resins [7]. A theoretical reaction scheme is shown in Fig. 2. Surprisingly, it was found that despite many potential side reactions, including the self-condensation of the melamine formaldehyde resins, the predominant reaction of α,β- and α,γ-diols with melamine formaldehyde resins is also single-ended. The resulting novel melamine polyols (MEPOs) have low viscosity and high reactivity. They are suitable for use in 1K and 2K, low VOC coatings.

This paper demonstrates how polyisocyanates and melamine formaldehyde resins, the most commonly used crosslinkers in coatings, can be converted, under controlled conditions, into hydroxyl

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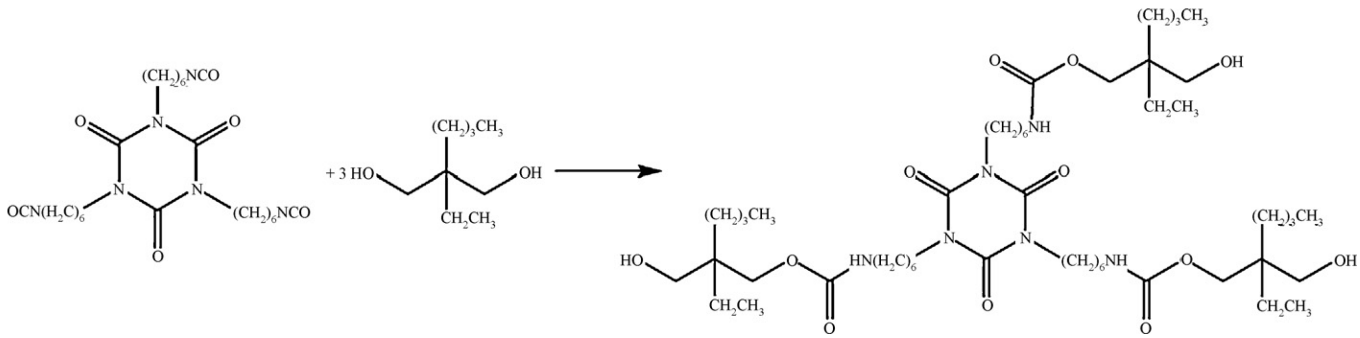

**Fig. 1.** Idealized reaction scheme of polyurethane polyol prepared from the isocyanurate trimer of hexamethylenediisocyanate (HDI) and 2-butyl-2-ethyl-1,3-propane diol (BEPD).

functional binders suitable for 1K and 2K coatings. Polyurethane polyols are low molecular weight, ester- and ether-free resins which can be used in coatings as sole binders or co-reactants with commonly used acrylic, polyester, and epoxy resins. The original work of Gardon et al. focused on the applications of PUPOs in 1K melamine, acid etch resistant, automotive coatings [3–6]. The work described here, dates from the early 1990s to present, including the development of new PUPOs and their corresponding coating formulations. Efforts to further reduce the viscosity of PUPOs and the development of PUPOs for rigid and flexible substrates are presented. We also describe the use of PUPOs in 2K urethane coatings and discuss how the basic technology can be extended to incorporate different functionalities in addition to hydroxyls.

Examples of two applications of melamine polyols in coatings are presented. The first application describes the development of a 2K, self-healing, scratch and mar resistant coating for the automotive refinish market. The second application demonstrates how water-reducible melamine polyols can improve the chemical resistance of waterborne 2K soft-touch coatings for automotive interiors.

## 2. Experimental

### *2.1. Synthesis of standard polyurethane polyol, PUPO-1*

The standard polyurethane polyol, PUPO-1, was prepared by mixing 961.6 g 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 411.7 g of n-butyl acetate in a 5 L round bottom flask equipped with a mechanical stirrer, nitrogen blanket, heating mantle, thermocouple, and condenser. The flask contents were then heated to 70 °C. Once a homogeneous solution was formed, a mixture of 1170.0 g of Desmodur N 3300 (HDI trimer), 500.0 g of n-butyl acetate, and 2.1 g of a 10% solution of dibutyltin dilaurate (DBTDL) in n-butyl acetate was fed to the flask over 3 h during which the temperature was maintained at 70 °C. The reaction mixture was then held at 70 °C until no isocyanate was detected by FT-IR. The resulting resin had a solids content of 70.3% and a Brookfield viscosity of 212 cPa s (25 °C, #4 spindle, 20 rpm).

### *2.2. Synthesis of polyurethane polyol modified with a monofunctional alcohol, PUPO-2*

The first step in the preparation of a monofunctional alcohol-modified polyurethane polyol, PUPO-2, involved combining 588.0 g of Desmodur N 3300, 210.4 g of n-butyl acetate, and 0.5 g of a 10% solution of DBTDL in n-butyl acetate into a 1 L round bottom flask equipped with a mechanical stirrer, nitrogen blanket, heating mantle, thermocouple, and condenser. The material was heated to 70 °C and 74.0 g of 2-butanol was added evenly over a 1 h period. At the end of the 2-butanol feed, the mixture was held at 70 °C for an additional hour before cooling to room temperature for the next step in the synthesis.

In a separate 2 L round bottom flask equipped with a mechanical stirrer, nitrogen blanket, heating mantle, thermocouple, and condenser, a solution of 320.0 g of BEPD in 210.4 g of n-butyl acetate was heated to 70 °C. The isocyanate prepolymer in the first step was added to the second flask over a period of 2 h, during which the temperature was maintained at 70 °C. The reaction mixture was then held at 70 °C until no isocyanate was detected by FT-IR. The result-

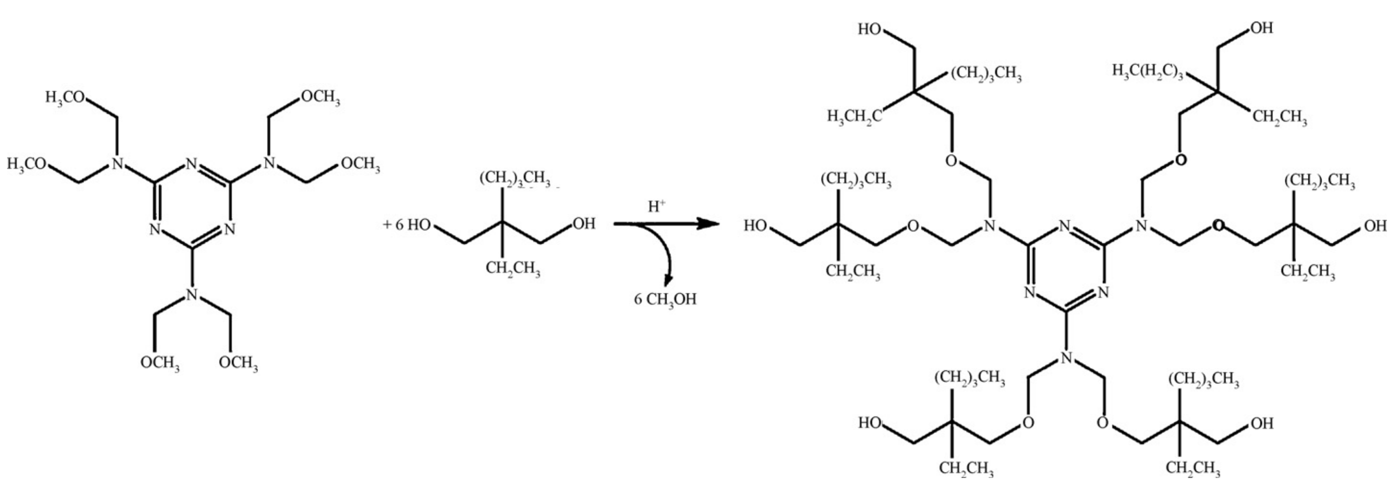

**Fig. 2.** Idealized reaction scheme of melamine polyol prepared from hexamethoxymethyl melamine (HMMM) and 2-butyl-2-ethyl-1,3-propane diol (BEPD).